Ionised Deposition for the Structural Control of Carbon Nickel Thin Films

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A thesis submitted for the degree of

Doctor of Philosophy

October 2012
Preface

This dissertation is submitted to the University of Cambridge for the degree of Doctor of Philosophy. The work described was carried out between October 2009 and October 2012 at the Department of Materials Science and Metallurgy, University of Cambridge. No part of this dissertation has been submitted for a degree to any other university. This dissertation is my own work, although some work was done in collaboration with others as specified in the Acknowledgements. The content of this thesis does not exceed 60000 words.
Acknowledgements

I would like to express my sincere thanks to all involved, directly and indirectly, with my work over the last three years. Both those inside the department who shared their expertise and those outside who helped make this time so enjoyable, without your friendship this thesis would not have been possible.

I am most grateful for the help and guidance from my supervisor, Dr. Zoe Barber. Her patience and support was invaluable. Special thanks go to Dr. Nadia Stelmashenko, her advice, skill and knowledge in guiding me through the technical aspects of my work were outstanding and this work would not have been possible without her. I would like to thank Mary Vickers and Andrew Moss for their help with the X-ray experiments. For his help with the SEM/EDX work I am greatful to Simon Griggs. I gratefully acknowledge all at the LENNF facility in Leeds but particularly Dr. Michael Ward for the TEM work and Dr. Alex Walton for the XPS work. The SQUID measurements would not have been possible without the guidance of Tony Dennis. I am grateful for the help of Fred Lord, as a Masters student he helped me with the early Raman work. Additionally Algirdas Baskys, a summer student, was of great help with the work on heat treatments.

I would like to thank all the members of the Device Materials Group, past and present. Their friendship and support has made my time here a pleasure and they were always available to answer my questions, listen to my complaints and encourage me onwards. A special thanks is reserved for all my friends at Robinson College and throughout the University over the last 7 years. They have been an amazing source of support and entertainment and I treasure all our memories (even the things I should rather forget!).

Last but not least I would like to thank my family, especially my parents. Their love and support for the last 26 years have helped me to achieve all that I have. This thesis would not have been possible without their love and it is dedicated to them.
Carbon encapsulated metal nanoparticles are an increasingly important class of materials due to the wide range of electronic, magnetic and mechanical properties they display. However, traditional deposition techniques are often complex or lead to a poor quality film. Ionised magnetron sputter deposition is a promising development to traditional magnetron sputtering which combines film deposition with ion bombardment. By adding an RF powered, inductively coupled plasma positioned between the deposition targets and the substrate, the ionisation fraction of the depositing flux is greatly increased. This additional ion flux can then be controlled through the use of an electrical substrate biasing. This controls the energy flux to the surface and therefore the resulting microstructure.

Carbon-nickel thin films were grown by ionised magnetron sputter deposition. The films themselves were characterised using a wide variety of techniques to measure not only their structure but their properties. Additionally, the inductively coupled plasma itself was characterised using a Langmuir probe. It was determined that upon application of a negative substrate biasing, the ion flux to the growing film remained constant, however the energy of the species increased. This resulted in a columnar structure of nickel carbide which coarsened as the bias (and therefore the energy of the ions) was increased. Conversely the application of a positive bias gives a large flux of low energy bombardment. This led to the formation of metallic nickel nanoparticles (≈ 30 nm diameter) which were surrounded by several layers of ordered graphitic shells forming a so-called “nano-onion” structure.

The transition between these phases is a result of an increase in adatom mobility when there is a high flux, low energy ion bombardment which allows the nickel and carbon to phase separate. Upon separating, the nickel templates graphite growth due to their similar bond lengths leading to the formation of the graphitic cages.

The transition between these two structures is measured through X-ray diffraction which shows a transition from the hexagonal carbide phase to the cubic...
nickel phase. This is accompanied by an increase in ordering of the carbon as the bias is increased as measured by Raman spectroscopy. Additionally, it is observed that there is an increase in carbon ordering when a negative bias is applied, due to the additional energy from ion bombardment leading to graphite formation.

Magnetic measurements showed a transition from a non-magnetic state when the structures were largely carbide, to a magnetic state when metallic. However at room temperature the structures display superparamagnetic behaviour due to the small size of the particles.

Measurements of electronic conductivity showed a negative temperature coefficient of resistivity for all samples demonstrating no metallic conduction path was present. A large drop in resistivity as the temperature increases was assigned to thermally activated conduction. At low temperatures the conductivity is dependent on tunnelling across small regions of amorphous carbon, while at higher temperatures it is possible to excite the electrons into a conduction band allowing them to conduct more easily.
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Chapter 1

Introduction

In this work carbon-nickel thin films were grown by ionised magnetron sputter deposition. The films themselves were characterised using a wide variety of techniques to measure not only their structure but their properties.

Nanostructured films consisting of multiple elements and phases have attracted much interest in recent years. These nanoscale systems offer unique combinations of properties which often greatly differ from the bulk properties of the constituent materials. A new generation of multifunctional materials is finding uses in catalysis, hard coatings, electronic and magnetic devices as well as drug delivery and biomedical applications. A great challenge remains in how to attain these properties in a reproducible and facile way.

The concept of graphitic encapsulation of nickel has been observed extensively in the past. The relationship between nickel and carbon has already been shown to be of interest in catalysis and carbon nanotube growth. It has frequently been observed \([1]\) that given sufficient energy, spherical coherent onion like graphitic shells will form around nickel nanoparticles to form structures which have become known as \(\text{“nano-onions”}\).

Kovacs \textit{et al} have investigated the growth of nickel carbon films. In addition to the variations seen with deposition temperature \([2,3]\), they have also investigated the role of ion bombardment to some degree \([4,5,6]\). They found film structure depends not only on composition (a minimum metal content is required to form metallic particles) but is also strongly dependent on incoming ion energy, incidence angle and flux composition. They propose that diffusion rate and growth velocity determine the microstructure. That is to suggest that diffusion distance of the depositing species is vital in controlling the growth.

The most common technique for growing these structures so far has been magnetron
1. INTRODUCTION

Sputtering. Sputtering has found applications in a wide range of fields due to its flexibility both in terms of scale (nanometre electronic interconnects and vias can be deposited, yet it can be easily scaled up to coat large panes of glass with high emissivity coatings) and control (defect free nanometre layers and dense tough layers can be deposited with high accuracy). Additionally, sputtering is flexible in terms of the materials which can be deposited. The deposition of complex alloys, oxides, nitrides as well as elemental films have all been widely investigated. However, increasing demands on materials and devices require new deposition techniques.

In traditional magnetron sputtering, a collision between the gas ion and the target generates a sputtered atom. However there is normally a low ion fraction in the flux reaching the substrate (resulting in a current of less than 1 mA cm$^{-2}$) [7, 8]. Ionized physical vapour deposition is the term used to describe a range of deposition techniques where the ionisation fraction of the depositing flux is significantly higher (>50%) [9]. The term encompasses various deposition techniques such as unbalanced magnetrons, high power impulse magnetron sputtering, microwave electron cyclotron resonance deposition, ionised hollow cathode magnetron sputtering and, the technique of interest here, radio frequency inductively coupled plasma deposition [10].

The term inductively coupled plasma (ICP) arises from the technique by which the secondary plasma is created. In order to raise the ionisation fraction, a second plasma (in addition to the glow discharge which causes the sputtering) is created in the space between the target and the substrate. This second plasma is typically larger than the mean free path of the atoms in the gas, increasing the number of collisions such that the depositing species are likely to become ionised [11]. In the case of an ICP, the inert gas in the chamber (and then the plasma once ignited) is inductively coupled to an RF voltage (typically at 13.56 MHz) applied through a coil.

In the late 1980s Yamashita [12] outlined a process for increasing the ion fraction of a depositing flux through this method. Then in the early 1990s Hopwood and Rossnagel published a series of papers detailing the current state of research [13] and further building on both the theoretical and practical nature of the technique [14, 15, 16, 11]. Originally devised as a technique to produce a collimated flux to allow for the coating of high aspect ratio vias in microelectronics [17], the control over ion energy made possible soon led to the use of the technique to control film microstructure [18].

The aim of this project is to build on the work by Kovacs et al and investigate how the
use of ionised sputter deposition can provide additional levels of control over the structure and composition of metal carbon films, through the independent control of deposition flux, ionisation rate and ion energy.
1. INTRODUCTION
Chapter 2

Metal Carbon Nanostructures

Nanostructured devices have become an increasingly important area of research over the last three decades. The opportunities created by the behaviour of structures at a nanometre scale have driven the electronic revolution and continue to promise great developments in the fields of energy production, microelectronics and health care. However the manufacture and control of these devices and materials is rarely trivial and so the development of new structures as well as new routes for production remain a continuous driving force of research. A wide range of such structures and manufacturing routes have been explored, an overview of which is outlined below.

2.1 Applications of metal-carbon structures

Metal-carbon structures have found applications in a range of fields due to the breadth of properties they can achieve. Hard coatings have attempted to mimic the mechanical properties of diamond for many years, and through diamond like carbon (DLC) coatings, very large values of hardness and wear resistance are possible [19]. However through the addition of a metal dopant [20] it is possible to reduce residual stresses and increase wear resistance further. Additionally, due to a well defined relationship between conductivity and applied stress, metal doped DLC films make very sensitive strain gauges [21].

Metal-carbon composites have also shown excellent catalytic properties for a variety of reactions including hydrogen oxidation [22], carbonylation of ethanol [23] and general hydrocarbon decomposition [24]. Alternatively, nanostructured materials often incorpo-
2. METAL CARBON NANOSTRUCTURES

rate magnetic behaviour [25] which allows for the careful control and tuning of magnetic properties and domain size [26].

Due to their size, nanoparticles can also be used for novel drug delivery systems [27]. Surface functionalisation of nanoparticles allows for the delivery of biomolecules and drugs directly into cells, while magnetic properties allow for external control over these particles. “Trojan Horse” drug delivery systems could carry proteins and DNA across the cell membrane and deliver them directly to damaged cells; inorganic nanomaterials are excellent candidates as carriers of these devices.

Finally nanoparticles are of interest in their own right as dimensionally confined systems [28]. The ability to make reproducible nanoscale systems in terms of chemistry, scale and composition, allows for the study of effects such as superparamagnetism, quantum tunnelling and other nanoscale phenomena.

2.2 Morphologies of metal-carbon structures

With growing demands being placed on the performance of devices, novel composites are being developed in an attempt to create new materials with useful properties. As seen in figure 2.1 nanostructures have been of increasing interest since the early 1990s. Many of these are based around metal and carbon due the range of properties each component can achieve.

A key area of interest for metal nanoparticles is catalysis. Metallic catalysts have been used for many years and there has been a constant pressure to increase their efficiency. One such option is through ordered mesoporous carbon (OMC). These structures consist of large pores and therefore have a high surface area to volume ratio, but also offer chemical stability [29] which makes them ideal for use in catalysis and energy storage. However in order to be used as catalysts and electrode materials, metal or metal oxide particles need to be incorporated into the centre of the OMC [30]. It is this incorporation which is challenging and a range of approaches have already been employed. The location of the metal particle is of particular interest as its relationship to the porous channels can dramatically alter the efficiency of the catalytic process. Initially [31], the growth of these structures was achieved by using a silica template into which the carbon precursor (typically sucrose) was injected and then reduced to form the OMC. The metallic particles were then deposited on the outer surface of the OMC. However this had the effect of
blocking the OMC pores and therefore reducing the overall efficiency. A later development was to incorporate the metallic particles in the silica template [32] so that they were embedded within the OMC.

While this later method provided good quality metal encapsulated OMCs, the production route was complex and involved a number of steps. A more direct approach was sought and two such approaches were developed. The first [30] involved mixing nickel nitrate hexahydrate with the sucrose solution prior to thermal treatment such that when heated the carbon reduced simultaneously with the formation of nickel oxide. This approach has the advantage that there was significantly less pore blockage as the nanocrystallites do not sit in pore channels but rather the walls of the OMC. This ensures the large surface area is maintained.

An alternative approach centres on using a soft template rather than a silica template [33]. By using a copolymer which phase separates it is possible to create a gel containing nickel nitrate as well as a block copolymer to act as the carbon source. Once the gel had been left to phase separate, it was then heated to break the polymer down and cause carbonisation resulting in a nickel containing OMC.

Figure 2.1: Graph to show the number of publications on nanostructures and nanoparticles by year (Source: Web of Knowledge)
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In addition to catalytic applications, metal containing OMCs have also been shown to have excellent capacitive properties \[34\] making them an attractive option for energy storage.

While OMC structures are promising for certain applications, bulk and thin film carbon structures have attracted by far the greatest attention due to the wide range of structures they can adopt. Carbon exists in a number of forms but is most easily categorised in terms of the chemical bonding of the carbon atoms. In graphite, the carbon forms covalent bonds in the graphitic planes via sp\(^2\) type bonding. In diamond, the carbon is tetrahedrally bonded, in an sp\(^3\) type hybridisation. Therefore man-made structures can best be described in terms of the relative amounts of sp\(^2\) and sp\(^3\) bonding. In addition to these forms of carbon, amorphous carbon is also often found. Amorphous carbon often consists of locally bonded sp\(^3\) carbon, but with no long range order, this form of carbon is known as tetrahedral amorphous carbon (ta-C) or diamond like carbon. Other forms of amorphous carbon exist in which the sp\(^3\) content is lower, and this is known simply as amorphous carbon (a-C). In each case, the structures can be hydrogenated to form tetrahedral amorphous hydrogenated carbon (ta-C:H) or hydrogenated amorphous carbon (a-C:H). The various forms of carbon with different levels of sp\(^2\) and sp\(^3\) carbon and hydrogen are best described through a ternary phase diagram as shown in figure 2.2 \[35\]. However due to the ill-defined boundaries between phases, the labelling of structures can be inconsistent and is open to individual authors’ interpretations.

As previously mentioned, diamond like carbon (DLC) has found uses in a range of applications. However of particular interest is the ease with which the electrical conductivity can be influenced by the addition of metal atoms \[36\]. Also of note is that the metal atoms do not distribute themselves uniformly as atoms, but rather cluster together to form nano-particles.

A range of deposition techniques has been employed to fabricate such structures. Pulsed laser ablation \[37\] using graphite and nickel targets, has been shown to produce DLC:Ni films containing around 50 at% Ni which forms as 100 nm nodules. These nodules were shown to consist of almost pure nickel with little carbon content, the carbon being found nearly exclusively in the DLC phase. In contrast, films grown via biased target ion beam sputtering \[38\] using methane as a carbon source have produced Ni:ta-C:H films incorporating some Ni\(_3\)C carbide nanoparticles. It was observed via Raman spectroscopy that the addition of nickel increases the sp\(^2\) carbon content which results in a decrease in
2.2. MORPHOLOGIES OF METAL-CARBON STRUCTURES

Figure 2.2: Ternary phase diagram for sp\(^2\) and sp\(^3\) carbon and hydrogen showing the various structural types possible [35].

The increase in sp\(^2\) content observed in metal containing DLC films is not surprising as the graphitising nature of nickel has long been known (since the 1970s) with many detailed studies having been completed [39]. Nickel [40], iron [41] and cobalt [42] have all been shown to catalyse the growth of graphitic carbon [43, 44] and have all been demonstrated to act as growth centres for carbon nanotubes (CNTs). Based on a CVD method [45], the metal catalysed breakdown of hydrocarbons such as benzene, acetylene or methane provide the carbon atoms which then dissolve in the metal particle due to the increased solid solubility possible at the elevated experimental temperature [46]. Upon cooling, the carbon precipitates out and, since the graphitic carbon-carbon bond length and the metallic nickel-nickel bond length are closely matched, the underlying metal particle acts...
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as a template for graphite growth or CNT growth.

2.3 Carbon encapsulated metal nanoparticles

Metal nanoparticles are a very active area of research due to their interesting physical properties and the applications they therefore lend themselves too (see figure 2.1). Research in the field has grown massively in the last decade. Magnetic recording, biomedicine, contrast agents for magnetic resonance imaging and many other magnetic applications have all been highlighted as potential applications. However pure metal nanoparticles are very reactive \cite{47} and so oxidise rapidly in air, they also agglomerate easily and dissolve in acid making them difficult to work with. By encapsulating these metal particles with carbon, the underlying nanoparticles are protected from environmental degradation \cite{25} while the magnetic properties are retained. Additionally if the carbon is in a graphitic form, the electronic properties of the metal nanoparticle are also still available. Carbon encapsulation also reduces agglomeration and increases the biocompatibility of the particles \cite{27} making them more suitable for biological applications.

By the late 1990s \cite{48} four classes of metals had been identified based on their reaction with carbon:

1. Materials such as B, V, Cr, Mn, Y, Zr, Nb and Mo that can be encapsulated by carbon but the underlying nanoparticle is a carbide

2. Elements which form separately to carbon cages such as Cu, Zn, Pd or Ag as they do not react with carbon

3. Elements which form as carbides without encapsulation such as Al, Si Ti and W

4. Iron group metals such as Fe, Co and Ni which actively stimulate the formation of graphite and so most readily form graphite encapsulated metallic particles

Schematics of these structures are shown in figure 2.3.

The different behaviour of the metal in response to carbon gives rise to a range of different structures. Metals which fall into the first category result in carbide particles surrounded by some graphitic cages but also amorphous carbon in contrast to the third
2.3. CARBON ENCAPSULATED METAL NANOPARTICLES

Figure 2.3: Schematic of nano-onion structures showing nanoparticles and graphitic cages

Spherical coherent onion-like graphitic shells will often form around metallic nanoparticles to form structures which have become known as “nano-onions”. The nano-onion structure can be distinguished from the more general carbon encapsulated metal structures by the presence of the graphitic shells as shown in frame 4 of figure 2.3.

2.3.1 Fabrication techniques

Given the attractive nature of carbon encapsulated metal, there have been a wide range of approaches employed for their production. Starting in the early 1990s, arc discharge was the first technique to be used to produce these “nano-onion” structures. The earliest
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work involved lanthanum [50], yttrium [51] and Fe$_2$O$_3$ [52] before attention moved to iron, nickel and cobalt [53].

Arc discharge consists of passing a large DC voltage between two electrodes such that an arc between the two removes material from the anode which then falls into a crucible below. Early methods [53] involved drilling a hole in the centre of a graphitic anode and packing it with metal powder. While this did produce some nano-onion structures, the crystallite size varied widely from 2 - 50 nm and the carbon encapsulation was uneven and of a low quality. There were also large amounts of carbon debris [54] and uncoated metal particles. While these could be removed through acid treatments, this led to an additional processing step and reduced the overall material utilisation.

A development of this method was to use a liquid hydrocarbon as the carbon source. This allowed for more careful control of the carbon supply and therefore reduced the amount of unwanted carbonaceous material. By injecting liquid alcohol between a bulk metal anode and graphite cathode [55] it is possible to create more uniform metal nanoparticles (30-70 nm) and have much better defined carbon encapsulation with significantly less excess carbon. An alternative method to limit the supply of carbon [28] is to use two metallic electrodes and a graphitic crucible into which the nanoparticles drop. Since the metal is molten when it drops into the crucible it is able to take up some of the surrounding carbon and form a graphitic layer.

Another technique for the production of carbon encapsulated metal nanoparticles is the thermal decomposition of organometallic precursors. Nickel (II) acetylacetonate is a common precursor [56, 57, 58, 59], which when heated along with oleylamine, breaks down to form nickel nanoparticles. However it should be noted that there is rarely a well defined graphitic onion structure, with the carbon forming within the particle to create a carbide. The exception to this result is the instant pyrolysis method [47]: combining nickel acetylacetonate with a heavy oil (to act as the carbon source) and then heating to 900°C produces well defined carbon encapsulated nickel magnetic nanoparticles. These face centred cubic (fcc) pure nickel particles were typically 10 to 30 nm in size with a 4 - 5 nm thick set of graphitic encapsulation layers. This coating layer was found to be both coherent and uniform.

Also of note, is a detonation process [60] in which nickel nitrate, carbamide and ethyl alcohol were mixed with the explosive pentaerythritol tetranitrate to form an explosive charge. Following detonation in a nitrogen environment, crystalline nickel nanoparticles
(approximately 10 - 25 nm) were found surrounded by 3 - 5 nm thick shells consisting of graphitic and amorphous carbon.

While these techniques show potential in the formation of nano-onions, they are energy and time intensive, and generally produce low yields of poor quality material. By far the most promising technique for the production of nano-onion carbon encapsulated metal nanoparticles are those based around magnetron sputtering which have been shown to produce these structures in a much more facile way.

### 2.3.2 Sputtering based techniques

Two physical vapour deposition methods have been focused upon: ion beam sputtering and magnetron sputtering. Early attempts \[61\] used ion beam sputtering of two solid targets, the metal and carbon. The use of a solid carbon target rather than gaseous or liquid precursors simplifies the deposition significantly and allows for excellent compositional control. Due to the interaction between the metal and the carbon, the graphitic ordering occurs at relatively low temperatures (300°C). However the structure is very dependent on composition and heat treatments \[62\]. Low deposition temperatures (200°C) result in a completely amorphous film. Heating to 300°C begins to generate some graphite but only for high (greater than 50%) carbon content films. For metal rich films, heat treatments of 400°C are required to produce crystalline metal with graphitic encapsulation.

However the transformation temperatures are not themselves fixed and are dependent on a range of kinetic and thermodynamic factors during growth and any subsequent heat treatments. Ion beam deposition of carbon-nickel films \[63\] using methane as the carbon source, generated a nickel carbide phase which was largely amorphous until annealed at 300°C, which then only generated crystalline nickel and amorphous carbon. Rf-sputtered \[64\] carbon-nickel films showed some graphitisation in the as deposited state, while a heat treatment of 300°C produced well defined nickel carbide crystallites which eventually broke down at 400°C to form metallic nickel nanoparticles with several layers of graphitic encapsulation. Similar results were observed in DC sputtered films \[65\] although the as-deposited films already showed a columnar nickel carbide structure, which transformed to a graphite encapsulated metallic nickel particle structure when heated to 400°C. Clearly the structures produced and the transformation of phases is strongly dependent on the energy of the deposited species. This is highlighted in an experiment involving carbon
encapsulated silver [49]. Using a two target ion beam sputtering system, the as deposited films phase separated due to the low solubility of carbon in silver, and the carbon formed an amorphous interlayer between the silver particles. When heated to 500°C, this carbon transformed into graphitic cages around the particles. However this transformation temperature could be reduced to 300°C when ion beam assistance was used.

Different metals have different affinities and solubility with relation to carbon. Transition metals form carbides with varying levels of ease [66]. Early transition metals such as Ti, W, V and Zr easily form very stable carbides while Cu and Zn form carbides with more difficulty. Interest often lies with the intermediate group of Fe, Co and Ni which form metastable carbides. Indeed a study [67] investigated the behaviour of a three metal system, (Ni$_{66}$Fe$_{22}$Co$_{12}$)$_x$C$_{1-x}$. While in the as-deposited film NiFeCo crystallites were observed to form, above 300°C Ni$_3$C was also observed, until at temperatures above 500°C the nickel carbide broke down and NiFeCo particles were encapsulated by graphitic shells.

Clearly the formation of the as-deposited and post-anneal structures is a complex process, dependent not only on the film composition in terms of the metal, but also in terms of the metal to carbon ratio. Due to its interesting magnetic properties and its carbide forming behaviour, nickel based metal-carbon nanocomposites will be the focus of this study. Therefore the growth mechanisms of these structures in particular will be explored further.

2.3.3 Nickel carbon growth mechanisms

a) Phase Structure

Nickel in its pure state exists as a face centered cubic phase [68] as can be seen by the phase diagram in figure 2.4. There also exists a hexagonal phase of pure nickel [69] which is a metastable phase and therefore does not usually appear on the phase diagram. Experimental details on hexagonal nickel are somewhat complicated. Counterintuitively this metastable phase has been reported [70] to form at elevated temperatures (in excess of 200°C) compared to the thermodynamically stable fcc structure. This metastable phase is then stable below 500°C, above which it decomposes back to the stable fcc phase [71, 72]. However it has also been demonstrated [73] that there is a size dependence on the phase of pure nickel. For particles smaller than 4 nm the hexagonal phase appears to be more stable, however for larger sizes the metal reverts back to its fcc phase [73].
2.3. CARBON ENCAPSULATED METAL NANOPARTICLES

![Phase diagram for the carbon nickel system showing a metastable carbide phase](image)

Figure 2.4: Phase diagram for the carbon nickel system showing a metastable carbide phase [68]

This complex behaviour extends to the case of carbon containing films. In the presence of carbon, a metastable carbide (Ni$_3$C) often forms [68] which due to it often being experimentally observed, is shown on the phase diagram as a dashed line in figure 2.4. The low solubility of carbon in nickel at elevated temperatures (2.7 at% at 1326°C) along with no ionic bonding and only weak covalent bonding allows for the formation of a metastable carbide [74, 75]. Due to the lower binding energy of a carbon-nickel bond compared to that of the carbon-carbon bond and the low diffusivity of carbon in nickel carbide [76] a metastable phase of Ni$_3$C can be readily produced. With an enthalpy of formation of around +10 kJ mol$^{-1}$ [77], at room temperature the energy of formation of Ni$_3$C is 27 kJ mol$^{-1}$ [78]. Therefore under certain conditions [79] (below 400°C), the carbon atoms lack the mobility to separate from the nickel and so become trapped and bond with the nickel to form the Ni$_3$C carbide.

However these relatively weak covalent bonds [75] are readily broken down at elevated temperatures and the diffusion rate of carbon also increases, leading to increased decomposition. Given the low equilibrium solubility limit of carbon in nickel, once the covalent
bonds are broken and the mobility increases, the carbon atoms diffuse from the carbide and two separate phases form: a pure nickel and pure carbon phase.

Nickel is also known to react with oxygen to form nickel oxide. Indeed NiO is a wide band gap semiconductor [80] and is often grown via magnetron sputtering. In this work the formation of nickel oxide would be an unwanted impurity and it is therefore important to ensure it does not form. While it is strongly thermodynamically favourable to form nickel oxide (at room temperature the equilibrium oxygen pressure is $10^{-78}$ Pa and the reaction has a free energy, $\Delta G$ of -420 kJ mol$^{-1}$ as calculated from an Ellingham diagram [81]), kinetically the formation of the oxide is very difficult [82]. For oxygen partial pressures of less than several percent in the sputtering gas, no oxide is formed and metallic films result [80].

In this work, prior to deposition the deposition chamber is evacuated such that the oxygen pressure is below $10^{-6}$ Pa, this corresponds to an impingement rate on the surface of around $5 \times 10^{16}$ m$^{-2}$s$^{-1}$ whilst the nickel and carbon impingement rate is closer to $1 \times 10^{18}$ m$^{-2}$s$^{-1}$ based on the average deposition rate. Additionally, oxide growth on the target when it is exposed to the atmosphere is very slow [82] at room temperature and will be removed by pre-sputtering. Oxide formation on the target at the low oxygen pressure inside the chamber is also not observed [80].

There is a fundamental problem in distinguishing between the hexagonal nickel phase and the hexagonal nickel carbide phase in that they have virtually identical structures resulting in a lattice parameter difference of just 0.001 nm [83]. This is because the two structures share the same sublattice, with the carbide having carbon atoms in a third of the octahedral interstices. The addition of the carbon atoms has negligible effect on the lattice spacing and so the X-ray diffraction patterns of the two structures are identical. X-ray photoelectron spectroscopy is often used to attempt to distinguish the two phases, however due to the large number of bond types (sp$^2$ and sp$^3$ bonds as well as different forms of Ni-C bonds and C-O bonds) the difficulty in the fitting of a model to this region means that this method is at best inconclusive.

Magnetic measurements are also ambiguous: reported values for the coercive field for hexagonal nickel vary from 0.3 to 30 emu/g [57], while others claim it to be non-magnetic [84] or even antiferromagnetic. This confusion most probably occurs as a result of the misidentification of nickel carbide as hexagonal nickel. It is most likely that nickel carbide is non-magnetic [85] due to the hybridisation of the Ni-C bond, however defects can lead
2.3. CARBON ENCAPSULATED METAL NANOPARTICLES

to locally nickel rich regions which may be magnetic. Hexagonal nickel is thought to have similar magnetic properties to cubic nickel [86], though it often shows superparamagnetic behaviour due to its stability as very small particles. Therefore magnetic measurements could offer a promising method to distinguish between the phases.

Like any metastable phase, the carbide can be converted to the stable nickel fcc phase under the correct conditions. Under bulk conditions, the carbide is stable below 419°C [87] and completely decomposes at 700°C. However for thin films this decomposition can begin at temperatures closer to 380°C [2] though the decomposition might not be complete until 600°C [65] depending on exact composition and growth conditions. This decomposition is often accompanied by the generation of nano-onion structures.

b) Nano-onions

There are a number of possible mechanisms for the formation of nano-onion structures. As discussed earlier, in the case of carbon nanotube growth, there is a supersaturation-precipitation mechanism. This requires a temperature variation in the process such that the carbon can dissolve in the nickel at high temperature and then precipitate out on cooling. In most physical vapour techniques no such gradient exists and so there must be an alternative formation mechanism. Additionally, having precipitated out the excess carbon, there will still be an equilibrium level of carbon dissolved in the metal, one would therefore expect to observe carbides in the centre of the graphitic cages.

A second growth mechanism has been proposed in the case where no such temperature variation exists [88]. Investigated by depositing nickel on amorphous carbon, it was observed that the nickel segregated into islands. The films were then heated to 670°C and some graphitisation was observed at the interface between the nickel and the carbon substrate. It was determined that when the nickel was deposited at high temperature (greater than 500°C) there was no increase in graphitisation and that this was because a graphitic layer had formed on deposition between the nickel and the amorphous carbon. This interlayer prevented diffusion between the nickel and carbon and so no further graphitisation could occur. This suggests that the graphitic layers cannot template further graphite layers, and any additional graphitisation would have to occur at the nickel surface and therefore carbon diffusion across the graphite would be necessary. Samples grown at lower deposition temperatures demonstrated a different behaviour [89]. Upon
annealing the carbon nearest the nickel particle diffuses along the surface and nucleates a graphitic layer as before. Carbon material from beneath the particle then diffuses up to reach the metal graphite interface where it too nucleated a new layer, creating a second layer inside the first as shown schematically in figure 2.5. This places a stress on the enclosed nickel particle which then faces one of two fates. If there is sufficient energy, for example from electron irradiation [1], then there will be defects in the graphitic layers and the nickel atoms can diffuse through the graphite, before recrystallising on the outside of the particle. These defects would also allow carbon material to diffuse towards the metal carbon interface and so graphitisation could continue. If, however, there are insufficient vacancies, then the stresses will continue to grow until the particle breaks out of the graphitic cage at a weak point [90]. It is possible to determine whether there are sufficient defects for atoms to diffuse across the graphitic layers; if there are defects then the creation of a carbon nickel crystalline phase on the outside of the graphitic cages and a carbon nickel phase at the boundary between the underlying particle and the first graphitic layer is observed. By contrast, a lack of mobility across the encapsulating layers results in a great number of “broken” cages and metal particles which have diffused across the surface leaving a thin graphitised layer behind them.

These models describe a static situation where the supply of carbon and nickel is fixed and growth is limited by diffusion. In the case of physical vapour deposition, there is a constant supply of nickel and carbon atoms arriving across the film. This gives rise to the
2.3. CARBON ENCAPSULATED METAL NANOPARTICLES

possibility of a different formation mechanism.

In physical vapour deposition, the structure depends on the interplay between surface diffusion, growth rate and elastic stress [91]. This process is made additionally complicated by the presence of metastable phases and graphitising materials. It has been observed in several studies [92, 5] that magnetron sputter deposition of carbon and nickel produces a columnar structure of Ni$_3$C at low deposition temperatures (less than 600 °C) [93]. The Ni$_3$C metastable carbide phase forms due to the low surface mobility of the carbon atoms on the nickel, therefore any carbon adatoms which deposit on to a growing nickel particle become stuck and form covalent bonds [94]. However when heated, this metastable carbide phase breaks down to form a face centred cubic phase of pure nickel. This variation in phase formation is shown schematically in figure 2.6.

![Figure 2.6](image-url)

**Figure 2.6:** Schematic of structural variation depending on growth conditions and heating. Black circles represent carbon atoms while grey circles represent nickel atoms.

At high deposition temperatures the pure nickel phase has very low carbon solubility and so carbon adatoms now diffuse across the surface of the nickel regions to the edges [65] where they form graphitic layers as shown in figure 2.7b. Nickel nanoparticles act as a nucleation point for graphitic carbon and encourage the formation of ordered layers. However these ordered layers of carbon then prevent nickel atoms which deposit on areas other than an existing nickel particle to diffuse to one in order for it to grow (2.7c). The ordered carbon therefore acts to prevent the growth of the nickel particles, forcing them to renucleate new particles instead (2.7d). This repeated renucleation and limited growth gives rise to a nanoparticle structure with ordered graphitic layers surrounding them, and...
2. METAL CARBON NANOSTRUCTURES

Figure 2.7: Schematic of phase separation occurring when there is high mobility. Carbon atoms which land on nickel particles (b) diffuse quickly across the surface to reach the carbon matrix. However nickel atoms landing on carbon (c) are unable to diffuse across ordered carbon and so are forced to renucleate a new nanoparticle (d).

This is indeed what is observed. The onset of graphitic ordering is observed to occur at temperatures around 200 °C, however the carbide does not break down until about 400 °C. This means there is a narrow temperature window where excess carbon which does not form a carbide phase can still form graphitic structures in the gaps between the carbide grains. The carbide grains themselves are strongly dependent on the initial nucleation of the nickel particles. As mentioned previously, nickel forms as island structures rather than a continuous layer \[95]. The size of these islands is strongly dependent on the deposition temperature as this determines the surface mobility of the nickel. At low deposition temperatures, both surface and bulk diffusion are negligible and so nucleation dominates over grain growth and a fine grained carbide structure forms. As the deposition temperature increases (provided it remains below the temperature at which the carbide breaks down) there is an increase in surface mobility and so the initial islands grow, which in turn coarsens the columnar structures. Another point of interest is the nature of growth of multiple graphitic layers. In the case of nickel being deposited onto a carbon substrate it was thought that the nucleation of the graphitic layers had to occur at the metal surface, as it was the metal which encouraged the graphitisation. However, since no nickel atoms, or nickel carbide phase is observed on the outer layers of the graphitic shells, and no broken shells are observed, this suggests that the graphitic layers grow outwards,
with the previous layer acting as a template for the next.

Clearly the control of graphite encapsulated metal nanoparticles is strongly dependent on the interplay between bulk and surface diffusion controlling the stable phase and growth mechanism. It is therefore vital that these factors can be controlled and varied.

While substrate heating in conjunction with magnetron sputtering offers a level of control, it is a very aggressive process which often involves post-deposition annealing. Utilisation of ionised sputter techniques and substrate biasing can offer the same control in a single step process [96].
2. METAL CARBON NANOSTRUCTURES
Chapter 3

Controlling Film Microstructure and Ionised Magnetron Sputter Deposition (IMSD)

Controlling film microstructure is key for a wide range of applications. Whether to produce single crystal films or nanostructured devices, microstructure is key to device properties. Therefore much work has gone into developing a range of techniques to produce thin films and investigating how deposition parameters effect film microstructure. An overview of these techniques and the theory behind film formation is outlined here.

3.1 Thin film deposition

DC magnetron sputter deposition is a widely used physical vapour deposition technique to produce thin films [97]. The process has been used for many years and in its most basic form consists of a bulk target of the material the coating is to be made from. This target is placed within a vacuum which is then backfilled with a “sputtering gas”. This gas should consist of inert atoms and so argon is typically used. A negative voltage is then applied to the target. This large electric field ionises the sputtering gas in the vicinity of the target and creates a “glow discharge” plasma near the target. Since the target is negatively biased, the positive argon ions are attracted to the target. When the ions strike the target they transfer momentum which then removes, or “sputters” a target
atom. This atom travels through the low pressure gas and lands on the substrate that is to be coated. The sputtering event also generates secondary electrons near the target surface as a result of the ion bombardment. This production of electrons due to the energetic collision of ions with the surface is vital to maintain the plasma as it increases the electron density near the target surface and therefore ensures the plasma is stable. For nickel, each energetic ion collision will produce approximately 0.03 electrons \[98\].

The introduction of magnetron sputtering in the 1970s \[99\] was an important development in making it the process of choice for a wide range of widely-used coatings. By adding a magnetic field perpendicular to the electric field near the target, both the glow discharge electrons and secondary electrons are confined to a helical path close to the surface of the target as shown in figure 3.1 \[97\]. Since the residence time of the electron near the target is increased, the minimum pressure required to sustain the plasma is decreased drastically from, typically, around 3 Pa to 0.1 Pa. Additionally, since the plasma is more closely confined, smaller bias voltages are required on the target (a few hundred volts rather than a few thousand volts) \[8\]. The lower pressure means the sputtered atoms undergo fewer collisions before reaching the substrate and so retain more of their kinetic energy, typically the sputtered atom has an energy comparable to the surface binding energy of the target material \[100\]. The reduced level of scattering also increases the deposition rate.

In traditional magnetron sputtering, collisions between the gas ions and the target generate sputtered atoms. There is a probability that these atoms will be ionised by the glow discharge. However, given that the target is negatively biased, ions will be strongly attracted back towards the target. Furthermore, the addition of a magnetic field confines the glow discharge to near the surface of the target. Therefore the size of the glow discharge will be smaller than the mean free path of the sputtered atoms, reducing the chance of ionisation occurring. The combination of an electric field attracting ions
towards the target and a low residence time of neutrals in the glow discharge leads to a low ion fraction (typically around 5% [101]) in the flux of traditionally sputtered atoms reaching the substrate [7].

The energy of the depositing flux is most often controlled via the target to substrate distance \((d)\) or the pressure \((p)\). By increasing \(p \times d\) the depositing species undergo more collisions with the cold sputtering gas and therefore lose energy. This also disrupts their trajectory resulting in a more random directionality and reduced overall deposition rate.

However in ionised sputter deposition, there is a greater fraction of ions in the depositing flux. The depositing species can therefore be manipulated using an electric or magnetic field, controlling the energy with which the deposit on the substrate. An additional level of control over energy flux to the growing film is made possible in order to gain better control over the resulting structures. One of the first methods to increase the ionisation fraction of the depositing flux was unbalanced magnetron sputtering [8]. By increasing the strength of the outer magnets as shown in figure 3.2, the magnetic field is no longer closed and now extends out towards the substrate. Since electrons travelling parallel to the magnetic field are not acted on by it, they may escape outwards, extending the plasma region away from the target. The ion flux is therefore proportional to the target current and so can be controlled by varying the power applied. Window [102] investigated a range of unbalanced magnetron designs, varying the field strength and the level of unbalance. He found it was possible to control the ion flux to the substrate through magnetron design, however there was a significant variation in ion current across the substrate depending on the intersection with the field lines. In order to increase the ion current without altering the magnetron design, larger powers need to be applied to the target. There is however an upper limit to the power that can be applied before the target overheats or begins to arc.

Gudmundsson et al [10, 7] reviewed a range of other deposition techniques which aim to increase the ion fraction in the deposition flux such as microwave electron cyclotron resonance deposition (ECR plasmas), ionised hollow cathode magnetron sputtering (HCM) and, the technique of interest here, radio frequency inductively coupled plasma deposition [10].

The issue of overheating the targets as the applied power increases, can be overcome to some degree through the use of high power impulse magnetron sputter deposition (HIPIMS). In HIPIMS, high plasma densities are achieved by applying very large (\(> 1000\))
W cm\(^{-1}\) powers to the target but for a very short period of time (up to a few hundred µs), which is then followed by a rest period before the short power pulse is applied again. This repeated pulsing produces a very high density plasma (10\(^{19}\) cm\(^{-3}\)) which can then be used to produce high quality dense films without over heating the target. However producing such large, short bursts of power requires complex power supplies and is therefore a rather expensive process. Additionally, the low duty cycle (the proportion of each cycle for which the power is applied) means that the overall deposition rate is often lower than that for traditional balanced magnetron sputter deposition [10].

ECR plasmas use microwave radiation to excite plasma electrons to their resonant frequency, making them very energetic [103]. This electron temperature varies greatly with pressure but is typically around 8 - 10 eV. The resulting plasma density is typically around 10\(^{18}\) m\(^{-3}\) [104]. However the high cost of operating microwave power supplies, the limited range of frequencies permitted by law and the large magnets required to control the power make ECR of limited practical use. HCM sputtering uses a novel magnet design to confine the plasma from a standard target into a cup shaped confinement. Ions are then extracted from the cup which then flow towards the substrate. This allows HCM to generate very large plasma densities (around 10\(^{19}\) m\(^{-3}\)).

A limitation of systems which use ions produced via collisions with secondary emitted electrons from the sputtering event is that the ion flux is directly related to the sputter rate. This means that a number of the variables which may wish to be controlled, ion fraction and ion flux for example, are interdependent and so the varying effects of different aspects of the deposition are hard to separate. By separating the ion production from the
sputtering, it is possible to more easily control the various parameters of the discharge which in turn allows easier control of film structure. A widely used approach to achieve this is the radio frequency inductively coupled plasma which offers independent variables to control the nature of the depositing flux.

### 3.2 Inductively coupled plasma sputter deposition

An inductively coupled plasma (ICP) describes a plasma sustained via coupling of the gas to a coil, itself submerged in the gas and then driven at RF frequencies. Discovered by Hittorf in 1884, ICPs were originally used for wafer etching and other processing applications, attention then turned to using these plasmas to ionise depositing species during film growth. Seminal works by Rossnagel and Hopwood during the 1990s built up the practical and theoretical understanding of the technique. Early applications of the high ion ratio flux used electric fields to draw the flux into a collimated stream which would then deposit uniform layers on high aspect ratio vias, though the control over ion energy made possible soon led to the use of the technique to control film microstructure.

The plasma occurs as the high frequency oscillating field fluctuates too quickly for the slow ions to respond and as a result only the electrons react. These electrons oscillate rapidly, drawing power from the oscillating electric field until they have sufficient energy to become free electrons resulting in a plasma.

For applications in film deposition, the coil is placed between the sputtering glow discharge and the substrates. This secondary plasma must be sufficiently large to ensure it exceeds the mean free path of the depositing species. This ensures the depositing species have a sufficiently long residence time (which is increased further by operating at pressures greater than 1 Pa typically) in the discharge such that a significant fraction (>50%) become ionised.

The mechanism of inductive coupling is best described using the transformer model as shown in figure 3.3.

This model uses the N turn coil as the primary winding of a transformer and models the plasma as a single coil secondary winding. As a time varying voltage \( V(t) = V \sin(\omega t) \) is applied, a current \( I(t) = I \sin(\omega t) \) flows in the coil. Ampere’s law tells us the alternating current creates a magnetic field within the coil:
CONTROLLING FILM MICROSTRUCTURE AND IONISED MAGNETRON SPUTTER DEPOSITION (IMSD)

![Figure 3.3: Schematic diagram of the transformer model of inductively coupled plasmas](image)

Figure 3.3: Schematic diagram of the transformer model of inductively coupled plasmas

\[ \oint B \cdot dl = \mu_0 I_{\text{enc}} \quad (3.1) \]

where \( B \) is the magnitude of the magnetic field generated along the length \( l \) of the coil due to the current carried, \( I_{\text{enc}} \), and \( \mu_0 \) is the permeability of a vacuum.

So for a coil of height \( h \) with \( N \) turns carrying a current \( I \) the resultant magnetic field is:

\[ B_{\text{coil}} = \frac{\mu_0 N I}{h} \quad (3.2) \]

Since the current varies with time, this magnetic field varies, creating a mutual inductance in the plasma as a result of the coil:

\[ L_{\text{coil}} = \frac{\phi_{\text{plasma}}}{I_{\text{coil}}} \quad (3.3) \]

Where \( L_{\text{coil}} \) is the mutual inductance in the plasma as a result of the magnetic flux \( \phi_{\text{plasma}} \) and the current flowing through the coil \( I_{\text{coil}} \). Given that the coil sits in the plasma, it is assumed that the magnetic field experienced by the plasma is equal to that created by the coil. Therefore the mutual inductance experienced by the plasma coil, as a result of the flowing current is:

\[ L_{\text{coil}} = \frac{B A}{I} = \frac{\mu_0 N \pi r^2}{h} = \frac{\mu_0 N \pi r^2}{h} \quad (3.4) \]

Where \( r \) is the coil radius, which is assumed to be equal to the plasma radius.

The magnetic field from the coil induces a current \( i \) in the plasma. This results in an additional self-inductance \( L_{\text{plasma}} \) so the magnetic field created by the plasma, \( B_{\text{plasma}} \) is therefore:
Given that the number of coils representing the plasma $N_{\text{plasma}}$, is assumed to be 1 we find the self-inductance to be:

$$L_{\text{plasma}} = \frac{B_{\text{plasma}} A}{i} = \frac{\mu_0 \pi r^2}{\hbar}$$  \hfill (3.6)

The total voltage across the plasma is therefore the sum of the two effects, the mutual inductance and the self inductance. The voltage across an inductor is given by $V_R(t) = I_0 \omega L \sin(\omega t)$, and so the voltage in the plasma, the plasma potential $V_{\text{plasma}}$, is given by:

$$V_{\text{plasma}} = \omega L_{\text{coil}} I + \omega L_{\text{plasma}} i$$  \hfill (3.7)

In terms of plasma production this means the application of an RF power source to the coil produces a magnetic field, which in turn induces a current in the plasma which itself oscillates. It is this oscillation which leads to the ionisation of the species and sustains the plasma. In an RF driven plasma it can be assumed that the ions themselves are largely stationary as a result of their larger mass.

Given the smaller mass of electrons, there are a large number of electrons oscillating which leads to ionisation through two main mechanisms [11]:

**Electron impact ionisation** A high energy electron ionises the metal atom directly:

$$e^- + M \rightarrow M^+ + 2e^-$$

**Penning ionisation** A high energy electron collides with an inert atom to form an excited metastable ion which then collides with, and ionises, a depositing metal atom:

$$M + Ar^* \rightarrow M^+ + e^- + Ar$$

Where $Ar^*$ denotes an excited argon atom and $M^+$ denotes a metal ion. Both of these mechanisms require a collision with the depositing species. At low pressures the mean free path will be greater than the size of the plasma, therefore ICP require relatively high pressures, typically between 0.5 and 5 Pa. At high pressures the sputtered atoms undergo a number of collisions and become thermalised, losing the energy they sputtered with (approximately their surface bonding energy, $\approx 2 \text{eV}$). The relative importance of the two ionisation mechanisms is then dependent on the electron density within the plasma. At
low electron densities \((n_e < 10^{11} \text{ cm}^{-3})\) there are insufficient electrons for electron impact ionisation to occur and so Penning ionisation dominates. Above \(n_e = 10^{11} \text{ cm}^{-3}\) most of the metal ions are generated by electron impact \([103]\). Typically in the case of an ICP, the electron density is approximately \(10^{12} \text{ cm}^{-3}\) \([11]\) and therefore electron impact ionisation is the dominant mechanism.

In order for ionisation to occur, the collision must be sufficiently energetic, and so the ion content in the plasma depends on the nature of the atoms being ionised. In the case of electron impact ionisation this is dependent on three factors: the ionisation cross sectional area, the ionisation potential and the mobility of the ion. The first two factors indicate how easy it is to form the ion, while the mobility of the ion governs how many are lost to the surroundings. Carbon, for example, is difficult to ionize \([103]\) due to its large potential (11.26 eV), small cross sectional area and high mobility (3.6 cm\(^2\) V\(^{-1}\) s\(^{-1}\)). Nickel, by contrast, has a much smaller ionisation potential (7.63 eV) and a low mobility (2.3 cm\(^2\) V\(^{-1}\) s\(^{-1}\)) making its ionisation fraction much higher.

To ensure a high ionisation rate, it is therefore important to make sure there is an efficient transfer of power from the RF supply connected to the coil and the plasma. Power supplies are designed with a specific impedance (usually 50 Ω) and only deliver the maximum power if this impedance is conjugate to that of the load attached to it. The load impedance is made up from the capacitance between the coil and plasma and the inductance of the coil itself. Further to these contributions, additional inductance and capacitance are introduced in the form of a “tuning” circuit \([97]\).

The tuning is achieved using a π tuning circuit as shown in figure 3.4. The natural impedance of the coil system is generally much greater than that of the RF source and since the electrons are much more mobile than the ions there is also a phase shift between the voltage and current. This leads to a significant reflected power unless the tuning circuit is adjusted to reduce the current. The circuit also brings the current and voltage back into phase, thereby making the whole system operate as a resistive load.

![Schematic diagram of a π tuning circuit](image.png)
3.2. INDUCTIVELY COUPLED PLASMA SPUTTER DEPOSITION

Having produced the ionised flux, the deposition proceeds to form the film. The overall process of deposition is outlined in figure 3.5. In this work two targets were used (nickel and carbon) and the ionisation process occurs for both, though for clarity the schematic shows the process for just one target.

![Schematic diagram of the 2 target IMSD process](image)

Figure 3.5: Schematic diagram of the 2 target IMSD process

The 4 main steps in the process are;

1. As with all sputtering processes, an inert gas ion strikes the target which acts as a cathode to create the glow discharge. The inert atom transfers momentum to the target which may cause a target atom to be ejected or “sputtered”.

2. The sputtered atom moves through the inductively coupled plasma which is created by passing an alternating electrical current through a coil.

3. Ionisation of the depositing atom then occurs within the secondary plasma.

4. The depositing ion can then be controlled by applying an electrical bias to the substrate holder.

Having produced an ionised flux in the secondary plasma, the ions then move towards the substrate. The behaviour of the plasma near the substrate holder is complex and worthy of separate attention.
3. CONTROLLING FILM MICROSTRUCTURE AND IONISED MAGNETRON SPUTTER DEPOSITION (IMSD)

3.3 Plasma behaviour at the substrate

In an inductively coupled plasma, the plasma itself is quasi-neutral \( (n_e \approx n_i) \) in that there are as many ions \( (n_i) \) as there are electrons \( (n_e) \). However, due to their very different masses and energies, their velocities are very different. Considering their thermal velocity:

\[
v_{\text{thermal}} = \sqrt{\frac{8k_B T}{m \pi}}
\]  

Where \( k_B \) is the Boltzmann constant, \( T \) is the temperature and \( m \) is the species mass.

We find that the velocities of the electrons and ions are:

\[
v_{\text{electron}} = \sqrt{\frac{8k_B T_e}{m_e \pi}} \quad v_{\text{ion}} = \sqrt{\frac{8k_B T_i}{M_i \pi}}
\]

Given that the ion mass \( (M_i) \) is many orders of magnitude larger than the electron mass \( (m_e) \), the inductively coupled oscillating electric field drives the electrons preferentially, heating them much more, such that the electron temperature \( (T_e) \) is in the range of a few eV, while the ion temperature \( (T_i) \) is two orders of magnitude lower \[111, 112, 10\]. These factors mean that \( v_{\text{electron}} \) is much larger than \( v_{\text{ion}} \). This higher mobility has dramatic effects on the charge distribution within the plasma, creating a sheath region near any conductive surfaces.

Initially \[108\] the distribution of ions and electrons is uniform within the chamber (which has earthed walls) as shown in figure 3.6a. Since the species are evenly distributed, there is no net electric field within the plasma and so the potential within the plasma, \( \phi \), is zero. However a very short time after, the more mobile electrons (the electron velocity it around 100 times the ion velocity \[108\]) reach the walls of the chamber and are lost to earth (figure 3.6b). This creates an electron deficient region near the edges of the chamber. This sheath region is very thin \( (s \ll w) \), a few millimetres, however it contains many more ions than electrons \( (n_e \ll n_i) \). This generates a potential profile shown at the bottom of figure 3.6b where the plasma potential itself becomes positive but falls to zero in the sheath region. This electric field then reflects electrons away from the sheath back in to the plasma, but accelerates ions towards the wall.

This situation arises for any earthed object placed within the plasma. In the case that the object is electrically isolated then a slightly different situation occurs as shown in figure 3.7.
3.3. PLASMA BEHAVIOUR AT THE SUBSTRATE

Figure 3.6: Schematic diagram of sheath formation (a) before the electrons have moved to the chamber walls and (b) once the sheath has formed. [108]

Figure 3.7: Schematic diagram of sheath formation for an electrically floating substrate where $V_p$ is the plasma potential and $V_f$ is the floating potential. [108]

Here the conductive object is initially bombarded by many more electrons than ions, again due to their greater mobility. This produces a negative charge on the object which
begins to repel further electrons from impacting on the surface and attracts ions. Eventually a potential is reached whereby the flux of ions and electrons is equal and so no net current flows, this potential is known as the floating potential. It is important to note that there is still an ion flux to the substrate and so ion bombardment still occurs. The low electron density within the sheath, means that the plasma cannot be sustained in the region closest to the surface and so a “dark space” is produced. The size of the potential drop across the sheath region can be calculated by balancing the flux of ions and electrons. The electric field in the region is defined as:

$$E = -\frac{dV}{dx}$$ \hspace{1cm} (3.10)

From Poisson’s equation we find:

$$\frac{dE}{dx} = \frac{\rho \cdot e}{\epsilon_0}$$ \hspace{1cm} (3.11)

Thus:

$$\frac{d^2V}{dx^2} = -\frac{\rho \cdot e}{\epsilon_0}$$ \hspace{1cm} (3.12)

Where the charge density \( \rho = |n_e - n_i| \), \( e \) is the charge on an electron and \( \epsilon_0 \) is the permittivity of free space. In order to determine the density of each carrier \( n_e \) and \( n_i \) we must consider the affect of the sheath region.

Consider an ion at the boundary between the sheath and the plasma. If we define this point to have a zero potential then the energy of the ion as it accelerates across the sheath (due to the potential that exists there) is given by:

$$\frac{1}{2}Mu^2(x) = \frac{1}{2}Mu_s^2 - qe\phi(x)$$ \hspace{1cm} (3.13)

Where \( M \) is the ion mass, \( q \) is the charge on the ion, \( u \) is its velocity and \( u_s \) is the velocity of the ions as they enter the sheath. The energy gained due to the potential across the sheath is given by the product of the charge on the ion \( qe \) and the potential \( \phi \). Given that no new ions are formed in the sheath (due to the low electron density), the number of ions entering the sheath must be equal to the number of ions in the sheath, \( n_i(x)u(x) = n_{is}u_s \). Here \( n_i(x) \) is the density of ions at a position \( x \) within the sheath, travelling at velocity \( u(x) \), and \( n_{is} \) and \( u_s \) are the density and velocity of ions at the
sheath boundary. Combining these two factors gives the ion density in the sheath to be:

\[ n_i = n_{is} \left( 1 - \frac{2e\phi}{M_u^2} \right)^{-1/2} \quad (3.14) \]

We then assume that the electron density follows a Boltzmann distribution \[^{113}\]:

\[ n_e(x) = n_{es} e^{\phi(x)/T_e} \quad (3.15) \]

Where \( n_{es} \) is the electron density at the sheath edge. Therefore, combining equations \[^{3.14}\] and \[^{3.15}\] with equation \[^{3.12}\] and assuming at the sheath edge \( n_{es} = n_{is} = n_s \), we find:

\[ \frac{d^2 \phi}{dx^2} = \frac{e}{\epsilon_0} (n_e - n_i) = \frac{en_s}{\epsilon_o} \left[ \exp \phi/T_e - \left( 1 - \frac{2e\phi}{M_u^2} \right)^{-1/2} \right] \quad (3.16) \]

This equation defines the shape of the sheath potential curve and as a result the ion and electron densities.

The size of this sheath region is dependent on a parameter known as the “Debye Length” or the electrostatic screening length. This characteristic length is the distance over which significant charge variations can occur, as such a sheath forming on a naturally floating substrate will be a few Debye lengths wide. This characteristic length represents the scale at which charge non-uniformity can spontaneously occur, since below this scale the charges can redistribute themselves. Using equation \[^{3.16}\] and assuming immobile ions (since we are interested in the scale at which electrons can move with respect to the ions) we find:

\[ \frac{d^2 \phi}{dx^2} = \frac{en_s}{\epsilon_o} \left[ \exp \phi/T_e - 1 \right] \quad (3.17) \]

Using the Taylor expansion for \( \exp(\phi/T_e) \) since \( \phi \ll T_e \):

\[ \exp \left( \frac{\phi}{T_e} \right) = 1 + \frac{\phi}{T_e} \quad (3.18) \]

Which when substituted back into equation \[^{3.17}\] gives:

\[ \frac{d^2 \phi}{dx^2} = \frac{en_0 \phi}{\epsilon_o T_e} \quad (3.19) \]
A solution to which is:

$$\phi = \phi_0 \exp \left( -\frac{|x|}{\lambda_{De}} \right)$$

(3.20)

Where

$$\lambda_{De} = \left( \frac{\epsilon_0 T_e}{e n_0} \right)^{1/2}$$

(3.21)

Such that $\lambda_{De}$ can be thought of as a decay length over which charge can redistribute itself. Any perturbation less than this length can be undone by the movement of electrons. This length provides a characteristic size over which plasma variations (such as the sheath size) can occur and is typically a few mm [108] in size.

### 3.4 Ion energy

While equation [3.16] describes the shape of the potential, we are also interested in the difference between the floating potential (the voltage which occurs due to the accumulation of charge on an object in plasma) and the plasma potential. To calculate this we must equate the flux of ions and electrons, since this is the condition which defines the floating potential.

The flux of electrons can be calculated using kinetic theory [108]. The number of electrons striking the floating object per unit area is given by $J = \frac{1}{4} n \bar{v}$ where $n$ is $n_e$ which we assume follows the Boltzmann distribution in equation 3.15. We also assume that they have a thermal velocity given by:

$$\bar{v} = \left( \frac{8eT_e}{m_e\pi} \right)^{1/2}$$

(3.22)

For the ions, we assume no new ions are produced in the sheath and so the ion density is simply $n_i$. The velocities can then be calculated from equation 3.16.

Multiplying equation 3.16 by $d\phi$ gives:

$$\int_0^\phi \frac{d\phi}{dx} \frac{d}{dx} \left( \frac{d\phi}{dx} \right) dx = \frac{e n_s}{\epsilon_0} \int_0^\phi \frac{d\phi}{dx} \left[ \exp \frac{\phi}{T_e} - \left( 1 - \frac{2e\phi}{M u_s^2} \right)^{-1/2} \right] dx$$

(3.23)
Integrating and using the assumption $\phi$ and $d\phi/dx$ are zero at $x = 0$ we find:

$$\frac{1}{2} \left( \frac{d\phi}{dx} \right)^2 = \frac{e_n}{\epsilon_o} \left[ T_e \exp \frac{\phi}{T_e} - T_e + \frac{M_u^2}{e} \left( 1 - \frac{\phi e}{M_u^2} \right)^{1/2} - \frac{M_u^2}{e} \right]$$  (3.24)

Given that physically $\frac{d\phi}{dx}$ must be positive, using a Taylor expansion to expand the right hand side of the equation gives:

$$0 \leq \frac{e_n}{\epsilon_o} \left[ T_e \left[ 1 + \frac{\phi}{T_e} + \frac{\phi^2}{2T_e^2} \right] - T_e + \frac{M_u^2}{e} \left[ 1 - \frac{\phi e}{M_u^2} + \frac{\phi^2 e^2}{M^2 u^4} \right] - \frac{M_u^2}{e} \right]$$  (3.25)

Which simplifies to:

$$0 \leq \frac{\phi^2}{T_e^2} + \frac{\phi^2 e}{M u^2}$$  (3.26)

Such that the ion velocity $u \geq \sqrt{\frac{e T_e^2}{M}}$.

Now, balancing the ion flux ($n_i u_i$) with the electron flux ($\frac{1}{4} n_e \nu_e$) we find:

$$n_i \left( \frac{e T_e}{M} \right)^{1/2} = \frac{1}{4} n_e \left( \frac{8e T_e}{\pi m_e} \right)^{1/2} \exp \left( \frac{V_p - V_f}{T_e} \right)$$  (3.27)

Assuming again that $n_i = n_e$ we find:

$$\left( \frac{e T_e}{m_i} \right)^{1/2} = \left( \frac{e T_e}{2\pi m_e} \right)^{1/2} \exp \left( \frac{V_p - V_f}{T_e} \right)$$

$$\ln \left( \frac{e T_e}{m_i} \right)^{1/2} - \ln \left( \frac{e T_e}{2\pi m_e} \right)^{1/2} = \left( \frac{V_p - V_f}{T_e} \right)$$

$$\ln \left( \frac{e T_e}{m_i} \right)^{1/2} = \left( \frac{V_p - V_f}{T_e} \right)$$

$$\ln \left( \frac{2\pi m_e}{m_i} \right)^{1/2} = \left( \frac{V_p - V_f}{T_e} \right)$$
3. CONTROLLING FILM MICROSTRUCTURE AND IONISED MAGNETRON SPUTTER DEPOSITION (IMSD)

Which gives us, for a floating substrate

$$\Delta V = |V_p - V_f| = T_c \ln \left( \frac{m_i}{2\pi m_e} \right)^{1/2}$$

(3.28)

Or if the substrate is biased at a negative voltage, $V_b$ then the potential across the sheath is given by $\xi$ where:

$$\xi = V_p - V_b = (V_f + \Delta V) - V_b$$

(3.29)

This potential across the sheath allows for careful control of the energy flux into the depositing film. Given that the depositing species retain some energy from sputtering $E_0$, we can define the overall ion energy as:

$$E = E_0 + qe\xi$$

(3.30)

Where $q$ is the charge on the ion and $e$ is the electric charge of an electron. It is therefore possible to control the energy of the depositing species through the application of an electrical bias to the substrate.

3.5 Controlling structure through energy flux

The properties and behaviour of a film are largely determined by the film microstructure. This in turn is a function of the energy available during growth. The key parameters are:

- The energy of incoming adatoms;
- The energy of any species reflected at the target and striking the substrate such as inert argon atoms;
- The flux density to the substrate of adatoms and inert species;
- The substrate temperature - this can be a function of the above factors, or can be the result of external heating.

The energy of the film surface is critical in controlling events such as adsorption, desorption, diffusion and surface reactions. In experiments where evaporation is used to
create the depositing flux, the energy of the depositing species is very low and so film energy is principally controlled by varying the substrate temperature. The first attempt to rationalise the variation in structure with growth temperature was performed by Movchan and Demchishin (M&D) [114] in 1969 using evaporated films. Their suggested “zone model” described the structures formed as a function of the homologous temperature (the fraction the deposition temperature $T_d$ is of the melting temperature $T_m$) and shows that three zones exist (figure 3.8a):

- **Zone 1 ($T_d/T_m < 0.3$)** - The film consists of fine scaled crystallites with domed tops and voided boundaries. This results in a poorly defined crystal structure with a high dislocation density. The crystallite size increases as $T_d$ increases and is mainly dependent on the nucleation density as there is insufficient mobility for significant rearrangement of the atoms. This leads to a film with a high hardness but low lateral strength.

- **Zone 2 ($0.3 < T_d/T_m < 0.5$)** - The films have a more clearly defined columnar grain structure which continues to coarsen with increasing $T_d$ as surface mobility increases. Crystallite boundaries are well defined and dense so the film overall has a smooth surface with increased ductility.

- **Zone 3 ($0.5 < T_d/T_m < 1$)** - Equiaxed grains dominate the structure resulting in a bright shiny film, the grain size is now only limited by the film thickness.

In the case of sputter deposition the sputtered species have much greater energy and sputtering gas pressure plays an important role in determining the number of collisions the depositing species undergo (which in turn determines how much energy they loose) and also the rate of bombardment of the film by neutrals. This effects the species energy and their mobility once deposited and so is an important parameter in any zone model. This led to the development of the Thornton zone model [115] as shown in figure 3.8b. The structures found in each zone are broadly similar to those in the M&D model however there is now an additional transition or “T” zone.

- **Zone 1** - Similar to that found in the M&D model however the zone persists to higher $T_d$ at high sputtering gas pressure due to the effects of scattering. Shadowing dominates due to low surface mobility. Shadowing is the term used to describe the
3. CONTROLLING FILM MICROSTRUCTURE AND IONISED MAGNETRON SPUTTER DEPOSITION (IMSD)

(a) The Movchan and Demchishin (M&D) zone model for evaporated films [114]

(b) The Thornton zone model for sputtered films [115]

(c) The Messier zone model for sputtered films with ion bombardment [116]

(d) The Kelly zone model for sputtered films with varying ion energies and ion fractions [117]

Figure 3.8: Zone models for thin film growth
formation of porous structures due to a non-uniform growth front. Preferential grains may grow faster and then block the area near or underneath them from the deposition flux thereby preventing these areas from growing.

- Zone T - This zone consists of tightly packed fibrous grains which create a relatively smooth surface. The energetic bombardment by depositing species and gas neutrals allows for better mobility and so the effects of shadowing are largely overcome.

- Zone 2 - Again, similar in nature to the M&D zone 2. The bulk features are largely independent of the pressure. At high deposition rates a higher $T_d$ is required for similar structures as greater mobility is necessary.

- Zone 3 - Rather than the equiaxed grains seen in the M&D model, broad, squat grains are observed with smooth surfaces. The columnar structure seen in zone 2 may persist even at high temperatures due to granular epitaxy.

Transfer of kinetic energy from bombarding atoms plays an important role in governing surface mobility of adatoms. When significant ionisation occurs and when the substrate is biased to encourage bombardment, then it is important to include these factors in any zone model \cite{118}. The energy with which the species strike the surface is given by equation \ref{3.30}, however only a fraction of this energy is transferred to the deposited atoms. The efficiency of energy transfer is dependent on the relative mass of the striking atom, $M_1$ and atom which it strikes, $M_2$. If the incident atom has energy $E_0$ then the energy transferred, $E$ is given by:

$$E = E_0 \frac{4M_1M_2}{M_1 + M_2} \cos^2 \theta \tag{3.31}$$

Where $\theta$ is the incident angle of the atom to the film. It is therefore clear that collisions between atoms with similar masses lead to much greater efficiency of energy transfer than those with significantly different masses.

This trend therefore suggests that bombardment by the film atoms themselves will have a greater effect than bombardment from background gas species. These effects were taken into account by Messier \cite{116} in his revised zone model as shown in figure \ref{3.8c}. For low bombardment the T zone is small, however as bombardment increases (controlled by increasing the substrate bias, $V_s$) the T zone widens. This can be rationalised by
assuming ion bombardment is only capable of improving short range mobility rather than large scale crystallinity, which is still dependent on thermal diffusion. However, a more detailed analysis [119] suggests that the situation is more complicated.

At first glance one might assume it is simply the energy input into the film which controls the structure, and $E_{\text{total}} = \sum_i E_i j_i$ where $E_i$ is the average energy of species $i$ which arrives as a flux $j_i$. However it is found to be more complex than this, indeed a large flux of low energy ions is not equivalent to a small flux of high energy particles. Petrov et al. [119] investigated the effect of varying ion flux as well as ion energy. They determined that high energy, low flux bombardment led to columnar growth but had little effect on nucleation, texture and surface mobility as the irradiation led mainly to large collision cascades. The films showed limited coarsening with a porous and open zone T-like structure. At higher ion energies there is some densification but the high energy ions create many defects and high compressive stresses which do significant damage to the films rendering this method of limited use.

Low energy bombardment may therefore be a more promising method for structural control. By ensuring the energy of the ions is less than the bulk lattice displacement energy, defect concentration is kept low. Low energy, high flux bombardment leads to an increase in surface mobility [120] however different crystallographic planes show different mobilities and hence this leads to strongly textured growth. Additionally, the increased mobility reduces the pore volume and produces more dense films.

The dependence of film structure on ion flux and ion energy as independent factors was investigated by Kelly et al. [117] and resulted in the creation of a new zone model as seen in figure 3.8d. This model used homologous temperature, bias voltage (linked to ion energy) and ion flux as three variables with which to control film structure. It was found that by increasing the flux of ions, structures traditionally found at higher homologous temperatures could be deposited at lower temperatures. Increasing the ion energy (by increasing the bias voltage) allows for the formation of these high temperature structures at lower flux rates still. However the relationship between flux and energy is not as simple as a “combined energy parameter” which is the product of these two values.

The full relationship between ion energy, ion flux and structure is not fully understood and there are likely additional considerations required when dealing with metastable phases and nanostructured materials. Studies [12] of transition metal-carbon films have shown that the structure is dependent on whether the growth is surface diffusion limited.
or bulk diffusion limited, the transition between which is strongly dependent on the nature of the energy input (high flux, low energy bombardment or low flux, high energy bombardment). In the case of silicon \cite{121} ion bombardment was used to control surface diffusion such that single crystals were grown, while Moafi et al \cite{122} showed that increasing the bias applied to the substrate can increase the sp$^2$ content of an amorphous carbon film. Further phase changes were observed in TiO$_2$ \cite{96} where control of ion energy was used to move between the rutile and anatase phases.

The mass of the bombarding species is also important \cite{123}, a fact which is often overlooked, as the momentum of the bombarding species and efficiency of energy transfer are important parameters also. The aim of this work is to investigate the effect of various ion bombarding conditions on the microstructure and growth of carbon-nickel thin films.
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Chapter 4

Experimental Methods

Carbon-nickel thin films were synthesised using direct current (DC) planar magnetron sputter deposition with an RF inductively coupled secondary plasma placed between the magnetrons and the substrate holder. The films were then characterised using a variety of methods to explore the effect of changing deposition parameters. A selection of films were heat treated to investigate their thermal stability and determine any phase changes.

Section 4.1 details the synthesis of the films and how deposition parameters were varied. Section 4.2 outlines how energy dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM), X-ray diffraction (XRD), Raman scattering, atomic force microscopy (AFM), superconducting quantum interference device (SQUID) magnetometry, vibrating sample magnetometry (VSM), X-ray photoelectron spectroscopy (XPS) and temperature dependent resistivity measurements were made. Section 4.3 describes how the films were heat treated to investigate the thermal stability of the structures.

4.1 Film deposition

C-Ni films were deposited using a dual target ionised magnetron sputter deposition system, shown schematically in figure 4.1a, with a photograph showing the actual setup in figure 4.1b. The system was composed of two independent sputtering targets above a 2½ turn copper coil. The targets and coil were placed within a shield to contain the plasma and sputtered material so that only a small area of the rotating substrate holder was exposed to the depositing flux. The target to coil distance is around 1 cm, the coil height is around
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(a) Schematic diagram of deposition system  (b) Photograph of system

Figure 4.1: Experimental setup of film growth equipment

3 cm and the substrate holder is approximately 2 cm below the bottom of the coil, giving a total target to substrate distance of 6 cm.

Prior to deposition, the chamber was evacuated using a diffusion pump to achieve base pressures of better than $1 \times 10^{-6}$ Pa as measured using a mass spectrometer. The quality of vacuum was confirmed by ensuring the nitrogen to oxygen ratio was well above 4:1. When isolated from the pump system, the chamber pressure was monitored to ensure any increase was due to outgassing rather than a leak.

For film deposition, the chamber was back filled with argon (99.997 %, BIP grade). A leak valve was used to control the flow of argon (when isolated, the chamber pressure increased by 0.1 Pa per second). A dynamic equilibrium pressure of 2 Pa inside the chamber was achieved by varying the gate valve. A voltage was then applied to each of the targets independently to light the glow discharge.

A 55 mm x 35 mm target was attached to each magnetron, made from carbon (99.95% purity 1mm thick graphite sourced from Goodfellow Limited) or nickel (99.99% purity 1mm thick Ni foil sourced from Advent Limited). A standard balanced magnetron setup (as defined in section 3.1) was used operating at 5.18 W cm$^{-2}$ and 0.26 W cm$^{-2}$ for the carbon and nickel targets respectively. The targets were water cooled throughout to avoid overheating. A balanced magnetron was used in preference to an unbalanced system so
that the plasma properties could be attributed to the ICP alone rather than a combination of the ion flux from the target and also the flux from the secondary plasma.

With the substrate holder positioned so that no substrates were exposed to the depositing flux, a pre-sputter stage of 10 minutes removed any surface contaminants and also coated the shield to avoid contamination of the films in the event of resputtering.

Following the pre-deposition step, a $2\frac{1}{2}$ turn copper coil was powered using a 13.5 MHz RF power supply to generate a secondary inductively coupled plasma. The enclosed area of the coil was larger than the magnetrons to ensure a uniform plasma and was positioned between the magnetrons and the substrate holder. The power supply was tuned to minimise the reflected power. The coil operated in an inductive mode as evidenced by net deposition onto the coil [103]. To avoid flaking as a result of build up of material on the coils and shields, the exposed surfaces were cleaned at regular intervals between deposition runs. The addition of the secondary plasma increases the electron content in the plasma and therefore the current flowing to the targets. Given that the power supply operated in a constant current mode, the target current was altered to ensure constant power (which altered by around 15%).

The substrate holder could be electrically floating, or biased using a DC power supply (-300 to +300 V). The substrate holder was thermally floating and, due to energy input from depositing flux, heated to approximately 150 °C as measured by a K-type thermocouple placed beneath a substrate. Once the deposition parameters stabilised the substrate holder was then rotated to expose the substrates to the deposition flux.

The RF power of 100 W was selected as it gave rise to a sufficiently high level of ionisation as explained in section 6.7.2. The range of applied substrate bias (-250 V to around 250 V) was selected to provide the widest possible range of deposition conditions. It has been previously been reported [124] that bias values of greater than -250 V lead to resputtering of carbon in TiC as the energy of the bombarding ions became comparable to the bond strengths. -250 V was therefore chosen as the lower limit so as to limit any resputtering. The upper value of +250 V was selected as it was the voltage at which a large increase in ion current was measured (see section 5.3). Based on the work by Matsumoto [125] it was these conditions that would result in a high flux ion bombardment.

A range of substrates and deposition times were used depending on the characterisation required. The various substrates are outlined in table 4.1. Deposition time was varied so that the required film thickness was achieved.
<table>
<thead>
<tr>
<th>Substrate Name</th>
<th>Substrate Material</th>
<th>Source</th>
<th>Substrate Size</th>
<th>Typical Film Thickness</th>
<th>Characterisations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon</td>
<td>Naturally oxidised (100) Si</td>
<td>Kyocera Fineceramics</td>
<td>10 mm x 5 mm</td>
<td>200–300 nm</td>
<td>Cross sectional TEM, Raman, resistivity measurements, VSM, XPS, EDX, AFM and SQUID</td>
</tr>
<tr>
<td>Glass</td>
<td>Boron Silicate</td>
<td>Agar Scientific</td>
<td>10 mm diameter</td>
<td>200–300 nm</td>
<td>XRD</td>
</tr>
<tr>
<td>Sapphire</td>
<td>R-Plane Sapphire</td>
<td>Kyocera Fineceramics</td>
<td>10 mm x 10 mm</td>
<td>200–300 nm</td>
<td>Raman and XRD for heat treatments</td>
</tr>
<tr>
<td>Carbon Grid</td>
<td>Holey-carbon coated copper TEM grid - 300 mesh</td>
<td>Agar Scientific</td>
<td>3 mm diameter</td>
<td>70 nm</td>
<td>Plan view TEM</td>
</tr>
</tbody>
</table>

Table 4.1: Overview of substrates used for a range of characterisation techniques
4.2 FILM CHARACTERISATION

In order to measure the film thickness a step was created in the film by masking a region of the silicon substrate with a permanent marker pen which was removed post-deposition using acetone to leave a step as shown in figure 4.2. The height of the step was then measured using a Veeco Dektak 6M Surface Profilometer.

![Figure 4.2: Schematic showing how steps were created in films in order to measure thickness](image)

4.2 Film characterisation

4.2.1 Energy dispersive X-ray spectroscopy (EDX)

The film composition was measured using a JEOL 550 scanning electron microscope with an Oxford Instruments energy dispersive spectroscopy detector. Composition was determined by measuring over a 20\(\mu\)m by 20\(\mu\)m square at three different sites on the sample and averaging. An accelerating voltage of 15 kV was used. It is difficult to measure carbon composition using a standard SEM due to the presence of background carbon as a result of hydrocarbon contamination. Additionally, since the interaction volume of the beam extends beyond the film into the substrate there is also a strong silicon peak present. This was partially overcome by using a background scan of a bare silicon wafer which was then subtracted from the scans for the films in order to account for the presence of background carbon and silicon. A typical EDX spectrum including the silicon peak is shown in figure 4.3.

Iron, argon and oxygen are all occasionally detected within the films but never in amounts exceeding 4 at%. The iron was largely attributed to contamination from the shields or the magnetron. Argon implantation, while possible, was rarely seen and is most likely an erroneous fitting element from the EDX analysis. Oxygen, like carbon, is always found in the vacuum chamber of the microscope and is likely to be present in small amounts due to the oxide layer on the silicon and also contamination on the surface.
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Figure 4.3: Typical EDX spectrum showing nickel and carbon peaks along with an intense peak showing the silicon substrate.

of the C-Ni film. When using INCA software to analyse the EDX spectrum, all elements except for carbon and nickel were ignored in the final fitting.

4.2.2 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) was performed at the LENNF facility at the University of Leeds by Dr Mike Ward, using a FEI Tecnai F20 FEGTEM (200 kV) fitted with a HAADF detector, a Gatan SC600 CCD camera and an Oxford Instruments X-max 80 mm² SDD X-ray detector. Samples were examined either as plan views or cross sectional views.

Plan view samples were deposited directly onto holey-carbon grids as detailed in Table 4.1. Cross sectional views were first deposited on to silicon substrates before sample preparation.

Figure 4.4 shows a view of the samples prepared for cross sectional imaging. The initial carbon nickel on silicon sample was loaded into a FEI Nova200 Nanolab dual beam FIB/SEM fitted with a Kleindiek micromanipulator. The film was coated with a thin (approximately 90 nm) layer of platinum using an electron dissociated gas injection system. This was followed by a thicker (approximately 1 µm) ion dissociated platinum layer (see Figure 4.5a). The initial electron deposited layer is much less energetic and so does less damage to the underlying film than if the ion layer had been deposited directly onto the film. These platinum layers are required to avoid damaging the carbon-nickel film during subsequent ion etching.
4.2. FILM CHARACTERISATION

4.2.3 X-Ray diffraction (XRD)

X-ray diffraction (XRD) was carried out using a Bruker D8 theta/2theta diffractometer with a position sensitive detector (LynxEye). Scans were performed from a 2θ angle of 10° to 67° in 0.025° steps with a 1 second per step dwell. Copper Kα radiation with λ = 1.5405 Å was generated at a voltage of 40 kV and a current of 40 mA. Glass substrates were used in preference to silicon to avoid overlapping background peaks complicating analysis. Despite having different conductivities the film structures did not vary depending on
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(a) Protective platinum layers deposited onto film

(b) Thin slice of wafer etched using ion milling

(c) Micromanipulator arm attached to sample which is then cut free

(d) Sample is attached to TEM grid with a small area of deposited platinum

(e) Several samples (highlighted in red squares) are attached to each TEM grid

Figure 4.5: SEM images showing the stages of cross section TEM sample preparation
4.2. FILM CHARACTERISATION

substrate type as shown in section 6.3. Analysis was performed using Philips Profit and X’Pert PRO software.

4.2.4 Raman spectroscopy

Raman Spectroscopy was used to determine the nature of the carbon in the films. A schematic showing the operation of the Raman spectrometer is shown in figure 4.6.

![Figure 4.6: Schematic diagram of Raman system](image)

Raman spectrometers measure the shift in wavelength caused by inelastic scattering of the incident laser light by the bonds in the material. It therefore gives structural information about a material in terms of the bonding.

In this study the aim of the Raman analysis was to measure the disorder of the carbon in the films. This was done by analysing the various peaks produced as a result of the bond structure in the carbon. The analysis centred on the D-G band region consisting of a D band, at around 1300 cm$^{-1}$, and a G band at around 1580 cm$^{-1}$.

The scans were performed using a Ramascope-1000 Raman Spectrometer. Data were collected using two scan types, either by a static scan centred around 1400 cm$^{-1}$ (which ranges from 957 cm$^{-1}$ to 1813 cm$^{-1}$) with a 10 second exposure time and summed over 10 accumulations. Alternatively a dynamic scan from 700 cm$^{-1}$ to 2000 cm$^{-1}$ summing 5 accumulations each of 10 seconds was used. In both cases a 633 nm laser was used.

4.2.5 Magnetic measurements

The magnetic properties of the films were measured at low temperature and room temperature. A Quantum Design MPMS-XL 7T Superconducting Quantum Interference Device
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(SQUID) was used for low temperature measurements at 4 K, 10 K and 100 K. Measurements were made by scanning from 0 to +40 kOe then to -40 kOe before returning to 0 kOe. This was completed in 1 kOe steps with a temperature stability of ± 0.02 K.

Room temperature measurements were made using a Princeton vibrating sample magnetometer, scanning the applied field from 0 to 10 kOe, then to -10 kOe before returning to zero. Scans were completed using 500 Oe steps, averaged over one second.
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4.2.6 X-Ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy is a method to determine the bonding states within a material. The technique works by irradiating the sample with X-rays of known energy. These X-rays excite electrons within the material, some of which escape to the vacuum level and leave the surface in a process known as photo-ionisation. The kinetic energy distribution of these escaped electrons can then be measured and, since the incident X-ray energy is known, the electron binding energy can be calculated using \( KE = h\nu - B_E \) \( (4.1) \):

\[
KE = h\nu - B_E
\]

Where \( KE \) is the kinetic energy of the emitted electron, \( h\nu \) is the energy of the incident X-ray and \( B_E \) is the binding energy of the electron. Since these binding energies vary depending on the bonding state of the atoms, the structural nature of the material can be derived. A schematic of the process is shown in figure 4.7. Since there are multiple electrons which could undergo a transition, XPS spectra analyse the transitions of certain electrons within the structure. For carbon it is the 1s electrons which are analysed while for nickel it is the 2p electrons. This leads to a so-called 1s and 2p envelope, a range of energies which correspond to the different bonds these electrons can form which are then measured by the photo-ionisation.

Figure 4.7: Schematic diagram showing the electron emission process in XPS. [126]
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Due to the relatively low energy of the emitted electron, only those created near the surface of the film escape and are measured, making XPS a surface analysis technique. Therefore XPS is often used in conjunction with ion milling in order to measure the bonding structure as a function of depth.

The experiments were performed using a ThermoFisher K-Alpha system. The data were then analysed by measuring the count rate of electrons incident on the detector as a function of binding energy as shown in figure 4.8. Using Thermo Fisher Scientific’s Avantage software, mixed Gaussian Lorentzian peaks were used to fit the data and the relative contribution of each bond type calculated. In order to minimise surface oxidation effects, ion milling was performed prior to measurement to remove the top layer of the film, the removed layer was around 5 nm in thickness.

Figure 4.8: Typical XPS survey scan of C-Ni thin film.
4.2.7 Temperature coefficient of resistivity

The resistivity of the films was measured using a 4-point probe as shown in figure 4.9.

![Figure 4.9: Schematic of 4-point resistivity measurement setup](image)

Consisting of 4 pins equally spaced across the film, this method removes many of the geometric factors which normally complicate resistivity measurements and also removes the dependence of the measurement on the quality of the contact with the film. By passing a known current through pins a and d, and measuring the resulting voltage across b and c, the resistivity of the film can be calculated as:

\[
\rho = \frac{V}{I} t k
\]

Where \(V\) is the measured voltage, \(I\) is the source current, \(t\) is the film thickness and \(k\) is a correction factor based on the ratio of the probe width to sample width, and sample width to pin separation. While the actual resistivity is difficult to measure (since it is dependent on the sample geometry), it is possible to measure the resistivity ratio (the ratio of the resistivity at a given temperature compared to that at room temperature) and compare these values between samples having normalised for any thickness variations. Additionally, through using the same measurement geometry it is possible to make direct, meaningful comparisons between different samples.

The probe was submerged in liquid nitrogen to cool it to 70 K. It was then removed slowly so that it warmed at a rate of a few K min\(^{-1}\). Warming data were used in preference to cooling data as the warming rate is more stable and therefore the data contain less noise. Data were collected as the probe warmed up to room temperature.
4. EXPERIMENTAL METHODS

4.2.8 Atomic force microscopy (AFM)

The surface roughness of the deposited films was measured using a Multimode Nanoscope III AFM from Digital Instruments. Samples deposited on silicon were used, with a typical film thickness of 400 nm. The AFM was used in tapping mode and the data were analysed using WSxM 5.0 software to determine the roughness.
4.3 Heat treatments

In order to investigate the thermal stability of the deposited films, and the effect on structure of post-deposition heat treatments, the films were annealed under vacuum. Consisting of a 0.5 mm thick tantalum foil strip tray, 10 mm across and 80 mm long, 4 samples were placed equi-distant along the strip which was then placed inside a vacuum chamber (as shown in figure 4.10) and evacuated to better than $1 \times 10^{-6}$ Pa.

![Tantalum Strip Heater](image)

(a) Schematic representation  (b) Photograph

Figure 4.10: Tantalum strip heater used for heat treating films

A high current power supply was then used to resistively heat the strip which in turn heated the films. Using an optical pyrometer to measure the current dependence on temperature, it was possible to calibrate the heater. The optical pyrometer is only reliable at temperatures above those we wish to use for heat treatments and so the relationship between current and temperature was measured at high temperatures and extrapolated back to the lower temperature range. Figure 4.11 shows the dependence of temperature on current. The data point at 20 A corresponds to the lowest current at which the strip is seen to glow, this is known to occur at around 475 °C.

The variation of heater temperature with current is dependent on a number of factors such as heater size, shape and heat loss to the chamber. However over this limited range this relationship may be approximated to a linear expression as shown in the plot.
4. EXPERIMENTAL METHODS

Figure 4.11: Temperature calibration of tantalum strip heater. The red line shows the best fit of the data while the green lines confine the 90\% confidence region. The hatched area shows the heater temperature required for the desired film temperature.

Additional complications arise from the fact that the film is separated from the heater by a sapphire substrate (sapphire was used rather than glass or silicon due to its high melting point and its low reactivity with tantalum). This creates a temperature gradient across the substrate and the film temperature has been measured to be 120\(^\circ\)C lower than the heater temperature. Therefore in order to heat the films to around 650\(^\circ\)C, a heater temperature of 770\(^\circ\)C is required. Samples were heated for one hour.
Chapter 5

Plasma Diagnostics

Before discussing the variation in structure with deposition parameters there is a need to quantify the deposition flux in order to determine the mechanisms behind any changes. There are a number of techniques used to quantify plasmas however the most widely used is the Langmuir probe and it is this method which will be discussed here.

5.1 Probe theory

In its most simple form the probe is simply a metal electrode inserted into the plasma. To this, a variable voltage is applied and the resulting current flowing through the probe is measured. However as was shown in section 3.3 the presence of the conductive object in the plasma has an effect on the plasma itself. As a result a small probe is used which has an easily modelled geometry. Most often this takes the form of a thin cylindrical wire. A single probe Langmuir setup measures the voltages and currents with respect to a second reference probe, which is much larger than the measurement probe, typically the chamber wall. A schematic of the setup used in this study is shown in figure 5.1.
5. PLASMA DIAGNOSTICS

Figure 5.1: A schematic of the Langmuir setup used to measure IV curves

The probe is placed as closely as possible to the substrate surface in order to measure the plasma properties at the point of film growth. This may differ significantly from the bulk plasma properties (the bulk properties are of less interest). In sweeping the applied voltage to the probe from negative to positive, it is possible to measure the current as a function of voltage as is shown in figure 5.2.

There are a number of key points to note on this curve.

**Ion Saturation Region** When a large negative bias is applied to the probe the electrons within the plasma are repelled and only the ions are collected. The current at very large negative bias is therefore known as the ion saturation current and is related to the ion density of the plasma. The ion current flowing to the substrate is typically a few mA cm\(^{-2}\) [18].

**Electron Saturation Region** Conversely, when a large positive bias is applied to the probe then all the ions are repelled and the current is due only to the electrons striking the probe. The current at this region is related to the electron saturation current from which the electron density of the plasma can be calculated.

**Transition Region** The intermediate region between the electron saturation region and the ion saturation region describes the range in probe bias where the current is made
5.1. PROBE THEORY

up of a mix of ions and electrons. As the probe bias is made increasingly negative, electrons of higher energy are repelled and therefore the variation in current with bias describes the energy distribution of electrons.

Floating Potential The floating potential is the potential an insulated object adopts when placed in the plasma so that there is an equal flux of ions and electrons and no net current flows. Given the much higher mobility of electrons than ions, this potential is typically negative which then repels further electrons and attracts ions in order to achieve zero net current. For a traditional magnetron sputtering system, a floating voltage of around -10 V is typical [127] however with the addition of a secondary plasma, the increased ion current can force the floating bias to become positive and can then reach up to +300 V [127]. In terms of the IV curve, this point is simply the potential at which the line crosses the zero current axis.

Plasma Potential The plasma itself is said to be quasi-neutral in that, while there are an equal number of electrons and ions, the electrons are more mobile and so are lost to the chamber walls. This results in the plasma having a positive potential, known as the plasma potential, and is the most positive object in the system. The plasma potential gives an indication of the energy of the most energetic ions, and is calculated as the point of the gradient change between the transition region and the electron saturation region where the highest energy ions have been repelled.

Electron Density The electron density is simply the number of electrons per unit volume. Typically, for an inductively coupled plasma, this will be in the region of $10^{11} \text{ cm}^{-3}$ [128]. It is possible that, in addition to the free electrons produced by the secondary plasma, there will also be secondary electrons formed by the high energy impact of ions with surfaces. However, while this is significant in the case of the magnetron plasma (see section 3.1) given the low pressure (less than around 5 Pa) and lack of magnetic field, these secondary electrons are highly mobile and diffuse away from the plasma and are lost to the side walls and therefore typically have little effect on the overall electron density [108].

Ion Density In most plasmas there is a mix of positive and negative ions. The true ion density is the total number of ions per unit volume, however since it is difficult to distinguish between negative ions and electrons, the ion density typically describes
Figure 5.2: Example of a typical IV trace from the Langmuir probe. The position of the 0 V axis is approximate, the floating potential can be positive or negative depending on the nature of the plasma.

The number of positive ions per unit volume. For a RF inductively coupled plasma, values of $10^{11} \text{ cm}^{-3}$ [9] are typical however measurements ranging from $10^{10} \text{ cm}^{-3}$ [129] to $10^{12} \text{ cm}^{-3}$ [11] have been reported depending on chamber size, coil power and deposition flux.

**Electron Temperature** The electron temperature is a measure of the mean energy of the electrons in the plasma. The electron temperature varies depending on the deposition gas, the gas pressure, the species being ionised and the mechanism of ionisation [103]. However typical values lie in the range from around 1 eV to 5 eV [9, 129, 11].

All of these parameters can be determined from the analysis of the IV curves measured using the Langmuir probe. A number of models for the interpretation of the data exist however they each have limited areas of application. Orbital motion theory can be used to parametrise the curves and is detailed extensively in the literature [130] however it is
only applicable under a very small set of parameters and is not valid here. Instead the Laframboise theory \[14\] will be used.

The ion density, \( n_i \), is calculated \[131\] from the saturation current, \( I_i \), in the ion saturation region:

\[
I_i = 0.6n_i eA \left( \frac{eT_e}{M_i} \right)^{1/2}
\] (5.1)

Where \( M_i \) is the mass of the ion, \( e \) is the charge on an electron, \( T_e \) is the electron temperature and \( A \) is the probe area. Calculation of the probe area is made somewhat more complicated by the fact that this is the area over which the probe collects current, which includes the sheath volume also, and so this must be factored in. An additional complication arises from the value of \( M_i \), in a single element plasma such as argon this is a straight forward parameter to know, however in a mixed plasma as is the case here it is not so straight forward.

In the case of multiple species \[128\] we need:

\[
I_i = n_i eA \sum_j f_j \left( \frac{eT_e}{M_j} \right)^{1/2}
\] (5.2)

Where \( f_j \) is the ion fraction for the ion of mass \( M_j \).

Having calculated the ion density it is also useful to know the electron density. In a similar manner to the ion density, this can be calculated by:

\[
I_e = \frac{1}{4} \varepsilon n_e \sqrt{\frac{8eT_e}{\pi m_e}} A
\] (5.3)

Where \( I_e \) is the electron saturation current, \( n_e \) is the electron density and \( m_e \) is the mass of an electron.

Both the ion density and electron density are dependent on the electron temperature, \( T_e \). This can be calculated from the inverse of the gradient of \( \ln I_e \) versus probe voltage for the transition region (having removed the ion current by extrapolating the ion saturation region) as shown in figure\[5.3 \] \[131\].

Therefore having measured the IV curve we can calculate the ion density, electron density, electron temperature, the floating potential and the plasma potential. These parameters will be vital in rationalising the trends seen in the structural evolution of the
5. PLASMA DIAGNOSTICS

\[ \ln(I_e) \] vs. Probe Bias (V)

Gradient = \( \frac{1}{T_e} \)

Plasma Potential \( V_p \)

\[ \ln(I_{esat}) \]

Figure 5.3: Schematic curve of \( \ln I_e \) versus probe bias showing the calculation of the electron temperature, plasma potential and electron saturation current films.

5.2 Experimental setup

The system involves inserting a cylindrical tungsten probe (length 7 mm and diameter 0.38 mm) into the plasma between the substrate holder and the copper coil and is based on the work by Hopwood et al [14] who performed much of the early work on the measurement of RF induction plasmas. The probe is housed in a ceramic block to isolate it except for the region in the plasma. A probe bias voltage was applied using a high voltage power supply independently of the bias voltage applied to the substrate holder. The voltage and the resulting current through the probe were measured using Keithley multimeters attached to a computer to log the data. All voltages were measured relative to the chamber wall which was itself held at earth. The probe voltage was varied from -200 V to a potential of +300 V or a current of 0.5 A, whichever occurred first (the ammeter used to measure the probe current was only able to measure up to 0.5 A, imposing an upper limit on the measurement range). These parameters were based on the work of Gonda et al [132] who
were also investigating the effects of positive and negative biasing on ion bombardment. Further details of the deposition parameters are also given in the experimental methods section on page 45.

5.3 Results

The technique of ionized magnetron sputter deposition focuses on the introduction of a secondary plasma which dramatically increases the ionization fraction of the depositing species. Therefore it is of interest to note the variation in ion current with RF power. Figure 5.4 shows the variation in IV curve with coil power.

![IV curve with coil power](image.png)

Figure 5.4: Variation in IV curve with coil power

The ion current density increases as the coil power is increased as shown clearly in figure 5.5a. Given that the sputtered flux and gas pressure were held constant, the increase in ion current is due to the increase in ionization fraction which is expected as the energy input into the secondary plasma increases. By supplying more energy to the electrons, they undergo increasingly energetic collisions and therefore are more likely to lead to an ionizing collision. There is also a variation in the floating and plasma potentials with both observed to increase with coil power as shown in figure 5.5b.
5. PLASMA DIAGNOSTICS

The increase in plasma potential indicates that the ions are much more energetic and as a result require a larger positive bias to repel them from the probe. There is also a transition from the floating bias being negative when there is no coil, to positive when the coil is active. This is an indication of the change in flux flowing to the substrate. When the coil is not active, there is a negative voltage accumulated on the substrate. This is due to the greater mobility of electrons as described earlier, generating a negative charge to repel electrons and equalize the flux of charged species to the substrate so no net current flows. This is particularly the case in magnetron sputtering, where any positive ions generated in the glow discharge will be rapidly accelerated towards the target due to its large negative charge. Additionally argon ions in the glow discharge are attracted to the target and so few ions reach the substrate. With the addition of the coil the floating potential increases from -10 V when the coil is inactive to 10 V for a 50 W coil and up to 45 V when the coil is powered at 110 W. The size of these potentials is typical of the technique and are similar to those reported elsewhere [133]. The transition to a positive voltage indicates that there is an increase in ion flux to the substrate such that the natural potential of a floating object is positive due to the bombardment with positive ions. Therefore, the increase in floating potential and increase in ion current both indicate an increase in ion density within the plasma and near the substrate surface.

Figure 5.5: Variation in plasma properties as a function of coil power
5.4  Effect of pressure and deposition flux

Having determined that a coil power of 110 W generates significant ionisation, it is then of interest to determine what effect deposition pressure, coil power and deposition flux have on the behaviour of the plasma. Figures 5.6-5.10 show how the ion current to the substrate varies as a function of these parameters.

Figure 5.6: Variation in ion current density with deposition pressure. A 110 W coil was used in each case.
Figure 5.7: Variation in ion current density with RF coil power

Figure 5.8: Detail of figure 5.7 showing the results for 0 W and 50 W
5.4. EFFECT OF PRESSURE AND DEPOSITION FLUX

Figure 5.9: Variation in ion current density with nickel target power. A 110 W coil was used in each case.

Figure 5.10: Variation in ion current density with carbon target power. A 110 W coil was used in each case.
5. PLASMA DIAGNOSTICS

Figure 5.6 shows that there is a decrease in ion current to the substrate as the pressure increases. While the ionisation fraction increases with pressure [11], the increased scattering leads to a lower flux to the substrate (as evidenced by a decrease in deposition rate at high pressure) and so the ion current decreases. Additionally [134] increased scattering will lead to more ions being lost to the chamber walls, reducing the ion content in the plasma.

Figure 5.7 shows that the ion current density increases with RF coil power as expected. The measured currents are consistent with values reported elsewhere [18]. This trend is a result of an increased number of sufficiently energetic collisions to result in ionisation. With no coil active, there is a very low ion current to the substrate as most ions which are formed in the magnetron plasma are attracted back towards the target. It is only when a significant number of ions are produced in the secondary plasma that a current flows to the substrate.

The variation in substrate current as a function of deposition flux is shown in figures 5.9 and 5.10 for changes in nickel and carbon target power respectively. The behaviour in each case is complex: it is observed that when the carbon target is powered at 100 W, increasing the nickel power from 5 W to 10 W actually leads to a decrease in ion current to the substrate. Conversely, if the carbon target is only powered to 50 W there is an increase in ion current as the nickel power is increased. With the nickel power fixed, generally a decrease in substrate current is observed as the carbon flux increases. The exception being in the case of a 5 W nickel power at 2 Pa, where an increase in current is seen. The corresponding conditions at 5 Pa however resulted in a decrease in current. Gas rarefaction [129, 12] may play a role in explaining these trends. As the sputter flux increases, the additional ionisation events cool the plasma thereby reducing the ionisation fraction. In the cases where there is a large flux of atoms through the secondary plasma, further increases in the flux leads to a decrease in ionisation fraction and therefore a drop in ion current. However when the sputtered flux is lower, a small increase in flux has little effect on the ionisation fraction and so the overall ion current increases (the same proportion are ionised but there are a greater number of atoms passing through the plasma). However all of these variations are small in scale and more data would be needed to confirm these trends and provide a more conclusive explanation.
5.5 Plasma Characterisation

While certain aspects of the plasma behaviour can be measured through the current flowing to the substrate, to analyse parameters such as the electron density and electron temperature of the plasma, a full Langmuir probe analysis was performed. In particular, the variation with substrate bias was investigated. Given the effect the substrate bias and probe is likely to have on the secondary plasma, a mesh was placed between the secondary plasma and the substrate as shown in figure 5.11. It was hoped this equipotential surface would isolate the secondary plasma from the substrate. The mesh was made of stainless steel wire, 0.5 mm in diameter with approximately 1 mm square gaps.

![Schematic of experimental setup with wire mesh placed between the plasma and the substrate holder](image)

Figure 5.11: Schematic of experimental setup with wire mesh placed between the plasma and the substrate holder

5.5.1 Floating mesh

Given that the mesh is electrically isolated from the rest of the system it naturally adopts a floating bias which should then screen the plasma from the substrate bias. IV traces were performed as a function of substrate bias, with positive biasing shown in figure 5.12 and negative biasing shown in figure 5.13.
Figure 5.12: Plot showing the variation in IV curve with substrate bias for a positive substrate bias and a floating mesh between the ICP and the substrate.

Figure 5.13: Plot showing the variation in IV curve with substrate bias for a negative substrate bias and a floating mesh between the ICP and the substrate.
5.5. PLASMA CHARACTERISATION

Clearly these traces do not display the smooth transition between regions shown in figure 5.2. Instead they show distortions and noise. This is likely due to the proximity of the probe to the biased substrate holder. Typically Langmuir probes are used to measure bulk plasma properties however in this case, the bulk plasma is of less importance, compared to the plasma near the substrate. Given the biasing, the plasma in these two areas will differ significantly. However analysis of the curves still has merit.

In the case of positively biased substrates, there is a significant variation in IV character as the bias is altered. As the bias is made more positive we observe a shift in the curves to a more positive potential. The shift in plasma potential is accompanied by a change in transition region gradient indicating a variation in electron temperature also. There is an increase in the ion saturation current (the curves shift down) with increasing positive bias. It is important to be aware that the floating bias now changes. When the substrate is left floating, the measured floating potential in the plasma will be equal to the floating potential of the substrate. However when a bias is applied to the substrate, the floating potential in the plasma will now be different to that measured before the bias was applied.

In the case of the negatively biased samples there is less variation between the curves with each showing very similar ion current. There is however a variation in the floating bias, particularly for the large negative biasing. The smaller biasing curves overlap to a large degree.

The clear trend is that the ion current increases as the substrate is biased more positively. For negative biasing and biasing below the floating potential there is no such variation. This trend is somewhat counter-intuitive. The application of a negative bias might be expected to attract positively biased ions, while a positive bias would attract electrons.

In order to better analyse the IV curves, key parameters were extracted. The plasma potentials were determined using the method set out in figure 5.3. Figure 5.14 shows this analysis for an actual data set, in this case for a -200 V substrate bias.

The intersection of the two lines gives the plasma potential, \( V_P \), on the x-axis and the electron saturation current, \( I_{\text{sat}} \), on the y-axis. The slope of the transition region gives the inverse of the electron temperature, \( T_e \). Using equations 5.1 and 5.3 it is then possible to determine the electron and ion density. Figure 5.15 shows the variation of the plasma potentials with substrate bias, figure 5.16 shows the variation of the ion density while
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Figure 5.14: Plot of ln I against probe bias to calculate electron temperature, electron saturation current and plasma potential near a substrate biased at -200 V with a floating mesh

Figure 5.17 shows the electron density, again as functions of the substrate bias.

There is a clear trend in the plasma potential, in that it increases linearly for positive biasing and approaches a steady value for negative biasing. The difference between the substrate bias and the plasma potential gives the voltage experienced by the ions as they cross the sheath (the sheath voltage), which is the critical value in determining the energy gained by the ions. To more clearly show the variation in sheath potential with substrate bias, the solid black line in figure 5.15 plots the substrate bias (found on the x-axis) on the y-axis. The sheath potential is constant for positive biasing but increases significantly as the bias is made more negative, from 25 V for biasing above 50 V up to nearly 450 V when a bias of -250 V is applied. This indicates that the bombardment of ions onto the film becomes increasingly energetic. Similar behaviour upon application of a positive bias has been observed elsewhere [135, 132].

The clear trend in figure 5.16 is that the ion density increases as the substrate is biased more positively (as was seen from the shifting down of the VI curves) from around $1 \times 10^{12} \text{ cm}^{-3}$ to $2 \times 10^{12} \text{ cm}^{-3}$ for biasing below 100 V up to $1 \times 10^{13} \text{ cm}^{-3}$ for a bias of +250 V. For negative biasing and biasing below the floating potential there is no such variation. This trend is somewhat counter-intuitive but similar results have been observed.
5.5. PLASMA CHARACTERISATION

Figure 5.15: Variation of plasma potential with substrate bias showing change in sheath voltage when a floating mesh is present

Figure 5.16: Variation of ion density with substrate bias when a floating mesh is present

Figure 5.17: Variation of electron density with substrate bias when a floating mesh is present
in other studies [125] and an explanation is possible. The application of a negative bias might be expected to attract positively charged ions, while a positive bias would attract electrons. However during deposition is it noticeable that there is a change in the bulk plasma when the positive bias is applied. Due to the large size of the substrate holder, the application of a positive bias does not simply effect the ions local to the substrate holder, rather it alters the plasma as a whole. Given that the electrons are responsible for maintaining the plasma, and are more mobile than the ions, upon the application of a positive bias the plasma electrons are attracted towards the substrate holder while the ion flux is suppressed. These accelerated high energy electrons will lead to large amounts of ionisation close to the substrate surface and so there is an observed increase in ion density due to the shorter distance the species need to travel. While the application of a negative bias will accelerate the ions across the sheath region, it does not alter the plasma potential and therefore the flux of ions into the sheath remains constant. By contrast the application of a positive bias severely disrupts the plasma and results in the observed variation in ion density.

However, while the energy of the ions colliding with the substrate increases for increasingly negative biasing, the ion density increases as the bias is made more positive. This suggests that the addition of the mesh did not have the desired effect when left floating as it would seem that the addition of a positive bias is still sufficient to attract electrons towards the substrate holder. This is further supported by the observed variation of electron density with substrate bias.

Figure 5.17 shows that the electron density increases as the substrate bias is made more positive from \(2 \times 10^{10} \text{ cm}^{-3}\) at -150 V up to \(4.5 \times 10^{10} \text{ cm}^{-3}\) for a bias of +250 V. While this in itself is not unexpected as electrostatic attraction would draw electrons towards the substrate, it supports the hypothesis that it is the increased electron density at positive biasing which generates a plasma close to the substrate surface and therefore generates the increase in ion density. Additionally the increased ion current will result in increased secondary electron production which will further increase the measured current.

The scatter in the electron density values is in part due to the difficulty in fitting the curve and also due to the dependence on the electron temperature. The electron temperature is also difficult to calculate accurately for some curves where there are limited data points at the area of interest due to the large gradient in the curve. The calculated electron temperatures are shown in figure 5.18.
5.5. PLASMA CHARACTERISATION

Here we see a trend that the electron temperature decreases significantly as the bias is increased. This is likely a result of the increase in ionising collisions reducing the energy of the electrons and cooling them, leading to a drop in electron temperature. However, as stated in section 5.1, typical electron temperatures in similar systems are found to be in the range of 1 eV to 5 eV. It is possible that electron temperatures rise in spatially confined systems as we have here [136] since a high electron generation rate compensates for a high loss rate to the walls. However, the values of 11 eV for the negatively biased case are likely erroneously high due to fitting uncertainty in the IV curves. With this in mind, even if these two highest values are excluded, we still observe a rise in electron temperature as the bias is made increasingly negative.

It is clear from the above results that having an electrically floating mesh between the substrate and plasma is not sufficient to isolate the effect of applying the substrate bias, in order to prevent the shifting of the plasma, since an increase in electron density is still observed. This is because the application of a substrate bias causes a change in the floating mesh voltage as shown in figure 5.19.

Therefore the mesh is not acting as an isolating plane between the substrate and the plasma as hoped. An additional possibility is to earth the mesh, holding it at 0 V so that the effects of the substrate bias are isolated from the plasma as there is a fixed
Figure 5.19: Variation of mesh floating potential as a function of substrate bias intermediate potential.
5.5.2 Earthed mesh

By earthing the mesh, and therefore holding it at 0 V, the electric field between the mesh and the plasma is constant, with only the field between the substrate and the mesh altering as a function of substrate bias. This should prevent the field generated by the substrate bias affecting the plasma within the coil.

The results of IV scans for a range of substrate biasing with an earthed mesh are shown in figure 5.20 for positive substrate biasing and figure 5.21 for negative substrate biasing. Once again, the curves appear severely distorted, much more in this case than was observed for the floating mesh.

In the case of the negatively biased substrates the trend appears to be largely similar to that for the floating mesh. The ion current however appears to vary much more as a function of negative bias than has been observed previously. The increase in floating potential and largely uniform plasma potential however is consistent with the previous results. The greatest difference is observed for the positive substrate biasing. Again, the ion current varies as observed previously however in the case of biasing above the floating bias we no longer observe an electron current. For the +150 V and +200 V substrate biasing the IV trace is constant with no transition or electron saturation region observed. In order to determine why this is the case, firstly it is important to analyse the ion currents. Figure 5.22 shows how the ion current varies with substrate bias.

While this is broadly similar to the results seen in figure 5.16 there are some variations. In the previous cases the ion current for negative biasing was largely constant, with an increase only being observed when a positive bias was applied. In this case a linear increase in ion current is observed across the bias range. Perhaps the most interesting result however is that the ion current continues to increase with increasing positive bias as before.

It was previously hypothesised that the application of a positive bias drew electrons towards the substrate, which in turn ionised species close to the substrate surface and therefore increased the ion density. If the earthed mesh IV traces are reliable then these results suggest an increase in ion concentration even when no electrons are present. We observe from XRD scans (the results of which are shown in section 6.3.4) that the addition of an earthed mesh has no effect on the film structure and has only a limited effect on the ion current, however it appears to have a dramatic effect on the electron current in
Figure 5.20: Plot showing the variation in IV curve with substrate bias for a positive substrate bias and an earthed mesh

Figure 5.21: Plot showing the variation in IV curve with substrate bias for a negative substrate bias and an earthed mesh
5.5. PLASMA CHARACTERISATION

Figure 5.22: Variation in ion current with substrate bias with an earthed mesh

the case of a positive substrate bias and earthed mesh.

This leads to uncertainty as to whether the IV measurements are accurate in the case of an earthed mesh. Due to the space constraints in the set-up there is only a small separation between the mesh and the probe. Given that the floating potential of the substrate is still +125 V when the earthed mesh is used, this indicates that the flux to the substrate is comparable to the floating mesh or no mesh case. Since the mesh is earthed, one might expect a large current to flow through the mesh away to earth however this does not appear to be the case. This is likely due to the large open nature of the mesh (see Conclusions). If a significant current were flowing through the mesh then the flux at the substrate would be electron deficient. This would lead to the floating potential being much more positive (in order to achieve equal flux of electrons and ions) however this is not observed. When a large positive bias is applied to the substrate there is a large electric field in the region between the mesh and the substrate due to the small separation and the fact that the mesh is held at 0 V. Given the large size of the substrate compared to the probe, it is possible electrons are preferentially attracted to the substrate at the expense of the probe, leading to inaccuracies in the probe measurements. There is a large current measured through the substrate (0.5 A at a bias of +300 V) and so there is clearly a large flux of electrons to the substrate even when the earthed mesh is present. The presence of the mesh may also increase the secondary electron content of
5. PLASMA DIAGNOSTICS

the plasma due to a high rate of bombardment by the ions. However it is likely these electrons would either be lost through the mesh or result in recombination with the ions to form neutrals. Independent measurement of the mesh current would have been of value however this was not experimentally possible.

While the results obtained for a positive bias and an earthed mesh appear to be inaccurate, the results for all other conditions agree with the expected trends and were reproducible over a range of experiments. Additionally the floating mesh results agree with the results for when no mesh was present and so the varying local electric fields do not appear to be a concern for these conditions.

5.6 Conclusions

Analysis of the plasma has proven technically difficult. The application of a positive bias dramatically alters the plasma and as a result the measurements made from the Langmuir probe near the substrate are distorted. That said, the scales of the numbers measured are typically in agreement with those observed elsewhere, as is the variation in plasma potential, electron temperature and ion density. With that in mind a semi-quantitative interpretation of the results is valid. It would have been of use to qualify these results with additional plasma characterisation. Optical emission spectroscopy (OES) or a gridded energy analyser (GEA) would have offered additional information regarding the plasma. Unfortunately, while attempts to make OES measurements were embarked upon, spatial limitation of the system prevented its use and a GEA system was unavailable. While the lack of these techniques is unfortunate, the methods employed (Langmuir probe and analysis of the substrate current) still provide an insight into the nature of the plasma.

Langmuir measurements of the plasma in the vicinity of the substrate holder highlight the importance of the applied bias. The presence of the secondary plasma, unsurprisingly, increases the ion current to the substrate significantly which confirms that the coil ionises the species to a much greater extent than the glow discharge alone. This is evidenced through the dramatic increase in floating potential, from a negative voltage (as expected for a flux arriving at the substrate consisting mainly of electrons) to a positive voltage when many more ions are now arriving at the substrate.

Having confirmed that the coil is increasing the ion content of the system as expected, the next important task was to determine the effect of applying a substrate bias.
5.6. CONCLUSIONS

the theory laid out in section 3.3 we know that the application of a negative bias has the effect of increasing the sheath potential but not affecting the ion current. This was confirmed through the plasma potential measurements and ion density measurements where we observed a constant ion density for a negative bias, while the sheath potential increased. Therefore the acceleration of the ions across the sheath increases, that is to say, the application of a negative bias results in a low flux, high energy bombardment.

The application of a positive bias on the other hand has a more complex effect on the plasma. The positive bias accelerates electrons towards the substrate and since the electrons are responsible for the formation of the plasma, this means the bulk plasma is shifted towards the substrate, increasing the plasma density in the region. This increases the ion current significantly to the substrate as observed through ion density measurements. Since the positive bias draws electrons from the plasma, the plasma potential increases as a result of the increased variation in charge distribution. This increase in plasma potential with bias maintains a constant difference between the two (a constant sheath potential) and therefore a constant (and small in comparison to the negatively biased case) acceleration across the sheath. Therefore as the bias is made more positive, the ion flux to the substrate increases significantly however the acceleration across the sheath remains constant. The application of a positive bias results in low energy, high flux ion bombardment.

Attempts to isolate the substrate from the plasma through the use of a fixed potential mesh were unsuccessful. The complex behaviour of the plasma in the case of an earthed mesh made IV measurements inaccurate and incomplete. The unsuccessful nature of the isolation is likely related to the dimensions of the mesh. Given that the Debye length describes the distance over which the charge carriers can redistribute themselves, if the mesh dimensions exceed the Debye length significantly then the plasma will penetrate the mesh and pass through it, largely unaffected [15]. The Debye length is calculated from equation 3.21 which can be approximated [108] to:

\[
\lambda_{De} (\text{mm}) \approx 7430\sqrt{\frac{T_e}{n_e}} \quad (5.4)
\]

Where \( T_e \) is the electron temperature in eV and \( n_e \) is given in units of \( \text{cm}^{-3} \). From this we can calculate the Debye length at the two extreme values, for a bias of -150 V where it is found to be 0.19 mm and for +250 V where it is 0.035 mm. In both cases this is much
smaller than the grid spacing ($\approx 1 \text{ mm}$) and so it is likely the plasma passed through the mesh. Given the large electron density at positive biasing it would prove experimentally very difficult to apply a sufficiently fine mesh to shield the plasma from the substrate.
Chapter 6

Control of Film Structure Through Deposition Parameters

The primary method of control for the structure of the films will be through varying the substrate bias and therefore the energy flux to the surface. However as with all PVD techniques, the various other experimental parameters (target power, pressure and deposition time) will all play a role too. It is therefore important to be able to distinguish between the effects of the various parameters in order to determine the role each plays.

6.1 Deposition parameters

Prior to determining the structure of the film it is important to quantify some basic film growth parameters.

6.1.1 Deposition rate

Film thickness is an important value to measure in order to ensure reproducibility between samples and to determine the effects of varying deposition parameters. Using the step method described in section 4.1 the film thickness was measured for a variety of deposition conditions. Figure 6.1 shows the variation of deposition rate with substrate bias. No error bars are shown as the variation between samples grown under the same conditions is comparable to the data marker size.
6. CONTROL OF FILM STRUCTURE THROUGH DEPOSITION PARAMETERS

Figure 6.1: Graph showing the variation in deposition rate with substrate bias for a 30 minute deposition with a carbon target power of 100 W, nickel power of 5 W, RF power of 100 W and a deposition pressure of 2 Pa

It is clear that the deposition rate in the positively biased case is significantly higher (almost double) than that for the negative biasing, rising from around 7.5 nm min\(^{-1}\) at -250 V up to 20 nm min\(^{-1}\) at +250 V. The deposition rate for large negative biasing begins to approach that for depositions without the RF coil which was found to be 6.3 nm min\(^{-1}\). This suggests that the addition of the RF coil dramatically increases the deposition rate for moderate biasing. However as the biasing becomes increasingly negative it is possible that resputtering occurs which reduces the effective deposition rate. This trend of increased deposition rate at positive biasing has been reported elsewhere [139]. There is a slight increase in the power applied to the target on positive biasing but this is insufficient (only around 15%) to explain this increase in growth rate. A likely explanation is the combination of changes in ion bombardment leading to changes in film density, along with a change in film crystal structure. While it is not thought that significant resputtering occurred at negative biasing, it is still possible that there was less desorption of deposited species at positive bias due to lower energy bombardment [137]. The relationship between biasing and deposition rate is maintained when different pressures are used as shown in figure 6.2.

It is observed that there is a decrease in deposition rate of approximately 50% as the pressure is increased from 1 Pa to 2 Pa with a further 50% decrease as the pressure is increased from 2 Pa to 5 Pa. This is a known effect due to the decrease in mean free
6.1. DEPOSITION PARAMETERS

Figure 6.2: Graph showing the variation in deposition rate with substrate bias for a 30 minute deposition at 1 Pa, 2 Pa and 5 Pa with a carbon target power of 100 W, nickel power of 5 W and a RF power of 100 W

path as gas pressure increases. At higher pressures, the depositing species undergo more collisions and so their path becomes randomised and fewer species arrive at the substrate.

While these rates were measured over 30 minutes, the deposition rate (as defined in terms of film thickness per unit time) is not constant with deposition time as shown in figure 6.3. There is large (apparent) increase in the deposition rate for short runs. The rate of film growth then appears to stabilise as deposition time increases. A similar trend is observed regardless of substrate bias (it was not possible to measure very short runs for negative biasing due to the lower deposition rate). These effects were observed regardless of the order in which the films were deposited. The same trend was seen if the short deposition time samples were deposited first and the longer deposition time samples grown later in the same run, or if the long deposition time samples were grown first. This suggests that the different growth rates are not a result of target contamination since this would result in a constant change in growth rate as the deposition proceeded which is not what was observed. Instead, given that the arrival rate of adatoms is constant (since the system is run for some time prior to deposition) this trend indicates that the density of the deposited film varies initially. This suggests that the first layers to form are not structurally similar to the later sections of the film and as a result there is a difference in measured deposition rate, a concept further explored in section 6.2.2. A quartz microbalance could have provided in-situ growth rates as a function of time. This
6. CONTROL OF FILM STRUCTURE THROUGH DEPOSITION PARAMETERS

Figure 6.3: Graph showing the variation in deposition rate with time for a deposition with a carbon target power of 100 W, nickel power of 5 W, RF power of 100 W and a deposition pressure of 2 Pa

Information would have been very useful to determine whether the deposition flux (the mass increase per unit time) was constant, which would then indicate a change in film density. However due to the complications related to the biasing it was not possible to perform these experiments.
6.1. DEPOSITION PARAMETERS

6.1.2 Film composition

Film composition is another critical parameter, in particular if it varies significantly with deposition parameters. Composition was measured through EDX analysis, primarily through the method described in section 4.2.1. Figure 6.4 shows the variation in composition with substrate bias.

![Graph showing the variation in composition with substrate bias for depositions with a carbon target power of 100 W, nickel power of 5 W, RF power of 100 W and a deposition pressure of 2 Pa.]

There is a slight increase in the nickel content of the film at large positive biasing but the composition is uniform for negative and small positive biasing. There are a number of possible reasons for this. Firstly, as seen in figure 6.1, the deposition rate varies with bias, the largest change being seen upon application of a positive bias. The increase in plasma density observed upon application of a positive bias increases the current flowing through the target (see section 4.1) and will therefore alter the deposition rate. Given that carbon and nickel have different sputter yields [107] it is likely the composition of the flux will change. However, given that the increase in target current is small (around 15%) the change in composition is limited. Additional complications arise due to the change in plasma properties which occur when the composition of the flux changes. As explained in section 5.4 changing the flux into the plasma can lead to cooling effects which alter the ionisation fraction [140] due to rarefaction of the plasma.

The composition also varies with deposition pressure as shown in figure 6.5. This diagram plots only the carbon content of the films to show the trends more clearly. The
6. CONTROL OF FILM STRUCTURE THROUGH DEPOSITION PARAMETERS

Figure 6.5: Graph showing the variation in composition with substrate bias at 2 Pa and 5 Pa for a deposition with a carbon target power of 100 W, nickel power of 5 W and a RF power of 100 W. The carbon content of these films is significantly higher than those shown in figure 6.4 as the substrate position was moved closer to the carbon target. The deposition conditions (target power and sputtering distance) were the same.

The most significant difference is that at higher pressure, the films are much more carbon rich (around 80 at%) compared to those grown at 2 Pa (approximately 45%). Comparing the results for the individual pressures we see the increase in nickel content with increasingly positive biasing also occurs at 5 Pa. However at 5 Pa the variation occurs across the whole biasing range in contrast with 2 Pa which appears to have a constant composition at negative biasing.

This change in composition is likely the result of a number of factors. The sputter rate from the targets will vary as a function of pressure [107], which results in a change in the sputtered flux. Additionally the motion of the two species through the chamber will be affected by the change in pressure in varying amounts. The lighter carbon atoms will be scattered much more [141] and so the increase in pressure will alter their paths by a greater amount than the nickel. This increased number of collisions will also alter the ionisation fraction of the two species. A larger pressure will likely increase the ionisation fraction of the carbon species more than the nickel. This will have an effect on the flux of ions crossing the sheath to the substrate, making the film more carbon rich at higher pressures (as is observed).
To confirm the composition of the films, further EDX analysis was performed using a TEM. This allowed for much better spatial resolution and for compositional mapping of cross sections of the film. Figure 6.6 shows the composition maps measured for samples grown at a negative bias and at a positive bias. The nickel distribution in the negative sample is very non-uniform, being found in vertical columns with virtually no nickel present in the inter-column space. In the positively biased case there is also segregation of the nickel, though on a much smaller scale. Measurements of carbon content are complicated by the presence of background carbon. In the carbon map for the negative sample a uniform distribution continuing in to the platinum layer is observed, despite this being deposited under vacuum. This implies that while both carbon maps show a largely uniform distribution of carbon with only minor fluctuations, this may be a result of background carbon rather than the actual content of the film.

There is however a clear variation in composition at the substrate-film interface. Both samples show a nickel rich layer at the substrate followed by a nickel deficient region adjacent to it. Section 6.2.2 compares these maps to TEM data to better explain this variation in composition.
### 6. CONTROL OF FILM STRUCTURE THROUGH DEPOSITION PARAMETERS

<table>
<thead>
<tr>
<th>Substrate Bias (V)</th>
<th>Electron Image</th>
<th>Nickel map</th>
<th>Carbon map</th>
<th>Oxygen map</th>
</tr>
</thead>
<tbody>
<tr>
<td>-150 V</td>
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<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
<tr>
<td>+250 V</td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
</tr>
</tbody>
</table>

Figure 6.6: EDX composition maps for samples grown at negative and positive biasing.
6.2 Microstructure variation with deposition parameters

It is well documented that deposition energy and resulting film microstructure are closely related [119]. It is therefore vital to understand how the microstructure of the films varies as a function of deposition parameters. TEM microscopy was undertaken to ascertain how the films varied.

6.2.1 Structural variation with substrate bias

Figure 6.7 shows a TEM image of the structure grown under positive bias conditions, with an overall composition of 25 at% Ni-C. Clearly visible towards the lower centre of the image is a Ni nano-particle (approximately 6 nm diameter) which, at higher resolution, is seen to be highly crystalline. The graphitisation effects of nickel have led to the formation of a number of ordered carbon layers which encapsulate the particle. These “nano-onions” are distributed throughout the film. Although similar structures have been observed elsewhere [142], we see clearly delineated crystalline Ni nano-particles surrounded by well defined carbon layers.

![TEM image of film grown at a positive bias showing nickel nanocrystals surrounded by layers of ordered carbon as seen in a 70 nm thick film of composition 25 at% Ni-C](image_url)

Figure 6.7: TEM plan view image of film grown at a positive bias showing nickel nanocrystals surrounded by layers of ordered carbon as seen in a 70 nm thick film of composition 25 at% Ni-C
In order to determine the relationship between microstructure and deposition parameters, further samples were deposited at a range of substrate biasing. Figure 6.8 shows cross section and plan views of the microstructural evolution as a function of applied bias. A number of trends are visible. In the cross sectional views there is a transition from a columnar structure for those samples grown at floating, grounded and negative biasing, to a particle structure for the sample grown at a positive bias. This structural evolution is very similar to that seen as a function of deposition temperature in works by Kovacs et al [2] where columnar structures were observed for low deposition temperatures which transform to a particle like structure for deposition temperatures above 400°C. The columns appear to coarsen as the bias is made increasingly negative and extend for a significant fraction of the film thickness. The horizontal lines running across the floating and grounded samples are thought to be artefacts of the sample preparation (ion beam milling) rather than renucleation of the columns. Upon closer inspection it is clear that the grains are continuous through this region and no new grain growth is observed. In plan view, largely similar structures were observed in both the positively and negatively biased cases, although the ordered carbon appears to form as better defined ring structures in the positively biased case, as seen in figure 6.9a. The interlayer spacing for the graphitic cages was found to be 0.335 nm, which matches the value for bulk pure graphite and suggests that there is little or no strain within the layers. The cages typically extend until impeded by another cage growing around a neighbouring crystallite. In the gaps between the cages there is amorphous carbon, with small regions of locally ordered carbon. For the columnar structures grown at negative bias there is little graphite visible from the plan views, although cross sectional images (figure 6.9b) show some graphitic ordering, with the planes running parallel to the crystalline columns (approximately vertically through the film thickness), and an inter-plane spacing of approximately 0.36 ± 0.01 nm. This spacing is slightly larger than the bulk value suggesting the structures have grown under strain.
Figure 6.8: Bright field TEM micrographs of films grown at different substrate bias. The top two rows correspond to 70nm films grown directly on to holey carbon Cu grids at the bias stated. The bottom two rows show micrographs of cross sections of 300nm films grown on naturally oxidized silicon, sectioned using FIB. All films had a composition of 25 at% Ni-C
6. CONTROL OF FILM STRUCTURE THROUGH DEPOSITION PARAMETERS

(a) Plan view of carbon-nickel nano-onion formed at +250V bias
(b) Cross sectional view showing layers of graphitic carbon aligned along nickel carbide columns at -150V bias

Figure 6.9: High resolution TEM images for films of composition 25 at% Ni-C

We also observe a variation in crystallite size with substrate biasing in the plan views. Figure 6.10 shows the distribution of particle sizes for a variety of substrate biasing as measured from the TEM images. A log-normal distribution curve was then fitted to the data to arrive at a value for the average particle size.

Figure 6.10: Particle size distributions as measured from TEM micrographs at a range of substrate biasings as measured from a 70 nm thick film of composition 25 at% Ni-C

The distribution of particle sizes is somewhat complex. For the samples grown at either large positive, or large negative biasing, there is a large distribution in particle sizes, 15 nm
6.2. MICROSTRUCTURE VARIATION WITH DEPOSITION PARAMETERS

to 45 nm and 6 nm to 30 nm respectively. Additionally in the case of the negatively biased sample there are a large number of small particles filling the gaps between the larger ones as shown in figure [6.11]. This variation arises in part due to the thinner nature of the plan view samples, meaning these images show an early stage in growth. Initially there will be a large number of grains nucleating before competitive growth occurs and certain grains win out and dominate.

Figure 6.11: TEM Micrograph showing bimodal distribution of particle sizes in a sample grown at -150 V substrate bias as seen in a 70 nm thick film of composition 25 at% Ni-C

Analysing the cross sectional views (figure [6.12]) we note that the column widths are in good agreement with the particle sizes measured from the plan views. We also observe competitive growth during the early stages of film formation, figure [6.13] shows the initial 150 nm of film growth for a negatively biased sample. Throughout the first 100 nm there are a number of smaller crystallites which are formed but fail to grow while others extend and then coarsen to form the large columns observed later in the film. The nucleation of many grains, followed by the selective growth of a few is often observed in thin film growth as a result of different crystallographic orientations growing at different rates, leading to the growth of certain grains being favoured over time.

This bimodal distribution is seen to a lesser extent in the positively biased samples and there is a smaller difference between the particle sizes. This is consistent with the
6. CONTROL OF FILM STRUCTURE THROUGH DEPOSITION PARAMETERS

Figure 6.12: TEM cross sectional images of films grown at various substrate biasing with composition of 25 at% Ni-C
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Figure 6.13: TEM cross sectional micrograph showing competitive growth at the initial growth area in a sample grown at -150 V substrate bias with a composition of 25 at% Ni-C.

The idea that these structures form as discrete particles as seen in the cross sectional views, so that there is no competitive growth forcing out smaller particles as larger grains grow. Instead continuous renucleation occurs forming new nickel clusters which then coarsen depending on local conditions but whose growth is soon limited by the formation of a graphitic coating. Those samples grown at a floating (≈ 120 V) or earthed substrate show a much smaller, but more uniform distribution of particle sizes, varying from 4 nm to 10 nm and 10 nm to 20 nm respectively. In conjunction with the cross sectional images it is clear that there is still columnar growth but due to smaller initial crystallites, the column size is narrower throughout the film and so there is more uniform growth.

TEM analysis also allows for the study of the crystallographic diffraction patterns from the films as shown in figure 6.14. The strong spots (which make up rings due to the varying orientation of the crystallites) show the reflections from the crystalline nickel with the positions for each sample being consistent with a face centred cubic nickel phase. These rings were indexed to determine the lattice parameter for the structure. The lattice parameters varied slightly for the different samples from 0.374±0.002 nm, for the +250 V sample to 0.371±0.002 nm, for the +175 V sample and 0.374±0.003 nm, for the -150 V sample.
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Figure 6.14: TEM diffraction patterns for plan view films grown at various substrate biasing with a composition of 25 at% Ni-C and a thickness of 70 nm.

V sample, meaning that within error they are consistent.

These values are however ≈ 6% larger than the bulk value of 0.352 nm [84] suggesting that they are in some way strained upon initial formation (this strain is measured in more detail on page 114). The diffuse ring towards the centre of the diffraction patterns arise from reflections from the ordered graphitic layers. The size of this ring is again consistent across the samples and represents a lattice spacing of 0.338 nm which compares well with the bulk value of 0.335 nm. The ring is stronger for the positively biased samples as there is a greater extent of graphite formation as shown in figure 6.7, however there is still some graphite in the case of the negatively biased samples as shown in 6.15.
6.2. MICROSTRUCTURE VARIATION WITH DEPOSITION PARAMETERS

Figure 6.15: TEM Micrograph showing graphitic layers in a sample grown at -150 V substrate bias of composition 25 at% Ni-C

6.2.2 Compositional variation

EDX maps (figure 6.6) showed that there was a non-uniformity in the initial layers of films growth. These may play a significant role in the nucleation of the first layers of the film and therefore lead to variations in the film structure. Figure 6.16 shows the first 50 nm of films grown at a range of substrate biases.

Comparing the EDX maps to the TEM images it is possible to identify the features related to the variation in composition. In the TEM images, the large crystalline region at the bottom of each image is the silicon substrate, this is followed by a bright layer which is the naturally occurring silicon oxide layer (around 5 nm thick). Adjacent to this is a nickel rich wetting layer, as observed in the EDX maps. This layer is clearly visible in each scan except the sample grown on a floating substrate (figure 6.16b) which appears to have a less pronounced nickel layer. In the grounded (figure 6.16c) and negative bias (figure 6.16d) sample we then observe a lighter region adjacent to the nickel layer. From the EDX map we can identify this to be a carbon rich layer forming on top of the nickel.

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Figure 6.16: TEM cross sectional images of the initial nucleation layers of films grown at various substrate biasing with a composition of 25 at% Ni-C
In the case of the positively biased sample (figure 6.16a) there may be a slight indication of a carbon rich layer above the nickel layer though this is not well defined and was not visible in the EDX map.

These initial variations in the composition may go some way to explain the difference in deposition rate observed for very thin films, since the initial layers are not representative of the bulk film. The relative wetting abilities of the carbon and nickel with respect to one another as well as the substrate may be an explanation both for the phase separation but also for the apparent spherical morphology of the nickel. The interaction and wetting between nickel and carbon is largely dependent on defect concentration and the extent of graphite formation [143] which will be particularly important for the first layers deposited. Nickel diffuses slowly on single layer graphene but the rate increases as the graphite thickens. Also, the presence of defects in a carbide slow the diffusion rate. These various factors will likely cause significant variations in the growth of the initial layers.

The non-uniform composition at the substrate may explain the observation from the TEM diffraction patterns showed a pattern consistent with a cubic phase for all the samples. The metal rich layer forming near the surface of the substrate contains negligible carbon and is therefore likely to be an fcc metallic nickel phase rather than a carbide phase.

While the initial sections of the film are not representative of the bulk, they are similar to the particle structures seen for positive biasing in that they contain fcc nickel and a separate carbon phase. Given that the densities of nickel carbide, cubic nickel, amorphous carbon and graphite are 7.13, 8.9, 1.9 and 2.2 g cm\(^{-3}\) respectively [144] we find that for a material of composition 25 at\% Ni-C forming as a carbide and amorphous carbon the density is around 2.53 g cm\(^{-3}\) while for cubic nickel and amorphous carbon it is 3.69 g cm\(^{-3}\). Therefore the observation in the negatively biased sample of a cubic nickel region at the substrate does not explain the apparent increase in deposition rate, since this first layer is more dense and therefore would occupy a smaller volume. Likewise, if the first layer was the same density as the bulk metallic nickel - amorphous carbon then the positively biased sample should show no variation in deposition rate.

The presence of graphitic carbon may explain some of this anomaly. Graphitic carbon is more dense than amorphous carbon and so, since the initial carbon layers are not neighbouring a nickel particle, little graphitisation is likely to occur (and none is observed through TEM) which would make these initial layers less dense and therefore occupy a greater volume. However this variation is minimal (2.2 rather than 1.9 g cm\(^{-3}\)) and so...
6. CONTROL OF FILM STRUCTURE THROUGH DEPOSITION PARAMETERS

is unlikely to explain the near 50% increase in deposition rate during the earliest stages of growth. A more likely explanation is that the true densities deviate significantly from these bulk density values and the films themselves are not fully dense which results in an increase in measured deposition rate. The large nickel clusters would likely cause significant shadowing which would generate under-dense regions.
6.3 Nickel crystallinity and phase variation

While TEM analysis shows a variation in the morphology of the films, it does not illustrate how the crystal structure varies over a range of substrate biasing. To investigate the nickel phase, X-ray diffraction was performed on 300 nm thick samples. Glass substrates were used in preference to silicon to avoid peak overlap as shown in figure 6.17.

Figure 6.17: θ-2θ XRD scans of a bare silicon and glass substrate showing background peaks.

Despite the different conductivities of the two substrates, it was found the substrate material had no effect on the film structure as shown in figure 6.18. This is likely due to the substrate holder being much larger than the substrates themselves and so the small area of different conductivity has no effect on the growth of the film.
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Figure 6.18: $\theta$-2$\theta$ XRD scans of films grown at positive and negative biasing on silicon and glass substrates.

Nickel is known to exist in one of three phases, a face centred cubic (fcc) nickel phase, a hexagonal nickel phase and a hexagonal nickel carbide ($\text{Ni}_3\text{C}$) phase. Figure 6.19 show the expected peak positions for each phase.

Figure 6.19: XRD reference peaks for fcc nickel (ICPD 04-0845), hexagonal nickel carbide (ICPD 04-0853) and hexagonal nickel (ICPD 45-1027)

As detailed in section 2.3.3 distinction between the two hexagonal phases is not possible via XRD due to the similarity of the structures: their lattice spacings differ by just $10^{-3}$ nm. This often leads to misidentification of the phase as highlighted by He [83] in a review article which determined that hexagonal nickel is very difficult to obtain experimentally.
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(particularly in the presence of carbon) and material identified as hexagonal nickel is often, in fact, nickel carbide.
6. CONTROL OF FILM STRUCTURE THROUGH DEPOSITION PARAMETERS

6.3.1 Effect of substrate bias

To further quantify the trends seen in the TEM images, XRD measurements were performed as a function of substrate biasing as shown in figure 6.20.

Figure 6.20: $\theta$-2$\theta$ XRD scans of 300 nm films on glass substrates for a range of substrate biasing. Deposition times were varied to ensure a constant film thickness and the composition was constant at around 25 at\% Ni-C.

In the case of the negatively biased samples, peaks at 39.2°, 41.6°, 44.6° and 58.5° 2$\theta$ are consistent with a hexagonal nickel or nickel carbide phase while for large positive biasing, peaks at 44.6° and 51.8° 2$\theta$ are consistent with cubic nickel. At intermediate biasing there is a steady transition between the two phases where samples grown at small positive biasing show both sets of peaks. Samples grown at floating or earthed biasing show reduced crystallinity and significant broadening of the peaks.

Perhaps the most useful parameter that can be measured from the XRD results are the lattice parameters. Using the Bragg equation ($d = \frac{\lambda}{2\sin\theta}$) to calculate the lattice spacing...
6.3. NICKEL CRYSTALLINITY AND PHASE VARIATION

of the plane (hkl), \( d_{hkl} \), for the reflection at angle \( \theta \) it is then possible to calculate the lattice parameter using equation 6.1 or 6.2 for cubic or hexagonal crystals respectively.

\[
\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \quad (6.1)
\]

\[
\frac{1}{d^2} = \left[ \frac{4}{3} (h^2 + k^2 + h k) + l^2 \left( \frac{a}{c} \right)^2 \right] \frac{1}{a^2} \quad (6.2)
\]

All visible peaks were fitted and for those with two or more hexagonal peaks (two peaks are required due to the two unknowns \( a \) and \( c \)) lattice parameters were calculated. Figure 6.21 shows the ratio of these lattice parameters and compares them to the value for the bulk material.

![Figure 6.21: Ratio of the c and a lattice parameters calculated from XRD data for a range of substrate biasings, the dashed black line shows the bulk value for Ni_3C. All samples were of comparable thickness and had a composition of approximately 25 at% Ni-C. The datapoints without error bars indicate only a single measurement was made at these biasings. Elsewhere the error bars denote the variation between samples grown at equal biasing.](image)

The horizontal line shows the expected ratio for the bulk parameters for Ni_3C of 0.265 nm, for \( a \) and 0.434 nm, for \( c \). The measured parameters agree to within 0.5% of the bulk values suggesting there is little strain in the crystallites. Values for the cubic lattice parameter varied from 0.352 nm, to 0.353 nm, which are also in agreement with the bulk
value of 0.352 nm, suggesting that there is little strain (less than 0.5%) in these films either. To measure the strain more carefully a Williamson-Hall plot was made.

If the films are grown without strain then the broadening of the diffraction peaks is due to the finite crystal size and can be described using the Scherrer equation:

\[ L = \frac{0.9\lambda}{\beta_s \cos \theta} \]  \hspace{1cm} (6.3)

Where \( L \) is the particle size, \( \lambda \) is the X-ray wavelength, \( \beta_s \) is the peak breadth due to finite size effects and \( \theta \) is the centre of the peak.

This would lead to a constant broadening, independent of diffraction angle. Broadening however also occurs due to strain within the crystals, where this can be described using the Wilson formula [145]:

\[ \beta_\varepsilon = 4 \varepsilon \tan \theta \]  \hspace{1cm} (6.4)

Where \( \beta_\varepsilon \) is the broadening due to a strain, \( \varepsilon \). There will also be an instrumental broadening \( \beta_i \) due to the effects of the diffractometer. The instrumental broadening is calculated by measuring the peak width of single crystal substrates which are assumed to be infinitely large crystals and therefore have zero size or strain broadening.

Combining these effects we find:

\[ \beta_{\text{total}} = \beta_\varepsilon + \beta_s + \beta_i \]  \hspace{1cm} (6.5)

\[ \beta_{\text{total}} = 4 \varepsilon \tan \theta + \frac{0.9\lambda}{L \cos \theta} + \beta_i \]  \hspace{1cm} (6.6)

Which can then be rearranged to give [146]:

\[ (\beta_{\text{total}} - \beta_i) \cos \theta = 4 \varepsilon \sin \theta + \frac{0.9\lambda}{L} \]  \hspace{1cm} (6.7)

So that a plot of \((\beta_{\text{total}} - \beta_i) \cos \theta \) versus \( 4 \sin \theta \) gives a straight line of gradient \( \varepsilon \) and intercept \( \frac{0.9\lambda}{L} \).

Figure 6.22 shows examples of Williamson-Hall plots for film data at a variety of biasing. For those films grown at negative biasing there are typically 4 peaks which allows for a satisfactory fit to be made, however given there are only two peaks available for the films showing cubic character, the accuracy of these plots is questionable.
6.3. NICKEL CRYSTALLINITY AND PHASE VARIATION

Figure 6.22: Williamson-Hall plots for three bias values.

From these plots the associated strain and grain size can then be calculated. The strains are shown in figure 6.23a while the crystallite sizes are shown in figure 6.23b.

From this analysis we can see that the films grown at large negative biasing show little or no strain, in agreement with the 0.5% measured via lattice parameter variation. However as the bias becomes increasingly positive there is an increasing compressive strain present in the nickel nanoparticles. This is consistent with other reported nano-onion structures [89]. The graphitic layers which form on the outside of the nano-particles confine the growth of the nickel crystals and so create a compressive strain within them.

There is a clear trend showing a decrease in particle size as the bias is made increasingly positive, as was also observed from the TEM results. However comparing the absolute values (shown in table 6.1) we note a discrepancy between the two.

There are a number of reasons why these values do not match well [147]. Primarily, there is a variation in the direction of measurement. XRD measures planes parallel to the film surface and so the crystallite size is a measure of the crystal size in the direction perpendicular to the surface of the film, while measuring precipitate size from plan view TEM images measures the size parallel to the film surface. In the case of the coarse columns in particular, these values may be very different, indeed the large crystal sizes measured via XRD match well with the typical film thicknesses implying that the grains run through the majority of the film. Additionally XRD measures crystallite size not
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(a) Strain values
(b) Crystallite size

Figure 6.23: Strain and crystallite size as a function of substrate bias as calculated by Williamson-Hall plots for films of composition 25 at% Ni-C and thickness around 300 nm

<table>
<thead>
<tr>
<th>Substrate Bias (V)</th>
<th>TEM Size (nm)</th>
<th>XRD Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>+250</td>
<td>6-20</td>
<td>40</td>
</tr>
<tr>
<td>+120</td>
<td>4-10</td>
<td>100</td>
</tr>
<tr>
<td>0</td>
<td>10-20</td>
<td>120</td>
</tr>
<tr>
<td>-150</td>
<td>30-50</td>
<td>200-220</td>
</tr>
</tbody>
</table>

Table 6.1: Comparison of the measured particle sizes from TEM and XRD. TEM measurements were taken from 70 nm thick plan views while XRD measurements were calculated from 300 nm thick films using the Scherrer equation. All films had a composition of around 25 at% Ni-C

particle size, it is possible that the structures are polycrystalline which will not necessarily be reflected in the TEM results. There is evidence of this from TEM images as shown in figure 6.24. The linear fringes relating to crystalline planes vary in angle at different sites across the column suggesting there is a variation in crystal orientation. There is the additional complication that for experimental reasons, the TEM plan views are taken from thin samples (around 70 nm) while the XRD data measures much thicker films (around 300 nm). From the TEM cross sections we see that there is a variation in feature size during the first layers of growth. This might also vary the measurements. There may also be a variation due to the bimodal distribution of particle sizes, since small particles will dominate the XRD scans by causing significant broadening. Therefore the choice
of “particle” size is dependent on what you specifically want to measure, the size of the nickel clusters or the size of the nickel crystallites. For different applications different values are required, and so both TEM and XRD results are of use.

There is also likely a variation in amount of crystalline material as shown by the variation in the intensity of the 44° reflection. Figure 6.25 shows the variation of the peak intensity with substrate bias.

The intensity of the main peak is observed to increase for highly biased substrates, both positively and negatively. At small or no biasing, the intensity decreases significantly indicating a decrease in crystallinity. The minimum in intensity is seen when the substrate is floating. This point represents the lowest energy input into the film where the ions experience their smallest acceleration across the sheath and also where there has been no disruption to the plasma due to a positive bias being applied (in excess of the floating potential).
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Figure 6.25: Variation in peak intensity for the reflection at 44° for a range of substrate biasing. All samples were of comparable thickness and had a composition of approximately 25 at% Ni-C

6.3.2 Pure nickel films

It was noted in section 2.3.3 that pure nickel forms in the fcc phase. It would therefore be of interest to determine what affect, if any, biasing had on pure nickel films. Figure 6.26 shows XRD traces for pure nickel films deposited under a range of conditions.

The lattice parameters measured from the position of the (111) peak at 44.5° show a relatively consistent value within 0.01 nm, of the bulk value of 0.352 nm. An analysis of the peak widths shows an approximately linear relationship between peak width and substrate bias (figure 6.27), suggesting a decrease in crystallite size as the bias is made more positive. While the film grown at -10 V appears to fit this trend well, it is important to note that this film was grown without the RF coil being active. There is still however clear evidence that ion bombardment which occurs during negative biasing, creates larger crystallite formation (approximately 3 nm at -150 V), while the effect of positive biasing appears to be to encourage nucleation and prevent crystallite growth (limiting the crystallite size to around 1 nm at +300 V). There is also a significant increase in the intensity of the (111) peak in the case of the negatively biased sample, while the intensity remains approximately constant for the other conditions. This suggests an increase in the crystallinity generally with negative biasing as would be expected due to the increase

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6.3. NICKEL CRYSTALLINITY AND PHASE VARIATION

Figure 6.26: XRD scans for pure nickel films grown at a range of deposition parameters. In each case the nickel magnetron was powered at 5 W and the background pressure was 2 Pa. Deposition time was varied to ensure equivalent film thickness. Each scan is shown at the same scale to illustrate the variation in peak height. Each film is approximately 200 nm in thickness.

in energy from ion bombardment \([148]\) from argon ions as well as from the nickel ions themselves. Another result of interest is the variation in floating bias: during deposition of 25 at\% nickel carbon films the floating bias was approximately 130 V, in the case of a pure nickel film this was significantly higher at around 210 V. For a pure carbon film the floating bias remained around 130 V. The increase in floating potential indicates an increase in ion flux to the surface. This is likely the case in a pure nickel deposition since the nickel ions are easier to ionise and in the absence of any carbon, the nickel atoms are more likely to undergo an energetic ionising collision.
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Figure 6.27: Plot showing the peak width and calculated crystallite size for pure nickel films grown at a range of substrate biasing. Each film had a thickness of around 200 nm.

### 6.3.3 Multilayer films

From the EDX mappings it was clear that the composition of the films is not uniform during the early stages of film growth. However it was not clear if this variation was related to the final structures. It was therefore of interest to investigate what would happen if films were deposited on to layers of pure nickel or carbon in order to exaggerate any effect. Figure 6.28 shows the XRD results for films which were grown on layers (approximately 200 nm thick) of pure nickel or carbon, deposited at a floating bias with a coil power of 110 W. The films deposited were approximately 300 nm thick.

As was shown in figure 6.26, pure nickel films form as a cubic phase. This explains the presence of a peak at 52° in both of the samples grown on top of the nickel layer. The sample consisting of a negatively biased film shows clear diffraction peaks consistent with those seen when the film is grown directly on silicon or glass. As with the previous films, it is not possible to definitively state these peaks are a result of the formation of the carbide, however given that the weight of evidence suggests that the carbide is formed when films are deposited on to bare substrates, it is likely these films have formed as carbides also. These films suggest that growth on a nickel substrate has had no effect on the resulting film morphology, and is the same as was observed for a silicon or glass substrates. It is not possible to definitively say that the cubic peak is from the underlying nickel (as opposed
6.3. NICKEL CRYSTALLINITY AND PHASE VARIATION

Figure 6.28: XRD scans for layers of approximately 25 at% Ni-C grown using a bias of either +250 V or -150V on top of a pure nickel or carbon layer (also shown) which itself was deposited at a floating bias. In each case, the pure layers were around 200 nm thick and the top films were around 300 nm thick.

to cubic nickel in the Ni-C phase), however given the significant amount of hexagonal material it would appear that any change in structure as a result of the underlying phase is negligible.

In the case of the positively biased film grown on the nickel layer there is no hexagonal carbide phase as expected. There is however a very strongly textured cubic phase, with the intensity of the (200) peak at 51.8° much greater than observed in a bulk powder pattern (where the ratio of the (111) intensity to the (200) intensity is 100:42). This texturing was not observed in the case of pure nickel films, suggesting that there is a preferential growth direction in the nickel phase which only occurs in the presence of carbon. The effect of substrate material and how texture can develop is explored further in section 7.6 on page 168.

The samples grown on carbon show no significant cubic phase in either the positively or negatively biased cases. In the case of the negative biasing this is not surprising and indeed the film appears to behave no differently from when grown on silicon. However in the case of the positively biased film, there also appears to be a hexagonal carbide phase. It is possible that the additional carbon from the first layer diffuses into the growing
nickel particle, as well as carbon arriving from the depositing flux \[89\]. This increase in carbon content would then mean additional mobility was required in order for the carbon to diffuse out, to leave a metallic particle. Additionally, studies involving the deposition of nickel onto a carbon substrate \[88\] have found that carbide layers form on the interface between the two materials which then prevents diffusion across the boundary. This would further inhibit the phase separation of the nickel and carbon, ensuring the carbide phase was observed regardless of biasing. Reducing the ratio of nickel to carbon atoms in the depositing flux might show whether it is an interface effect or a bulk saturation effect which prevents the phase separation. due to the very high deposition rate of nickel compared to carbon, it would be necessary to fit baffles to reduce the deposition rate further. However the effect of the baffles on the ionisation of the flux would add additional complications to the experiment and may make comparison of the resulting films difficult.

An additional factor to consider is the difference in conductivity between a nickel layer (high conductivity) and a carbon layer (low conductivity). However films grown on glass (an insulating substrate) showed a carbide phase at negative biasing and a cubic phase at positive biasing (see figure 6.20) and so the poor conductivity of the carbon layer is unlikely to be the cause of this variation.

An alternative method to determine if there are any templating effects is to grow a positively biased film on top of a negatively biased film and vice-versa. The results of such an experiment are shown in figure 6.29. In the top two traces a thick (approximately 400 nm) film was grown on a thinner film (75 nm - thicker than the transition region seen in the cross sectional TEM) while in the lower two traces the films were approximately equal thickness (15 minute depositions resulting in 150 nm of negatively biased film and around 250 nm of positively biased film).

In the case of a negatively biased film being grown on a thin positively biased film we observe a standard pattern for a negatively biased film showing a well defined hexagonal carbide structure. Likewise for the positively biased film grown on a thin negatively biased layer we observe a good quality cubic phase film. This suggests that a thin layer with comparable composition to the growing layer has little effect on the resulting microstructure.

In the case of two layers deposited for equal time we observe that the sample with a negatively biased section on the top surface shows a carbide peak at 41.5° but also a cubic peak at 51.8°. We would therefore expect to observe a similar pattern if the layers
Figure 6.29: XRD scans for layers of approximately 25 at% Ni-C grown using a bias of either +250 V or -150V on top of films grown using the opposite bias. (a) the lower layers were around 75 nm thick and the top films were 400 nm thick. (b) layers were deposited for 15 minutes resulting in the positively biased layers being slightly thicker due to the increased deposition rate.

were reversed, however when the positive bias layer is on top, no carbide phase peaks are observed. While the two layers were deposited for equal time, the deposition rate is higher for positive biasing meaning that the positively biased layer will be thicker. However given the presence of substrate peaks in the scans when silicon substrates are used, we can state that penetration depth of the X-rays includes the whole film. Therefore the difference in layer thickness is not important and the absence of the carbide peaks is therefore likely due to low intensity of these peaks. There appears to be no evidence of the layer below altering the growth of the layer above.

6.3.4 Structures grown with mesh

As mentioned in section 5.5.2, the application of an earthed mesh did not alter the structure of the films. Figure 6.30 shows XRD scans for a positively and negatively biased substrate when an earthed mesh is placed between the substrate and the plasma. An
fcc phase is observed at positive biasing as expected and the hexagonal carbide phase is observed at negative biasing. The increase in noise in the scans compared to previous results is due to the films being thinner since the presence of the mesh decreases the deposition rate significantly, longer deposition runs were not possible as the mesh became blocked over time due to the build up of film material.

Figure 6.30: XRD scans of films grown at positive and negative biasing when an earthed mesh was placed between the secondary plasma and the substrate. The films had a composition of approximately 25 at% Ni-C but were only around 100 nm due to the decreased deposition rate as a result of the mesh.
6.4 Carbon structure and ordering

In order to better understand the changes to the structure of the carbon within the films, Raman spectroscopy measurements were performed. Raman spectroscopy measures the inelastic scattering of the incident photons which occurs through the interaction with molecular vibrations within the structure. While the bonding in carbon is predominately categorised as either being sp\(^2\) graphite like bonded or sp\(^3\) diamond like bonded, there are a variety of forms of sp\(^2\) carbon, each with varying levels of short and long range order. Raman performed using visible light excites two main modes, described as a D mode and G mode.

The D mode is produced by the breathing motion of A\(_{1g}\) symmetry, or the in-plane expansion of the 6 atom carbon rings. In perfect bulk graphite, this breathing mode is not possible since it is constrained by the presence of neighbouring rings and so is often used as a measure of disorder (since the presence of defects allows limited expansion). However, in the case of nanocrystalline graphite, lateral expansion is possible due to the lack of bulk graphite constraining the rings. Therefore while the D band is absent for bulk graphite (where the expansion is confined) and for amorphous carbon (where there are no ring structures to expand), for intermediate cases this mode is possible and so a D band is observed. This distinction is important when interpreting the results for structures containing nanosized graphitic material. The D peak itself is observed in the spectra at around 1355 cm\(^{-1}\).

The G mode of the E\(_{2g}\) symmetry is related to the in-plane stretching of bonds between sp\(^2\) bonded carbon atoms; however these atoms need not be in a sixfold ring. This mode is therefore a measure of the total sp\(^2\) content of the film, not just those in ring like structures. The Raman peak for this mode is found at approximately 1581 cm\(^{-1}\).

6.4.1 Fitting schemes

While Raman has been used for carbon based materials for many years, the fitting of Raman spectra to models is still a complex and varied process. Reports of a wide variety of fitting schemes have been recorded \[150\], however they generally employ combinations of three curve types:
6. CONTROL OF FILM STRUCTURE THROUGH DEPOSITION PARAMETERS

A Gaussian function

\[ I_G(\omega) = I_{G0} \times e^{-\left(\frac{\omega - \omega_0}{\Gamma}\right)^2} \]  

(6.8)

Where \( I_G \) is the peak intensity as a function of the frequency, \( \omega \), \( I_{G0} \) is the peak amplitude, \( \omega_0 \) is the peak position and \( \Gamma \) is the full width at half maximum (FWHM).

A Lorentzian function

\[ I_L(\omega) = \frac{I_{L0}}{1 + \left(\frac{\omega - \omega_0}{\Gamma}\right)^2} \]  

(6.9)

Where \( I_L \) is the peak intensity as a function of the frequency, \( \omega \), \( I_{L0} \) is the peak amplitude, \( \omega_0 \) is the peak position and \( \Gamma \) is the FWHM.

A Breit-Wigner-Fano (BWF) function

\[ I_{BWF}(\omega) = \frac{I_{BWF0}[1 + 2(\omega - \omega_0)/Q\Gamma]^2}{1 + [2(\omega - \omega_0)/\Gamma]^2} \]  

(6.10)

Where \( I_{BWF} \) is the peak intensity as a function of the frequency, \( \omega \), \( \Gamma \) is the FWHM and \( Q \) is the BWF parameter which is a measure of skewness of the function. As \( Q \) tends to infinity, a Lorentzian function is recovered. \( I_{BWF0} \) is the intensity of the peak at \( \omega_0 \), however \( \omega_0 \) is not the peak position due to the curve asymmetry, instead the maximum of the function occurs at:

\[ \omega_{max} = \omega_0 + \frac{\Gamma}{2Q} \]  

(6.11)

Ferrari et al. [35] outlined the principles behind selecting the different fitting schemes. Since no function can be derived a priori for the fitting of the spectra it is only possible to describe which functions work best in which situations. The most simple fitting schemes employ two curves, one for the D peak and one for the G peak. These are usually two Lorentzians or two Gaussians. It has been found that Lorentzian functions work best for crystals which have finite lifetime broadening (the excited states prior to the re-emission of a photon exist for a finite time and so there is an uncertainty in the energy of the photon emitted) and so are often used for disordered graphite. Gaussian functions describe cases where there is a random distribution of phonon lifetimes which is more often the case in more disordered materials.
However, often a two function fit is insufficient, particularly in fitting the low frequency tail, and so a four peak model is used. Adding an additional peak at around 1100 cm\(^{-1}\) and one at around 1400 cm\(^{-1}\) allows the model to fit the data much more closely. However the addition of two additional peaks can lead to over-fitting, with the uncertainty of each peak position becoming considerable. A more popular option is to employ the BWF function, which has an asymmetry making it useful to fit the low frequency tail without the need for additional peaks. This makes the combination of a BWF and a Lorentzian a very useful “general purpose” fitting scheme which is capable of fitting a wide range of structures.

The complication caused by the variety of fitting strategies available is that it makes results difficult to compare. While the BWF function is used to fit the higher frequency G band, the low frequency tail extends into the region describing the D band and therefore shifts the D peak position to a lower value than if two Gaussian curves had been used. This means that a decrease in D peak position indicates increasing order if a BWF and Lorentzian scheme is used, but is indicative of a decrease in order if two Gaussian curves are used. The actual shift is due to the softening of the vibrations as more defects arise which lowers the frequency with which the mode operates. These effects also arise due to finite size factors since smaller clusters push the modes to higher frequencies.

### 6.4.2 Variation with substrate bias

Figure 6.31 shows a series of Raman scans for samples grown at a range of substrate biasing.

Clearly there is a significant variation between the spectra as a function of substrate bias however it is now necessary to determine the most appropriate fitting scheme. Figure 6.32 shows a variety of fitting schemes applied to typical Raman scans for a sample grown at a negative and positive biasing.

Figures 6.32a and 6.32b show the spectra fitted by two Lorentzian functions. The fit for the negatively biased sample is in good agreement however for the positively biased sample the inter-peak region in particular is not reproduced very well. Additionally the high frequency tail is misfitted. A two Gaussian fit as shown in figures 6.32c and 6.32d also works fairly well for the negatively biased sample but again, the interpeak region of the positive biased sample is not well matched. While the high frequency tail is better
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Figure 6.31: Raman spectra for a range of substrate biasing for films with a composition of approximately 25 at% Ni-C and thickness of around 400 nm

matched than before, the low frequency tail is now poorly modelled due to the faster decay of the function. Finally figures 6.32(e) and 6.32(f) show the results of using a Lorentzian function for the D peak and a BWF function for the G peak. Here we see this model works well for both spectra, positive and negative. As mentioned before, it is important to have a consistent fitting scheme for all samples in order to make them comparable. Given that the BWF-Lorentzian scheme reproduces the whole of both curves accurately it is this model which will be used for the rest of the analysis.
6.4. CARBON STRUCTURE AND ORDERING

(a) Two Lorentzian fit for negative biasing  
(b) Two Lorentzian fit for positive biasing

(c) Two Gaussian fit for negative biasing  
(d) Two Gaussian fit for positive biasing

(e) BWF and Lorentzian fit for negative biasing  
(f) BWF and Lorentzian fit for positive biasing

Figure 6.32: Various fitting schemes applied to the Raman scans for samples grown at positive and negative biasing for films with a composition of approximately 25 at% Ni-C and thickness of around 400 nm
6. CONTROL OF FILM STRUCTURE THROUGH DEPOSITION PARAMETERS

Having fitted the Raman spectra for a range of samples it was then possible to identify some trends in the spectra. Figures 6.33a and 6.33b show how the peak intensity ratios and peak positions vary as a function of substrate bias.

(a) Variation in ratio of intensities for G and D peaks
(b) Variation in Raman peak positions
(c) Variation in Raman peak width

Figure 6.33: Raman fitting parameters as a function of substrate bias for films with a composition of approximately 25 at% Ni-C and thickness of around 400 nm

As seen in figure 6.33b, the G peak position decreases from a value of around 1568 cm\(^{-1}\) for a large negative bias to around 1564 cm\(^{-1}\) for the floating sample, before increasing to 1570 cm\(^{-1}\) when a positive bias is applied. Additionally the ratio of the intensities of the two peaks (I\(_D\)/I\(_G\)) decreases steadily as the negative bias is decreased and reaches a minimum for the floating sample before increasing with positive bias as shown in figure.
This increase in $I_D/I_G$ has also been observed for nickel carbon structures deposited at higher temperatures \[94\] suggesting that there is an increase in mobility occurring for positively or negatively biased samples. These studies also observed the associated increase in G peak position and generated spectra with comparable peak positions and widths (direct comparisons are not possible due to a different laser wavelength being used).

Ferrari et al. [35, 151] proposed a three-stage model for the interpretation of the G band position and intensity as shown in figure 6.34. Stage 2 describes the transition between nanocrystalline graphite and sp$^2$ amorphous carbon. In moving from amorphous carbon to nanocrystalline graphite, the sp$^2$ groups become larger and topologically ordered, moving into a more ring-like structure.

Ferrari et al suggest that the shift in G position on ordering can be from around 1510 cm$^{-1}$ to nearly 1600 cm$^{-1}$, and is due to a reduction in the weaker disordered bonds which have a lower vibrational mode. The increase in G peak position as the bias is made more negative therefore suggests an increase in the ordering of the carbon. It would be surprising if the carbon was only present within the carbide particles (since this cannot form ordered structures), however as observed from TEM there is significant carbon found between the carbide columns. In fact a significant amount of ordered carbon was observed in samples grown at negative biasing as shown in figure 6.15. As the applied bias decreases, and the energy input in to the film decreases, the carbon becomes less ordered and the G peak moves to a lower position. When the substrate is floating (and there is the smallest potential across the sheath) the carbon reaches its minimum of ordering before increasing again as the bias is made positive. Again, we have observed through TEM (figure 6.9a) that samples grown at positive biasing show well defined graphitic shells which contain few defects and therefore would have a high G peak position.

In addition to the peak position itself, the intensity ratio between the D and G peaks is another indicator of increasing order. The ratio of $I_D$ to $I_G$ is known to be related to the number of aromatic rings, that is the amount of ordered material. This shows that, in addition to there being an increase in ordering (as demonstrated through the increase in G peak position) there is also an increase in the amount of ordered carbon in both the negatively and positively biased samples. We can therefore state that by making the bias more positive, or more negative, the carbon moves up the ordering trajectory and becomes more graphitic.
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Figure 6.34: Diagram from Ferrari et al. [35, 151] showing the expected variation in G peak position and $I_D/I_G$ ratio with increasing amorphization.
6.4.3 Effect of varying composition

If the ordered carbon observed in the negatively biased samples is to be attributed to the excess carbon found in the spaces between the carbide columns, rather than the carbide itself, then it stands to reason that the Raman spectra should vary with the amount of excess carbon present. Therefore a set of films was deposited that consisted of $\approx 50$ at% nickel (compared to the $\approx 25$ at% nickel content of the normal films). These nickel rich films would be expected to have less excess carbon and so the ordering at negative biasing would be reduced. Figure 6.35 shows the variation of a variety of fitting parameters with substrate bias for the two sets of films, those containing $\approx 50$ at% nickel and $\approx 25$ at% nickel.

For the metal rich samples (50 at % Ni) there is no increase in G peak position when a negative bias is applied, suggesting that it is not possible to order the carbon in contrast to the graphitisation of the excess carbon observed in 25 at% Ni films. Instead the peak position is virtually constant for negative biasing but increases much more dramatically for positive biasing, reaching 1584 cm$^{-1}$ compared to the 1570 cm$^{-1}$ value for the films containing less nickel. The lack of ordering on the application of negative biasing suggests that most of the carbon is now “locked up” in the carbide phase and so cannot order to form graphite. Conversely, the presence of more nickel appears to encourage the formation of graphite on positive biasing. This supports the hypothesis that the nickel particles template the graphite growth and therefore by increasing the amount of nickel present, a greater proportion of carbon finds itself neighbouring a nickel particle and is therefore subject to the templating effect. These findings are re-enforced by the intensity ratio data which show a very low value at negative biasing, suggesting that these samples contain very little graphitic carbon.
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(a) Variation in ratio of intensities for G and D peaks

(b) Variation in Raman peak positions

(c) Variation in Raman peak width

Figure 6.35: Raman fitting parameters as a function of substrate bias for films with a composition of approximately 50 at% Ni-C and thickness of around 400 nm

6.4.4 Pure carbon films

The presence of nickel has a dramatic affect on the structure of carbon in the film. However the ion bombardment and ionisation effects will play a role in the carbon formation also. In order to investigate this a series of carbon only films was grown. Figure 6.36 shows the resulting scans while figure 6.37 shows some key fitting parameters as a function of substrate bias. Note that one sample was grown using traditional sputter deposition without an additional coil to provide a comparison.

Clearly there is a significant variation in the structure of the films as deposition pa-
rameters are varied. Of particular interest is the sample grown without biasing. This sample shows the highest G peak position, the narrowest peaks and the highest $I_D$ to $I_G$ ratio. With the coil active and a floating substrate, there is a relatively small variation compared to the sample grown without a coil, with the G peak position shifting from around $1588 \text{ cm}^{-1}$ to $1583 \text{ cm}^{-1}$ and the intensity ratio falling from around 1.18 to 1.16. Upon the application of a negative bias a greater variation is seen, the G peak position moves to a lower frequency of around $1579 \text{ cm}^{-1}$ and the peaks broaden significantly. Additionally the intensity ratio falls to just 1.03.

Application of a large positive bias decreased the G peak position to a value comparable to that for the sample grown at negative bias and produced a similar peak broadening, however the intensity ratio did not decrease as significantly, only reaching 1.12. The apparent disordering of the carbon upon application of both a positive and negative biasing indicates that in the case of pure carbon, additional energy is detrimental to graphitic formation. In the case of high energy bombardment (occurring at negative biasing) it is possible the ions damage the film. Comparison of the deposition rates may also shed light on these variations. In the case of no secondary ionisation the deposition rate was $5.6 \pm 0.2 \text{ nm min}^{-1}$ while for a negative bias this fell to $3.9 \pm 0.4 \text{ nm min}^{-1}$.

![Figure 6.36: Raman spectra of pure carbon films grown at a range of substrate biasing, each with a thickness of around 400 nm](image-url)
In the case of a floating substrate with the coil active the deposition rate was nearly twice that for a negative biasing \((7.2 \pm 0.3 \text{ nm min}^{-1})\) suggesting that resputtering may be occurring with the negative bias applied. This suggests that the ion energy is sufficient to disrupt the local structure and introduce the disorder observed through the Raman analysis. Conversely when a positive bias is applied the deposition rate increases to \(11.9 \pm 0.7 \text{ nm min}^{-1}\). This higher deposition rate, though combined with an increased mobility due to the low energy bombardment, may result in lower graphitisation due to insufficient time to form an ordered structure before being covered by the next layer of carbon.

(a) Variation in ratio of intensities for G and D peaks  
(b) Variation in Raman peak positions  
(c) Variation in Raman peak widths

Figure 6.37: Raman fitting parameters as a function of substrate bias for pure carbon films of thickness around 400 nm
6.5 Film roughness

Given the variation in growth morphology observed in the TEM results, the surface morphology of the films is of particular interest. Additionally surface topology is important for low wear rates, an important parameter for hard coatings. Atomic force microscopy (AFM) was therefore performed to determine the surface roughness and surface morphology. Figure 6.38 shows the variation in measured RMS roughness with substrate bias.

![RMS roughness graph](image)

Figure 6.38: Graph showing the variation in RMS roughness with substrate bias as measured over a 5 micron square area. The films had a composition of approximately 25 at% Ni-C and thickness of around 400 nm

The variation in sample roughness appears to form a minimum for low biasing before rising slightly if a negative bias is applied, and rising significantly upon application of a positive bias. For the most positively biased samples we see a large particle size in the AFM scans as can be seen in figure 6.39.

There is an increase in surface feature size from around 100 nm for the +100 V biased samples to around 150 nm for the +200 V biased samples. This trend supports the observations from TEM which suggested that there is an increase in particle size for increased biasing, though the values measured by AFM are significantly larger than those measured by TEM. The larger particles create a more varied surface, such that the surface roughness increases, likely due to the height of a particle being much greater than that of an inter-particle space (as a result of different growth rates). As the particle size decreases with decreasing bias, the surfaces become more uniform and smoother as is the case for the earthed sample which shows very low surface roughness.
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Figure 6.39: AFM scans for samples grown at positive biasings for films with a composition of approximately 25 at% Ni-C and thickness of around 400 nm.

Of note is the similarity in surface roughness of the +100 V sample and the -150 V sample. While having similar surface roughness, we can see in figure 6.40 that the two samples have very different particle sizes.

Figure 6.40: AFM scans for samples showing similar surface roughness but different surface particle size for films with a composition of approximately 25 at% Ni-C and thickness of around 400 nm.
The surface features of the positively biased sample are around 100 nm, yet the negatively biased sample has features of just 45 nm. It is therefore important to remember that surface roughness is not directly related to particle size. Surface roughness continued to increase for increasingly negative biasing though it remained significantly lower than was seen in the positively biased case.

This variation in roughness with particle size and type is not unexpected. As the column size increases there will be greater disparity between grains that have grown at slightly different orientations and rates, therefore leading to a rougher surface. In the case of smaller columns (as seen at lower biasings) the variations exist at a smaller scale leading to a smoother surface overall.
6. CONTROL OF FILM STRUCTURE THROUGH DEPOSITION PARAMETERS

6.6 Nickel-carbon bonding and chemistry

X-ray photoelectron spectroscopy (XPS) is a widely used tool for determining the chemical structure and bonding within a material. By analysing the bonding within the films it should be possible to determine how the nickel and carbon bond to one another and differentiate between a nickel carbide phase and a hexagonal nickel phase. However, since XPS is a surface analysis technique, it is important to test a representative area. The samples had been exposed to air prior to testing and so were likely to include a surface oxide layer. To remove this and expose a surface representative of the bulk, an ion beam etch was used to mill away the surface 5 nm of material. The variation in XPS scans, before and after milling for both the C1s and Ni2p regions are shown in figure 6.41 (see section 4.2.6 for an explanation of the 1s and 2p envelopes).

![Figure 6.41: XPS Scans showing the effect of milling for films grown at positive bias with a thickness of around 400 nm](image)

The etching removed much of the noise from the nickel region, a result of the post-
milling surface having a much higher nickel content. The carbon envelope has also changed significantly, likely a result of carbon oxygen bonds having been removed. In order to determine how the bonding changed with substrate bias, a range of samples were tested with the post-milling scans shown in figure 6.42.

In order to quantify the changes a series of pseudo-Voigt functions were fitted to the data. Fitting of XPS profiles, and the carbon 1s envelope in particular, is a complex and inexact process. In the case of the carbon 1s envelope there are many bonds at very similar energies which can easily lead to overfitting or misfitting. One solution to this problem [38] is to fix the peak position to within a narrow range around a known value for common bonds. By fixing the peak position but then allowing the peak width and intensity to vary, it is possible to fit a model to the measured curves. In total 9 peaks were used to fit the areas of interest, the corresponding bonds and approximate positions are listed in table 6.2.

<table>
<thead>
<tr>
<th>Carbon Peaks</th>
<th>Nickel Peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond</td>
<td>Binding Energy (eV)</td>
</tr>
<tr>
<td>C=O</td>
<td>288.5</td>
</tr>
<tr>
<td>C-O</td>
<td>286.2 - 286.6</td>
</tr>
<tr>
<td>sp³ C</td>
<td>285.2 - 285.3</td>
</tr>
<tr>
<td>sp² C</td>
<td>284.5 - 284.8</td>
</tr>
<tr>
<td>Ni₃C</td>
<td>283.3 - 283.5</td>
</tr>
<tr>
<td>Ni₂C</td>
<td>281.5</td>
</tr>
</tbody>
</table>

Table 6.2: Expected bonds within the films and the associated binding energy [152, 38]

The two Ni-C type bonds correspond to the different possible bonding structures between nickel and carbon. Kovacs et al [152] suggest that within a carbide (Ni₃C) the nickel-carbon bonding will be significantly different to the bonding between a nickel atom at the edge of a nickel (or nickel carbide) particle and the neighbouring carbon phase (the bond denoted Ni₂C). The bonding between these two phases will result in a shift of the peak position away from 281.5 eV (for Ni₃C) to around 283.4 eV (for Ni₂C).

Figure 6.43 shows how the ratio of the sp³ to sp² peaks and how the fraction of total peak area the Ni₂C peak represents, varies as a function of substrate bias. The sp³/sp² ratio measured acts as a useful compliment to the Raman data. While the Raman measurements suggested an increase in sp² (graphitic) bonding within the carbon it does
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Figure 6.42: XPS scans for films grown at a range of substrate biasing for films with a composition of approximately 25 at% Ni-C and thickness of around 400 nm
not give information about the sp$^3$ bonding state. Figure 6.43a shows a decrease in sp$^3$/sp$^2$ ratio as the substrate bias increases, however closer examination of the peaks show that this is due to an increase in sp$^2$ peak height rather than a decrease in sp$^3$ content. This agrees with the Raman results which demonstrated an increase in graphitic ordering with positive bias. The low sp$^3$ content also confirms the TEM observations that graphitic ordering dominates the structures. This supports the use of visible light Raman analysis to parameterise the carbon structure as any sp$^3$ content is small.

![Figure 6.43: Fitting parameters of XPS data as a function of substrate bias for films with a composition of approximately 25 at% Ni-C and thickness of around 400 nm. Also shown are the model curves used to fit the spectra.](image)

Figure 6.43b also shows an increase in the prevalence of the bonding state associated with the interface between the nickel (or nickel carbide) structures and the carbon rich phase as the bias is made increasingly positive. This in itself is not surprising, as given the decreasing size of the particles with increasing bias, there is greater amount of interface and therefore more Ni$_x$C bonds would be expected.

However it is also important to note the apparent complete absence of any Ni$_3$C bonding states. The corresponding peak, expected at around 281.5 eV is not present in any form for any of the measured samples. This raises the issue of whether the samples grown at negative biasing do, in fact, consist of a carbide phase.

The solution to this discrepancy may lie in the variation between the compositions measured by EDX and those measured by XPS. While EDX results (both from TEM and SEM experiments) show a film composition of around NiC$_3$ for all biasings, XPS results
show widely varying compositions as a function of substrate bias. The positively biased samples show a larger nickel content and significant oxygen contamination \((\ce{C_{40}Ni_{34}O_{26}})\), while negatively biased samples shows a smaller nickel composition \((\ce{C_{40}Ni_{26}O_{34}})\). In each case the oxygen content is much larger (around 30 at\%) than measured by EDX (\(< 2\ \text{at}\%)\). While the presence of oxygen may be a result of surface oxidation, the XPS values for oxygen content appear to increase with ion etching (prior to ion etching the composition of the samples grown at positive and negative bias are both around \(\ce{C_{75}O_{25}}\) with only trace amounts of nickel detected). Clearly these compositions do no match those measured by EDX in either the SEM or TEM systems (which give compositions consistent with one another). Neither do these compositions match the volume fractions and phases observed via TEM.

It is therefore highly likely that the XPS results are not representative of the actual film. This error is likely a result of differences in the ion etching rate for the different phases and microstructures. The lower carbon content than expected may be caused by preferential removal of the carbon phase. While the exact reasoning behind the anomalous observations are not certain, it is highly likely that the surface being measured is not a true representation of the bulk structure and therefore the XPS results are of limited use in characterising the films. Further work is required to ensure the measured surface is free from oxidation but also to ensure any milling does not disrupt the film. Using a synchrotron XPS allows for higher energy x-rays to be used which penetrate beyond the surface, without the need for ion etching. This would allow for better characterisation of the films as it would probe the bulk structure without the risk of uneven etch rates resulting in an unrepresentative surface being measured.

### 6.7 Effect of Varying Coil Power and Deposition Pressure

The structural variations observed as a function of substrate bias stem predominately from the nature of the secondary plasma, which in turn is dependent on two factors, the background gas pressure and the power supplied to the RF coils. Through varying these parameters it is possible to alter the nature of the plasma and therefore the effect of varying substrate bias.
6.7. EFFECT OF VARYING COIL POWER AND DEPOSITION PRESSURE

6.7.1 Gas pressure

Varying gas pressure is a technique widely used in traditional magnetron sputtering to control deposition. Increases in gas pressure increase the number of argon ions (though not the ionisation fraction) and therefore the number of collisions with the target, increasing the sputtering rate. However it decreases the mean free path within the chamber and so depositing atoms undergo more collisions. This reduces the deposition rate and decreases the energy with which the atoms deposit. This can have dramatic effects on the film structure and internal stresses and so gas pressure is often used as a tool to control film structure.

However with the introduction of an additional ICP the role of gas pressure becomes more complex. The increase in pressure decreases the mean free path and therefore increases the residence time of the depositing species within the secondary plasma. This in turn increases the likelihood of an ionising collision occurring and so an increase in ionisation fraction is observed [16]. Even though only a small proportion of the depositing energy (see equation 3.30) comes from the energy the atom has as it enters the plasma sheath, the reduction in this energy that occurs as a result of the increased number of collisions may be important in cases of low biasing where there is little additional energy due to acceleration across the sheath.

To investigate the effect of pressure on the film structures, samples were deposited at 1 Pa and 5 Pa (compared to the 2 Pa typically used). Figure 6.44 shows how the nickel structure varies as a function of substrate bias as measured from XRD data.
Figure 6.44: XRD scans for samples grown at 1 Pa, 2 Pa and 5 Pa at a range of substrate biasing, deposition times were altered to achieve films with thickness of 300 nm and deposition powers altered to ensure a composition of around 25 at% Ni-C. *Except for the sample grown at 5 Pa with a bias of +250 V which was thinner (200 nm) for reasons described in the text.
6.7. EFFECT OF VARYING COIL POWER AND DEPOSITION PRESSURE

Additionally it is of interest to compare these samples to films grown in the absence of a secondary plasma, where ion bombardment effects are minimal. The XRD data for these films is shown in figure 6.45.

![XRD scans of films grown without secondary ionisation. Due to a lower deposition rate, these samples were grown for a longer time such that the thickness was comparable to samples grown with the coil active.](image)

Figure 6.45: XRD scans of films grown without secondary ionisation. Due to a lower deposition rate, these samples were grown for a longer time such that the thickness was comparable to samples grown with the coil active.

In the case of the low pressure depositions (at 1 Pa) we observe that the hexagonal phase remains present even when a positive biasing of +250 V is applied. Additionally the crystallinity of the structures appears to be higher quality than comparable films grown at 2 Pa for equivalent biasing as demonstrated by an increase in peak intensity. While reducing the pressure increases the fraction of the sputtered energy the atoms retain, we see from the samples grown without the coil (which are largely amorphous) that this effect is insufficient to explain the high crystallinity. Therefore there must be ionisation occurring within the secondary plasma, leading to an increase in the energy of the depositing species. Since the deposition is occurring at lower pressure, a greater fraction of this energy is then maintained until the ions deposit. However since each sputtered atom undergoes fewer collisions, the ion density decreases. This means that regardless of the biasing, there is a low flux bombardment occurring since the ion fraction is never sufficiently high. This explains why well defined peaks are observed for all bias voltages compared to samples grown at 2 Pa (which display poor crystallinity at intermediate...
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biasing voltages due to the low energy of the depositing species). Yet no cubic phase is found for positive biasing due to the low ion flux not generating the required increase in mobility which occurs for high flux bombardment (as discussed further in section 7.1).

The samples grown at 5 Pa show a different trend, one more comparable to that seen at 2 Pa. At negative biasing we observe the carbide formation in a crystalline state, however at a floating bias (when the energy input into the film is smallest) there is no crystallinity. This suggests that the higher pressure has been sufficient to thermalise the depositing species and so, without significant acceleration across the sheath as a result of an applied bias, the species have very low energy and so form amorphous structures. The ionisation fraction is now sufficiently high that the application of negative bias causes ion bombardment which leads to the crystallisation of the nickel carbide phase, while the plasma density is large enough so that the application of a positive bias causes the phase change to the cubic phase. The sample grown at +180 V shows the onset of the cubic phase, this is not apparent in the sample grown at +250 V. This is likely due to the sample grown at +250 V being significantly thinner than the other samples. This is due to a decrease in deposition time which was required to avoid the film fracturing due to the tensile stress which occurs at higher pressures 153.

To further analyse the affect on structure, Raman spectroscopy was performed on each of the samples with the main fitting parameters shown in figure 6.46.

Figure 6.46: Variation of Raman fitting parameters as a function of substrate bias for a range of deposition pressures for films with a thickness of around 300 nm (with the exception of the 5 Pa, +250 V sample which was 200 nm thick).
6.7. EFFECT OF VARYING COIL POWER AND DEPOSITION PRESSURE

The variations observed in the carbon ordering largely reflect the findings of the XRD characterisation in terms of the varying levels of crystallinity. For the 1 Pa deposition there is a relatively small variation in the ordering parameters as a function of bias, suggesting that bias has a negligible affect. The intensity ratios (figure 6.46a) for the 1 Pa case follow the general trend seen for the 2 Pa case, however to a much smaller degree, suggesting any effects have been minimised (the intensity ratios for the 1 Pa deposition only vary by around 0.1 in moving from -150 V to 130 V while for the 2 Pa case there is a change of over 0.2). However it is interesting to note that the 1 Pa sample sees an increase in carbon ordering for positive bias despite there not being an associated nickel phase change, as evidenced by an increase in G peak position from 1565 cm\(^{-1}\) at 130 V to 1575 cm\(^{-1}\) at -150 V. This suggests that it is possible to order the amorphous carbon found between the carbide clusters through the application of a large positive or negative bias, without requiring a nickel phase change from carbide to metallic nickel which would then template the graphite growth.

For the case of the 5 Pa deposition, the variation between samples is much greater than that seen in both the 1 and 2 Pa case, with the ratios increasing by over 0.3 as the bias is changed from 130 V to either +250 V or -150 V. As with the XRD analysis, we see for the floating substrate there is a much lower degree of ordering (lower I\(_D\) to I\(_G\) ratio and lower G peak position) which again suggests these conditions result in a very low energy flux to the surface. Upon application of a large negative or positive bias, the effects of the increase in pressure are reduced and the level of order returns to a comparable value for the samples grown at lower pressure.
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6.7.2 RF power

The power applied to the coil is expected to have a direct effect on the ionization fraction of the depositing species. By increasing the RF power the ionization fraction increases for a given flux of atoms through the plasma \[15\]. In this regard, altering the coil power has similarities with changing the background pressure, however while increasing the pressure increased the ionisation fraction, but also thermalised the depositing species and reduced the deposition rate, increasing the coil power only alters the ionisation fraction. Increasing the coil power increases the electron temperature and therefore increases the likelihood of an electron collision resulting in ionisation. We should therefore observe some subtle differences between the two cases. To investigate this, XRD (figure 6.47) and Raman analysis (figure 6.48) was performed on films grown at a range of coil powers.

In decreasing the coil power to 50 W we observe that the level of crystallinity across all biasing has decreased significantly. In the case of a -150 V biasing there is evidence of a carbide phase while at positive biasing there is some slight evidence of the onset of a metallic cubic phase. However for samples grown at around the floating potential, the films are largely amorphous, particularly in the case of a floating substrate. In the case of a coil at 100 W the carbide phase is virtually absent at 180 V and not detectable at +250 V. When the coil power is increased to 150 W the carbide phase, while clearly visible at negative biasing, is not well defined at biasings above +132 V. The asymmetry of the peak at 44° suggests there may still be some carbide present at a floating bias, however the broadness of the peaks implies any crystalline particles are very small in size. At +180 V there is a detectable amount of cubic phase present while at +250 V the cubic phase is clearly present, more so than in the 100 W case.
Figure 6.47: XRD scans for samples grown at coil powers of 50 W, 100 W and 150 W at a range of substrate biasing, all films had a thickness of around 300 nm and composition of around 25 at% Ni-C
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Changes in the carbon structure were analysed using Raman spectroscopy with the key fit parameters shown in figure 6.48. Samples grown at 50 W show a decreased G peak position across all biasing values, implying a decrease in ordering. For those samples grown at 150 W, the G peak position is comparable to the 100 W samples, suggesting that the quality and defect density of the graphitic structures is broadly similar.

![Graph](image)

(a) Ratio of peak intensities  
(b) Peak positions

Figure 6.48: Variation of Raman fitting parameters as a function of substrate bias for a range of RF coil powers, each film had a thickness of around 300 nm.
6.8 Film Properties

The variation in film structure has a dramatic effect on the material properties. These properties are not only important for any potential applications, but they also provide additional insight into the behaviour of the structures, which can then be used to further build up a picture of the interaction between the nickel and carbon phases. Two key parameters for many potential applications are the magnetic and electronic behaviour. For this reason, these two characteristics will be explored further.

6.8.1 Magnetic measurements

The distinction between hexagonal nickel carbide and hexagonal nickel is a difficult task as has been stated previously. One approach that makes this distinction possible is to analyse the magnetic properties of the film. Cubic nickel (and hexagonal nickel) is known to be strongly ferromagnetic, while nickel carbide is thought to be non-magnetic (see section 2.3.3). Therefore measuring the variation in magnetisation with substrate bias should give an indication of the underlying structure.

Figure 6.49 shows room temperature Vibrating Sample Magnetometer (VSM) measurements for samples grown at a range of substrate biasing, the samples have been normalised for thickness, however due to the differing densities of the phases, no attempt has been made to give magnetisation per atom or per gram of nickel. The films each have a composition within 2.5 at% of one another, and so having been normalised for thickness, the results are comparable.

While none of the samples show hysteresis, there is a clear variation in saturation magnetisation with substrate bias which is consistent with the varying levels of fcc nickel and nickel carbide as seen from the XRD results. Given that nickel carbide is non-magnetic we see the magnetisation of the samples decrease as the carbide content increases and the metallic nickel content decreases. To better see this variation, figure 6.50 shows the magnetisation at 3000 Oe for each of the curves.
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Figure 6.49: VSM showing magnetic properties of films grown at a range of substrate biasing for films with a composition of approximately 25 at% Ni-C and thickness of around 400 nm

Figure 6.50: Variation in saturation magnetisation as a function of substrate bias for films with a composition of approximately 25 at% Ni-C and thickness of around 400 nm
Nickel carbide is non-magnetic due to the Ni-C hybridised bonding, however some magnetic behaviour persists due to residual fcc nickel and from defects which can lead to locally nickel rich regions which form as fcc nickel. From the TEM-EDX results it appears that there is also some fcc nickel near the interface with the substrate and so it seems likely that there will always be some amount of magnetisation, which becomes smaller as the bulk film increasingly adopts the carbide phase.

However as previously noted, none of the curves show hysteresis, suggesting that the normally ferromagnetic nickel has undergone a superparamagnetic transition due to the small size of the particles, leading to the closed curves observed. Superparamagnetism occurs when the energy barrier to magnetic reversal becomes comparable to the thermal energy and so the magnetic moment is able to rotate freely [154]. The process does not occur at a single temperature, but rather the inverse spin-reversal frequency decreases rapidly at lower temperatures. Therefore at lower temperatures the rate at which the spins rotate is slowed and so ferromagnetic behaviour is recovered. To confirm this, low temperature magnetisation measurements were performed on a sample grown at positive bias (and therefore containing the most amount of metallic nickel) using a SQUID as shown in figure [6.51].

Figure 6.51: SQUID curves showing magnetic hysteresis as a function of temperature for a sample grown at +250 V with a composition of approximately 25 at% Ni-C.

There does not appear to be a significant variation with temperature with all three
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scans showing very similar behaviour. We do however see hysteresis indicating a ferromagnetic behaviour with a saturation magnetisation of around 70 emu cm\(^{-3}\). This value is in agreement with values reported for carbon encapsulated nickel elsewhere \cite{155, 156} which report values of around 74 emu cm\(^{-3}\). (This value is derived from the quoted saturation magnetisation of 20 emu g\(^{-1}\) and taking a density of 3.69 g cm\(^{-3}\), assuming bulk values of density and perfect phase separation). Upon closer examination we can observe a variation in coercivity with temperature as expected (figure 6.52).

Figure 6.52: SQUID data showing magnetic hysteresis at low temperature for samples grown at at +250 V with a composition of approximately 25 at\% Ni-C.

There is a clear variation in coercivity with temperature with the value rising from 85.5 Oe at 100 K to 490 Oe at 10 K and reaching 570 Oe at 4 K. The coercivity remains non zero at higher temperatures indicating superparamagnetism has not occurred. Given that the blocking temperature (the temperature at which materials become superparamagnetic) is a function of particle size it is possible to calculate a bounded estimate of the nickel crystallite diameter.

The particle size is related to the blocking temperature \cite{142} by:

\[
T_b = \frac{KV}{25k_B}
\]  \hspace{1cm} (6.12)

Where \(k_B\) is the Boltzmann constant, \(T_b\) is the blocking temperature, \(V\) is the particle volume and \(K\) is the magnetocrystalline anisotropy energy. Therefore, given that the
samples grown at positive bias (consisting of nickel nanoparticles) are ferromagnetic at 100 K and superparamagnetic at 300 K and taking the bulk value for $K$ of Ni to be $5 \times 10^5$ erg cm$^{-3}$, we find that a significant fraction of the particles must be larger than 24 nm in diameter but smaller than 35 nm, which is in agreement with the TEM results.

6.8.2 Electrical properties

The structure of the deposited films has been observed to alter greatly with varying substrate bias. This has a significant effect on the magnetic properties of the films but it also has an effect on the electrical properties. Therefore 4-point resistivity measurements were performed on samples grown at various biasing as described in section 4.2.7.

Figure 6.53 shows the variation in resistivity as a function of temperature, normalised to the resistivity at 273 K. The normalisation is required due to the difficulty in measuring the true resistivity of the film as this is largely dependent on the sample geometry.

A useful parameter to measure is the variation in resistivity with temperature, or the temperature co-efficient of resistivity (TCR). A positive TCR indicates a metallic like structure, where resistance increases with temperature due to additional electron scattering. In semiconductors and dielectrics, a negative TCR is observed, typically due to an increase in available charge carriers at high temperature and the thermal activation of excitations across the band gap, both of which increase conductivity.

From figure 6.53 we observe that each curve has two distinct regions. The first extending from 70 K up to around 180 K (hereafter referred to as the low temperature region) and a second region extending from 180 K up to 300 K (the high temperature region).

Resistivity curves which alter dramatically with temperature have been observed for molybdenum-carbon, copper-carbon and nickel-carbon films elsewhere. It has been suggested that there are two conduction mechanisms; thermally activated conduction and tunnelling. The thermally activated conduction describes the high temperature region where the dependence on temperature is much greater, while tunnelling conduction dominates at lower temperatures. Tunnelling likely occurs at the higher temperatures also, but is a much smaller effect and so is masked.

The high temperature region shows a very large change in resistivity with temperature. The TCR measurements for this region are shown in figure 6.54.
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Figure 6.53: Variation in resistivity with temperature for samples grown at various substrate biasing with a composition of approximately 25 at% Ni-C. Resistivities have been normalised for thickness and then to the resistivity at 273 K.

Figure 6.54: Temperature co-efficient of resistivity in the high temperature region for films grown at various biasing with a composition of approximately 25 at% Ni-C.
The value of TCR for the negatively biased samples ranges from $-2 \times 10^{-3} \text{K}^{-1}$ to $-6 \times 10^{-3} \text{K}^{-1}$. This is comparable to a value reported for amorphous carbon when no nickel is present ($-8 \times 10^{-3} \text{K}^{-1}$) [160]. The TCR for amorphous carbon is seen to increase with nickel content, however for tunnelling limited conduction between nickel carbide particles and amorphous carbon, a TCR of $-3.5 \times 10^{-4} \text{K}^{-1}$ to $-4 \times 10^{-4} \text{K}^{-1}$ has been recorded [36], almost an order of magnitude lower than the value measured here. This suggests that rather than tunnelling effects (which would then be dependent on the nickel carbide), at higher temperatures thermally activated conductivity dominates.

At higher temperatures electrons can be excited into the extended state of the amorphous matrix through the Poole-Frenkel effect. This effect allows localised electrons to move into the conduction band due to thermal fluctuations [161] before relaxing back into a localised state on a neighbouring atom. This results in normally insulating materials (in this case the amorphous carbon) being able to conduct. Poole-Frenkel conduction has been observed [162] in amorphous carbon at near room temperature for moderate electric fields and so is a likely explanation for the observed variation in resistivity with temperature.

The TCR value for the positively biased sample is much greater still at $-0.022 \text{K}^{-1}$. This value is negative, implying dielectric like behaviour, but is much larger than can explained by either amorphous carbon or the presence of graphite and metallic nickel which have TCR values of $-0.0005 \text{K}^{-1}$ and $0.006 \text{K}^{-1}$ respectively [65]. This anomalous result may be due to the presence of a graphitic percolation path (as discussed later) which complicates the higher temperature behaviour.

Upon cooling (below $\approx 180 \text{K}$) the temperature dependence drops significantly. This is indicative of a transition to a tunnelling mechanism for conduction [159]. In this regime the conduction is controlled by thin amorphous layers of carbon between the conductive particles. To better analyse this region, the TCR values are plotted in figure 6.55.

The TCR for the most positively biased sample is now found to be $-4.8 \times 10^{-4} \text{K}^{-1}$. The fact that this value is still negative implies that there is not a continuous pathway through the sample of adjoining nickel nanoparticles - no percolation path is formed. Indeed the value of TCR for the positively biased sample is approaching that of pure graphite. This suggests that the conduction path is predominately made up of graphite, which is not surprising given the TEM and Raman data. It is possible that a graphitic carbon percolation path has been formed and therefore the conductivity properties of
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Figure 6.55: Temperature co-efficient of resistivity in the low temperature region for films grown at various biasing with a composition of approximately 25 at% Ni-C.

the graphitic carbon dominate. At high temperatures it may be possible for conduction to occur between the graphite layers via a thermally activated process [163]. Given the normally very anisotropic conductivity of graphite (\(2 \times 10^4 \Omega^{-1} \text{cm}^{-1}\) parallel to the layers and \(2 \Omega^{-1} \text{cm}^{-1}\) perpendicular to them [164]) this cross layer conduction would significantly reduce the resistivity.

For samples grown at negative biasing, the low temperature TCR values are also negative, albeit smaller in magnitude. This is likely due to the presence of amorphous carbon between the carbide columns, indeed the value of \(-3.5 \times 10^{-4} \text{K}^{-1}\) to \(-4 \times 10^{-4} \text{K}^{-1}\) is comparable to those reported for nickel carbide in amorphous carbon elsewhere [36] when no percolation path is present. These regions of amorphous carbon prevent conduction and therefore tunnelling is required [159]. The temperature dependence of this effect can be described [165] by:

\[
\rho = \rho_0 \exp \left(2 \sqrt{\frac{C}{k_B T}} \right) \tag{6.13}
\]

Where \(\rho\) is the resistivity, \(\rho_0\) is the resistivity at room temperature, \(k_B\) is the Boltzmann constant, \(T\) is the temperature and \(C\) is the tunnelling activation energy. Figure 6.56 shows a plot of \(\ln \rho/\rho_0\) against \(1/\sqrt{T}\) for samples grown at a range of biasing, the gradient of these lines is equal to \(2 \sqrt{C/k_B}\) from which \(C\) can be calculated.
Figure 6.57 shows how the tunnelling activation energy, \( c \), varies for the films in the low temperature region (<180 K).

The model from which the equation for the activation energy, \( C \), is derived assumes

![Figure 6.56: Plot of \( \ln(\rho/\rho_0) \) against \( 1/\sqrt{T} \) for samples of composition 25 at% Ni-C grown at a range of biasing, each sample is around 400 nm thick.](image)

![Figure 6.57: Variation in tunnelling activation energy in the low temperature regime for samples grown at various biasing](image)
6. CONTROL OF FILM STRUCTURE THROUGH DEPOSITION PARAMETERS

spherical particles in a cubic array, while this is of limited application here, qualitatively it still gives an indication of the ease of tunnelling.

The tunnelling itself occurs across any insulating layers, with the areas of amorphous carbon likely dominating. The value of C for the sample grown at +250 V is found to be the smallest, which is unsurprising since this structure is made up predominately of conductive metallic nickel and an extensive graphitic carbon network. The carbon network forms a near complete pathway (as shown by the similarity of the TCR to that of pure graphite) and so any tunnelling distances will be minimal.

The activation energy is dependent on a number of factors including the conductive particle size, the conductivity of each component, the tunnel length and the nature of the interface between the two. Therefore it is not possible to calculate the tunnel distance since too many parameters are unknown.

However with these factors in mind is is possible to explain the decrease in tunnelling energy as the bias is made increasingly positive. At large negative biasing, the coarsening has lead to larger carbon regions between the carbide particles. This increases the tunnelling distance, therefore making the process more difficult. While the tunnelling distance decreases as the bias is made smaller, the extent of graphitic ordering also decreases. This means there will be more amorphous carbon present which also makes tunnelling difficult. Finally, as the bias is made positive, the tunnelling distances become much smaller as a near complete graphitic pathway is formed. Combined with the change in conductivity of the metallic nickel compared to the carbide, this explains why the tunnelling activation energy decreases.

The complex nature of the structures make analysis of the electronic properties difficult. While the explanation given here offers one potential solution, it is by no means definitive. It is however clear that in addition to the electronic properties of the individual components, the structure of the composite is also important.
Chapter 7

Controlling Growth Through Deposition Parameters

The structure of the deposited films varies significantly as a function of deposition parameters. However as seen from the measurements of the plasma properties, the flux of species to the surface also varies significantly. By drawing together the various trends and observations made, it is possible to rationalise the results.

As discussed in section 3.4 the energy input into a film is a major driving force in determining its microstructure which in turn determines the film properties. Ion bombardment is a widely used tool to control energy input into a film along with variation of homologous temperature. There are many drawbacks to simply varying the deposition temperature, such as interdiffusion with the substrate, or substrate degradation but also that for many materials with high melting points it can be a technical challenge to achieve the required high temperatures. Ion bombardment is therefore an attractive option to controlling microstructure.

7.1 Energy input into a growing film

The energy input into a film from ion bombardment is dependent on two factors, the ion flux, and the ion energy. However it became apparent that film structures did not correlate with a simple product of these two factors [117]: low flux high energy bombardment was not equivalent to high flux low energy bombardment. This fact is shown clearly in the
work seen here.

The film structures varied fundamentally as a function of substrate bias, in terms of morphology, crystallinity and crystal structure. The transition from hexagonal nickel carbide at negative biasing through to cubic metallic nickel for positive biasing is comparable to that seen during heating of similar structures [92]. Upon heating, the carbon nickel bonds can break and the increased mobility due to higher temperatures allows the carbon atoms to diffuse out of the carbide and form a separate phase. However, the different films here are all grown at comparable temperatures (150 °C) which do not approach those temperatures required for the thermal breakdown of the carbide phase (600 °C). The resulting structures must therefore form upon deposition as a result of the bombarding ion flux, and not as a result of a temperature induced transformation.

The samples grown at negative biasing show an increase in crystallinity as the bias is increased, as observed in both the TEM cross sections (figure 6.12) and XRD results (figures 6.20 and 6.23b). The columnar structure of the films coarsens as the bias is made more negative and a transition to a zone T (as described by the zone models discussed in section 3.5) type structure is observed. In the case of the earthed and floating substrates the column width is very narrow (5 to 20 nm in diameter) but this increases to nearly 50 nm as the bias increases. This coarsening is due to the increase in energy as a result of the ion bombardment leading to grain growth. The energy of the bombarding ions can be calculated from:

\[ E = E_0 + qe(V_P - V_B) \]  

(7.1)

Where \( E_0 \) is the energy of the ion as a result of the sputtering process and \( qe(V_P - V_B) \) is the additional energy gained by the ion as it is accelerated across the sheath as a result of the potential between the substrate (\( V_B \)) and the plasma potential (\( V_P \)). This sheath potential can be calculated from figure 5.15. It is clear that the energy of the impinging ions increases significantly as the bias is made more negative, however from figure 5.16 we see that there is a relatively low ion density. These films are therefore grown under a high energy low flux bombardment. High energy bombardment leads to linear cascades [119]; the incident bombarding ion strikes a surface adatom and transfers momentum, and this adatom then transfers momentum to a neighbouring atom and so on. This means that the energy input into the film extends beyond the surface layers and
7.2. DISTINGUISHING HEXAGONAL NICKEL FROM NICKEL CARBIDE

can have bulk effects. Increasing the bias increases the energy input into the film and leads to the observed coarsening and increases the crystallinity of the structure. However this increase cannot extend indefinitely. Increasing the energy of the bombarding species too much can lead to the generation of defects in the crystal and ion implantation as the bombarding species drive into the film. This implantation can occur from both the inert gas species (argon) but also the depositing ions themselves. From EDX analysis there was little argon measured in the films and so it is unlikely significant implantation of the background gas occurs. Implantation of nickel or carbon ions would likely increase the defect density of the films however from the XRD data in figure 6.20 there is a continued trend towards improvement in crystallinity from an increase in peak intensity and narrowing of peak width. This indicates that at the biasing applied (up to -200 V) there is no measurable damage to the film structures and so ion implantation is unlikely to occur in any significant amount. A similar limit was observed in TiC films where biasing above -250 V led to resputtering [124].

7.2 Distinguishing hexagonal nickel from nickel carbide

Despite the increase in energy input into the film, the crystal structure of the nickel containing phase remains constant for negative biasing. As mentioned, identifying this phase is non-trivial. Typically XRD data is used for phase identification of such structures however as shown in figure 6.19 the peak positions for the hexagonal nickel phase and the hexagonal nickel carbide phase are virtually identical. However there is an array of evidence to suggest that this phase is indeed a carbide phase rather than a hexagonal nickel phase.

A simple observation of the TEM results gives a strong clue towards the identification of the phase since the images show large volumes of a single phase with some inter column second phase. Given the composition of 25at% Ni-C, if there was a pure nickel phase (since EDX data shows nickel to only be present in the column forming phase) then one would expect a significant volume fraction of secondary, carbon rich phase, which is not observed.

Magnetic data from the literature for the carbide phase and hexagonal nickel phase is incomplete and mixed (partly as a result of misidentification of the phases), however
7. CONTROLLING GROWTH THROUGH DEPOSITION PARAMETERS

theoretical calculations suggest hexagonal nickel would have similar magnetic properties to cubic nickel. The measured magnetic properties are therefore consistent with carbide formation at large negative biasing, and metallic nickel being formed at positive biasing. The transition from low magnetisation to high magnetisation is linear with bias, which is what would be expected given that there is a continuous variation in the relative amounts of each phase as observed through XRD measurements. While not definitive, the weight of evidence implies that at negative biasing a carbide phase is formed.

7.3 Growth of the carbide phase

The presence of the carbide phase is an indication of the carbide forming power of nickel. Nickel carbide is considered a weak carbide former, with the Ni$_3$C phase being metastable at room temperature [83]. Nickel and carbon have a low, but non-zero chemical affinity and so at low temperatures form as carbides [5].

While high energy, low flux ion bombardment aids grain growth it does not significantly increase surface mobility. Initially nickel atoms deposit and migrate to form nickel islands. Carbon depositing on nickel islands lacks the mobility to diffuse away and therefore forms covalent bonds with the nickel to produce the resulting carbide. Once formed this carbide phase is then stable to higher temperatures.

This lack of surface mobility is likely responsible for the bimodal distribution of particle sizes seen in figure [6.11]. While nickel atoms which adsorb onto an existing carbide particle will remain there, those which fall on the inter column spaces may have insufficient mobility to reach the nearest column and therefore nucleate a new inter column carbide particle which may then either grow or become blocked by the growth of a neighbouring larger carbide column.

However, given that the carbide phase is Ni$_3$C and the overall composition is closer to NiC$_3$ there is still significant excess carbon which segregates between the columns as seen in the TEM images. The Raman analysis of negatively biased films implies that this inter column carbon can have varying levels of graphitisation. There is an increase in graphitisation as shown by the I_D to I_G ratio increasing as the bias is made more negative. This suggests that increasing the bombardment energy promotes the formation of ordered graphite. Comparing these results to those for the pure carbon films (where we observed ion bombardment damaging the graphitic structures) and the results of other studies [166],
we can determine that the nickel in the depositing flux and the carbide particles still play an important role. The presence of the nickel in the deposition flux cools the plasma as ionisation occurs which therefore decreases the energy of the bombarding atoms. It is possible that while in the case of a pure carbon film the application of a -150 V bias generates damaging bombardment, when a mixed film is being deposited, the -150 V bias provides insufficient energy to damage the film and instead promotes graphitisation.

As discussed previously, in nanocrystalline graphite the presence of a D band in the Raman spectra indicates the presence of ordered carbon rather than a presence of defects. Therefore the presence, but small size, of the D peak in the negatively biased samples indicates there is some graphitisation. This is confirmed in TEM analysis as seen in figure 6.15 where some graphitic layers are visible adjacent to the carbide columns. This suggests that the additional energy as a result of ion bombardment is sufficient to promote the graphitisation of the amorphous carbon even without the catalytic properties of the nickel metal. As the bias is made more positive, the ion bombardment becomes less energetic, and so graphitisation becomes less extensive, as evidenced by the falling $I_D/I_G$ ratio. The widths of the Raman peaks are often thought to represent the phonon lifetimes of the excitation, however given their large values measured here (greater than 100 cm⁻¹) it is more likely that the width represents a variation in the excitation frequency [94]. The excitation frequency reflects the quality of the ordering and so a large peak width implies that there is a significant variation in the quality and extent of graphitisation. This is not surprising given the non-uniform nature of the structures which would result in large local variations.

7.4 Transition to metallic nickel

The transition to a positive biasing generates a significant change in both plasma behaviour and film structure. A change from a carbide to a pure nickel fcc phase is observed along with a transition from a columnar to particle like structure. Additionally, we observe several key changes in the plasma behaviour. Figure 5.15 shows how the plasma potential increases upon positively biasing the sample. As the applied bias exceeds the plasma potential, rather than the plasma potential becoming less than the substrate bias, the plasma potential rises since electrons will always be lost to the substrate forcing the plasma potential to become more positive. This means there is never a state whereby
the ions are repelled from the substrate, since the substrate is always more negative than the plasma. Therefore ions will always move across the sheath and bombard the growing film.

However the positive biasing dramatically alters the nature of the plasma. By accelerating the more mobile electrons towards the substrate, there is an increased number of collisions with depositing species in the vicinity of the film surface. This increases the plasma density near the substrate significantly as shown by the increase in electron and ion density (figure 5.16 and figure 5.17). The electron density doubles from approximately $2 \times 10^{10} \text{ cm}^{-3}$ for negative biasing to $4.5 \times 10^{10} \text{ cm}^{-3}$ for positive biasing, and this results in a factor of 10 increase in ion density, increasing from $1 \times 10^{12} \text{ cm}^{-3}$ to $1 \times 10^{13} \text{ cm}^{-3}$. From figure 6.1 we see that although the deposition rate does increase for positive biasing, it only increases by a factor of 2, not the ten times increase seen for the ion density. Since the sheath potential is relatively small, the ions striking the film have a relatively low energy and are unlikely to cause re-sputtering. Therefore it is most likely that a significant fraction of the plasma ions are inert argon ions, which contribute to the energy flux to the film.

In terms of resulting film structure, a low flux of high energy ions is not equivalent to a large flux of low energy ions. In the case of the negative biasing there were fewer ions but they were of higher energy. At positive biasing, the film is bombarded with a larger flux of lower energy ions, and the effect of this bombardment is to promote surface mobility. By providing a constant energy input to the film surface, the adatoms are significantly more mobile. This allows them to segregate more completely: carbon atoms which deposit onto nickel islands are able to diffuse across to the edges where their diffusion rate slows once they reach the carbon phase. Due to the template affect of the cubic nickel, the carbon forms graphitic structures which then surround the metal nanoparticles. These carbon structures envelop the particles and prevent them from growing (since doing so would cause a large strain in the graphitic cages) and therefore limit the size of the particles. This results in the eventual encapsulation of particles by carbon structures, leading to the need for repeated nucleation of the nickel nanoparticles. This change in growth mechanism leads to a transition from a columnar structure to the particle structure. The size limiting graphitisation generates the small particles observed in TEM, and also explains the increase in graphitsation seem via Raman.
7.5 Formation of the graphite encapsulation

From the TEM analysis for the positive biasing, we see particles of 5 to 20 nm surrounded by well defined layers of graphite. The XRD data in figure 6.20 clearly shows the presence of a fcc pure nickel phase while the EDX maps in figure 6.6 shows that the distribution of carbon and nickel is not uniform, supporting the fact that in this case the nickel and carbon have phase separated.

The Raman results also show a significant increase in the $I_D$ to $I_G$ ratio and a shift in the G peak position to higher values. These two trends follow the stage II graphitisation trajectory (figure 6.34) as proposed by Ferrari *et al.* [35] which describes the transition from amorphous carbon to nanocrystalline graphite. Ferrari *et al.* suggested that in the case of complete nanocrystalline graphite formation the G peak position could reach 1600 cm$^{-1}$ before shifting back to 1581 cm$^{-1}$ for bulk graphite. It is not practical to compare the absolute values to our data as these will vary for excitation (laser) frequency and fitting scheme, however the value for a large positive bias (1583 cm$^{-1}$) represents a significant proportion of sp$^2$ ordering.

The production of pure metal nanoparticles with several layers of low defect concentration graphitic cages is a significant and important result. This is the first time such good quality structures have been produced in a process that did not require either high temperature deposition or post-deposition annealing. The material produced is generally of a much better quality than seen from other growth techniques.

Comparing the Raman results to those for pure carbon samples (figure 6.37) we note that the highest quality graphite films are actually produced in the absence of the RF coil, in which case the G peak position reaches 1588 cm$^{-1}$ before dropping to below 1580 cm$^{-1}$ in the case of large positive or negative biasing and an active RF coil. In the case of pure carbon films, it is possible that ion bombardment introduces defects as discussed earlier. However, even though negative biasing decreases the intensity ratio and G peak position, the quality of graphite in the highly biased pure carbon films is comparable with the graphitic quality for positively biased samples in films containing both carbon and nickel. This suggests that while nickel encourages graphitisation, in order to overcome the carbide formation (which naturally occurs in the presence of nickel), a positive biasing is required to increase the mobility of the deposited species.
7. CONTROLLING GROWTH THROUGH DEPOSITION PARAMETERS

7.6 Role of substrate material and initial growth layers

It is important to note that through the use of various substrates and also through depositing different initial layers on the substrates, we can see that there is negligible effect on the film structure from the substrate. The structures are not dependent on any substrate induced epitaxial effects. They are however dependent on underlayer composition. Figure 6.28 showed XRD scans for films grown on a layers of either pure nickel or pure carbon. When films were deposited onto thick carbon layers they appeared to show a carbide phase regardless of bias.

In the positively biased case, where a cubic phase of nickel would be expected, it is possible that the increased mobility (which occurs for positive biasing) led to diffusion of the underlying carbon into the growing film which led to greater carbon saturation of the nickel particles, meaning carbon which deposited onto the growing nickel particles was not able to diffuse out to the surrounding carbon before being covered by the next layer.

For films deposited on a pure nickel surface, the growth was largely as expected, with a carbide phase growing when a negative bias was applied and a cubic phase when a positive bias was applied. Given that the carbide forms due to poor mobility when a negative bias is applied, it is logical that an excess of nickel from an underlying layer would not affect the growing film as it is unable to diffuse into the growing region.

However in the case of positive biasing a strong (200) texture was observed. Normally one expects the close packed plane to form parallel to the substrate, in the case of an fcc crystal this is the (111) plane. However it has been observed in TiN depositions [167, 168] that the application of an ion flux alters mobility and can lead to a transition to a (001) texture. This is because the mobility of the titanium atoms is reduced on the (001) planes and so migrating atoms cannot diffuse as readily and are more likely to react with the depositing nitrogen. The mobility of nickel atoms depositing on a pure nickel substrate is likely to differ from those depositing onto a carbon nickel surface. This variation in mobility may lead to the (200) face being preferentially grown due to nickel atoms diffusing more slowly, and therefore reacting with more carbon. However in order for this effect to continue throughout the film it would require a columnar structure rather than a particle structure (since texture cannot be passed on between particles). The narrow width of the (200) peak suggests there may be non-particle type growth, however without further
TEM analysis it is not possible to conclusively state this.

Deposition of carbon onto bulk nickel is often used to produce graphene and carbon nanotubes [169] however this uses a saturation-precipitation mechanism which requires a temperature variation. This is therefore unlikely to be relevant here since no thermal cycle occurs. Varying mobilities are much more likely to be responsible for the change in observed structure.
7. CONTROLLING GROWTH THROUGH DEPOSITION PARAMETERS

7.7 Role of RF power and deposition pressure

In the absence of the secondary plasma, increasing the background gas pressure would have the effect of decreasing the mean free path of the sputtered atoms. With each collision the energetic sputtered atoms lose energy to the cold gas. This process, known as thermalisation, leads to a decrease in energy of the depositing species and therefore generally reduces crystallinity in the film. With the addition of the coil there is an additional source of energy, acceleration across the sheath potential, which is dependent on the applied bias. Figure 7.1 shows how the phase of the deposited films varies with substrate bias for a range of deposition pressures.

![Figure 7.1: Variation in phase as a function of substrate bias for a range of deposition pressures](image)

Increasing the pressure reduces the energy the deposited atoms retain from the sputtering process ($E_0$), hence when the applied substrate bias is small, the sheath potential ($V_p - V_b$) is also small and so there is little energy input in to the growing film since:

$$E = E_0 + qe(V_p - V_b)$$  \hspace{1cm} (7.2)

This explains the observation that many of the films grown at high pressures are amorphous. However upon applying a sufficiently large negative bias (greater than -100
V at 5 Pa), the ion energy becomes sufficiently large to drive crystallisation and produce ordered material. The ordered carbon material grown at negative biasing is of good quality (as demonstrated from the Raman data) since at high pressures the ionisation fraction is large enough to cause significant ion bombardment (though not so high as to cause increased mobility at negative biasing). This increase in ionisation fraction also explains why the cubic phase is present in samples grown at positive biasing. Given that this phase forms due to high flux bombardment, increasing the ionisation fraction by increasing the deposition pressure will in turn increase the bombarding flux.

By contrast, in reducing the pressure, the ionisation fraction drops and so the \(qc(V_p - V_b)\) term becomes less significant. However the samples grown without a secondary plasma show virtually no crystallinity. Therefore the \(E_0\) term from the original sputtering is not sufficient to explain the crystallinity observed. Even at 1 Pa, the coil free sample shows no crystalline features. Therefore the presence of the secondary plasma plays a significant role, even at low pressures, as shown by the minor change in floating potential from 130 V at 2 Pa to 105 V at 1 Pa. This suggests that the ions are excited by the secondary plasma, increasing their energy even before any acceleration across the sheath region occurs. At low pressures the ions are able to retain much of this energy, due to there being fewer collisions, and so more crystalline films are grown even at small bias values.

The observation that the floating sample at low pressure showed significant crystallisation whereas the floating samples at higher pressures did not, suggests that even though increasing the ionisation fraction, the increased number of collisions at high pressures reduces the energy of the depositing species unless a bias is applied. The lack of a cubic phase at low pressures implies that the ion flux is small (since the ionisation fraction is reduced) and so even a large positive bias is insufficient to increase the surface mobility and allow the formation of the metallic nickel.

Increasing the ionisation fraction is useful since a smaller positive bias is then required to cause a change to the cubic nickel phase. However achieving this through increased pressure has the associated problem of decreasing the deposition rate and causing films grown at intermediate biasing to be amorphous. This is limiting if a fine scale columnar structure was required for a particular application. An alternative method to increase the ionisation fraction, without increasing the pressure, is to increase the power supplied to the coil, with the effect on structure shown in figure 7.2.

Increasing the coil power has the effect of increasing the plasma density (the number
7. CONTROLLING GROWTH THROUGH DEPOSITION PARAMETERS

Figure 7.2: Variation in phase as a function of substrate bias for a range of RF coil powers of ions and electrons in the system). Therefore the bias required in order to achieve either sufficiently high energy bombardment to cause the carbide phase to crystallise, or to attract sufficient ions to cause a transition to a cubic metal phase would be expected to be lower. In the case of the samples grown at 150 W we observe increased crystallinity compared to lower coil powers, particularly at a floating bias. While the peaks are not very intense, the sample grown at +180 V appears to have cubic character rather than a carbide structure. This suggests that as the coil power increases, the increase in ion density becomes sufficient that even without the application of a large positive bias, there is sufficient bombardment to increase the surface mobility and promote the formation of the cubic phase. Upon negative biasing at 150 W, the increase in energy of the ions, combined with a greater number of ions, drives the crystallisation and growth of the carbide phase hence the well defined carbide peaks observed.

When the RF power is reduced to 50 W, the ionisation fraction is decreased significantly (see figure 5.5a). This results in a relatively amorphous sample regardless of bias since there are fewer ions. In the case of a floating potential (when both the energy of the bombarding ions, and the number of bombarding ions is low compared to the positively biased case) there is virtually no crystallisation visible and the sample is comparable to that grown without a secondary coil. This is of particular interest since the deposition
rates for a sample grown with an active coil and a floating substrate is around twice that for a sample grown without a secondary plasma (12 nm min$^{-1}$ for a 2 Pa, 100 W coil power deposition compared to 6 nm min$^{-1}$ when the coil is not active). This indicates that the deposition rate alone is unlikely to be responsible for the observed variation in the film structures. When a negative bias is applied then there is some increase in crystallinity, though less so than for higher coil powers. This is consistent with there being fewer ions and therefore less bombardment occurring which promotes the crystallisation. The lack of significant cubic character at positive bias suggests that the requirement for a high flux of ions is not fulfilled due to the lower ionisation fraction and so the transition to a cubic phase is less evident.

It is therefore apparent that decreasing the coil power and decreasing the pressure have very different effects on the growing film. Both reduce the ionisation fraction such that there is an insufficient flux at positive bias to drive the transition to a cubic phase. However decreasing the pressure has a smaller effect on the ionisation fraction, and additionally allows the ions to retain much more energy resulting in a crystalline sample regardless of bias. Conversely, reducing the power (but maintaining a higher pressure) reduces the ionisation fraction and ion energy such that the resulting films are largely amorphous unless a significant bias is applied to accelerate the ions across the sheath.

At all biasing values, the samples grown at 50 W show poorer quality graphitic ordering compared to those grown at higher powers, as demonstrated by the lower G peak positions. Given the low energy available during growth, the carbon will largely be locked up in the carbide phase and the excess carbon will have insufficient energy to form graphitic structures. In terms of G peak position, the 150 W samples are largely comparable to those grown at 100 W. This suggests that the quality (in terms of containing fewer defects) of the samples grown at 100 W and 150 W are similar, however the intensity ratio of the peaks is found to be lower for the samples grown at higher powers, suggesting the ordered cluster size is reduced. XRD data suggest that the particle size decreases for higher coil powers when positively biased, which would explain the smaller cluster sizes as the particles they are encapsulating will be smaller. This decrease in size is somewhat surprising since greater bombardment would normally lead to increased mobility and therefore larger structures. However it is possible that the additional energy leads to the formation of the graphitic shells more easily (due to the higher mobility of the carbon) which therefore encapsulates the particles faster, preventing them from growing and forcing renucleation.
For negative biasing the sample grown at 150 W shows the lowest intensity ratio but a relatively high G peak position. This suggests that while the extent of ordering is reduced, the quality of the graphitic material remains high. This observation may be explained by the narrowing and increased intensity of the XRD peaks, which suggests there is increased coarsening of the carbide structures and therefore less excess carbon bordering the columns to form graphite. So while the graphite present is of high quality, it is made up of smaller regions, hence the decrease in intensity ratio. Conversely at positive biasing, the high coil power sample shows a significant increase in both peak position and intensity ratio over the lower coil power samples. This suggests that the increase in ion density which occurs at higher coil powers has led to additional low energy bombardment of the surface which has led to a further increase in graphitisation as compared to the 100 W sample.

These results demonstrate how, through the addition of the ICP, there are a range of deposition parameters available to control film morphology and therefore properties. Utilising various pressures and RF powers it is possible to independently control not only the nickel phase and morphology but also the extent of carbon ordering. This provides an additional level of control over the resulting microstructures without the need for substrate heating.
7.8 Conclusions

Overall the variation in structures observed can be explained by considering the energy flux to the surface and therefore the varying surface mobilities. Low flux, high energy bombardment, as seen for negative substrate biasing, leads to cascade events which drive bulk diffusion and coarsening of grains. However it does not significantly increase surface mobility. As a result the depositing species bond to sites close to where they land resulting in a carbide structure. Additional energy from higher energy bombardment allows for grain growth and increased crystallinity, but is insufficient for the carbon to diffuse out of the carbide and segregate as its own phase. By contrast, high flux, low energy bombardment, gives rise to increased surface mobility, by providing energy to more of the individual atoms. This allows the nickel and carbon to phase separate, with the nickel then acting as a template for graphitisation. This graphite formation prevents further nickel nanoparticle growth leading to repeated re-nucleation of nanoparticles. This different behaviour occurs despite the overall energy input into the film being comparable. Figure 7.3 shows the product of the ion density and the sheath potential as a function of substrate bias.

![Figure 7.3: Graph showing the total energy input to the surface as a result of ion bombardment](image)

While undergoing a minimum around zero biasing, the energy flux to the film is comparable for both negative and positive biasing. This provides clear evidence that the
ion flux and ion energy must be treated as two independent variables for film growth.

All the measured trends, including magnetic properties, XRD and electronic measurements show a continuum between the virtually pure metallic nickel state at high positive biasing and virtually pure carbide phase at negative biasing. Indeed XRD results show a transition region where both coexist. This suggests that there is an intermediate level of mobility where it is possible for carbon which deposits onto smaller nickel islands to diffuse to the edges leaving a pure nickel particle. Upon reaching the boundary of the particle carbon forms a graphitic layer, preventing the particle from growing further. However if a carbon atom deposits onto a larger nickel island then there is insufficient mobility for it to phase separate and so a nickel carbide column is formed.
Chapter 8

Effect of Heat Treatments on Films

The structure of the deposited films is clearly dependent on the substrate bias applied during growth. However it has been shown that post deposition heat treatments can have a significant effect on the film structure [2, 3], breaking down the metastable carbide phase to form a fcc nickel phase and a carbon phase. To investigate this effect, the as-deposited films were heated as described in section 4.3. The results of this heat treatment are discussed below.

8.1 Thermal decomposition of nickel carbide

If we assume that the phase present at negative biasing is in fact the carbide phase then XRD clearly differentiates between nickel carbide and metallic nickel phases. Therefore XRD scans were performed before and after annealing with the results shown in figure 8.1.
8. EFFECT OF HEAT TREATMENTS ON FILMS

Figure 8.1: XRD scans showing structural changes with heat treatment for films with a composition of approximately 25 at% Ni-C and thickness of around 400 nm grown on sapphire.
8.1. THERMAL DECOMPOSITION OF NICKEL CARBIDE

In order to heat the films it was necessary to deposit them onto a sapphire substrate in order to avoid reaction at higher temperatures. The complication of this is that R-sapphire has a diffraction peak at around 52° which masks the fcc peak at a similar position. In order to overcome this an offset between the source and detector of the XRD was added. While this reduced the peak intensity significantly (figure 8.2), the broad peak at around 52° in each of the pre heat treatment scans should be assigned to the substrate and not the fcc nickel phase (with the exception of the positively biased sample where the 52° peak is narrower and a result of the cubic nickel particles). With that in mind we find that the pre heat treatment films follow the same structural evolution as was observed for those samples grown on glass. What is of interest however is that following heating at 650 °C for one hour, each of the films had transformed to a fcc phase as shown by the absence of peaks at 42° and the onset of a peak at 52°. In order to better quantify these changes figure 8.3 shows the parameters of peaks fitted to the scans.

Figure 8.2: XRD scan of bare sapphire substrate with an offset to minimise signal

The XRD scans were aligned by fixing the position of the substrate peak, the peak positions in figure 8.3b then show the corrected position of the peaks. The slight shift in peak position to a lower value is characteristic of the transition to the cubic phase. The lack of shift for the positively biased sample (which was already in the cubic phase) implies that there was little change in lattice parameter with annealing. Given that the structures were not thought to grow under any strain this is not surprising as there would not be any relaxation upon heating. The peak widths (figure 8.3c) are inversely proportional to
crystallite size and so the pre heat treatment results are in line with the TEM observations, namely the characteristic length becoming smaller (and the FWHM becoming larger) as the bias is made more positive. What is noticeable is the limited change in crystallite size for the negatively biased substrates. The peak widths are virtually identical before and after heat treatment. The exception is the case of the positively biased substrate where the peak narrows significantly. Given that the films are of similar thickness (each is around 200 nm thick) the intensity of the peaks (figure 8.3a) for the earthed and negatively biased samples suggest that there is a significant amount of cubic nickel formed.

![Figure 8.3: XRD parameters for heat treated films](image_url)
8.2 Change in carbon structure with annealing

To quantify the changes in carbon structure with heat treatment, Raman scans were performed before and after heating. The results of these scans are shown in figure 8.4. Prior to heat treatment of the films, the Raman scans were consistent with those observed previously, again supporting the fact that substrate has no effect on film structure. Figure 8.5 shows the key fitting parameters for the scans, before and after heat treatment.
8. EFFECT OF HEAT TREATMENTS ON FILMS

+125 V (Floating) 0 V (Earthed) +250 V -150 V

Pre-heat treatment

Post-heat treatment

Figure 8.4: Raman scans before and after heat treatment for films grown at a range of biasings. All films had a composition of around 25 at% Ni-C and were around 400 nm thick.
8.2. CHANGE IN CARBON STRUCTURE WITH ANNEALING

(a) Peak intensity ratios
(b) Peak positions
(c) Peak Widths

Figure 8.5: Raman model parameters for heat treated films

While there has been a noticeable change in the scans for all the biasings, there has been a more substantial change for the samples grown using an earthed or floating substrate. For films grown at large positive or negative biasing, the intensity ratios, peak positions and peak widths are constant to within the error or the value. In contrast, the samples grown at intermediate biasing have shown a significant variation upon heating.

Both the earthed and floating samples see a relatively large shift in peak positions with the D peak moving down and the G peak moving up, indicating an increase in ordering. However in terms of the intensity ratio, the earthed sample ratio decreases while for the floating sample the ratio increases. Perhaps the largest change on annealing is the narrowing of the peaks. The earthed sample sees a reduction in peak width from 220 cm\(^{-1}\) to 101 cm\(^{-1}\) and from 157 cm\(^{-1}\) to 88 cm\(^{-1}\) for the G and D peaks respectively.
8. EFFECT OF HEAT TREATMENTS ON FILMS

A similar, though smaller effect, is also seen for the floating sample with the G and D peaks narrowing from 210 cm\(^{-1}\) to 167 cm\(^{-1}\) and from 166 cm\(^{-1}\) to 148 cm\(^{-1}\) respectively. The variation observed may be related to the size of the columns prior to heat treatment. The increase in G peak position implies an increase in graphite quality as there is less damping of the Raman signal caused by defects. However the different trend in intensity ratio raises complications. An increase in intensity ratio implies an increase in order and a larger ordered cluster size. While the higher frequency peak position suggests that there is a higher degree of ordering, the lower value intensity ratio for the grounded samples suggests that the clusters are very small. This is consistent with the TEM images of the films, where the very fine structure of the columns would lead to small inter-column spacings which would limit the size of the ordered carbon produced.

In contrast to the earthed and floating samples, for the positively and negatively biased cases the intensity ratio and peak positions are constant to within the variation seen across a sample and the decrease in peak widths is much smaller, typically only around 10 cm\(^{-1}\).

8.3 Discussion

The thermal breakdown of the carbide proceeds by the carbon precipitating from the columns to form a distinct phase. This requires significant mobility of the carbon atoms, hence the phase separation occurring at elevated temperatures. The positively biased sample already consists of metallic nickel and a separate carbon phase and, since carbon diffusion in graphite is slow due to the stable bonds formed, further growth of graphite is difficult. It is not therefore surprising that annealing of the positively biased samples does not lead to noticeable structural change. The dramatic decrease in XRD peak width for the post heat treatment film could have implied coarsening of the nickel particles. However the presence of the graphitic shells would most likely prevent diffusion of nickel found in the inter-particle spaces into the existing nickel particles. They would also act to constrain any growth. Therefore the decrease in width might be more accurately interpreted as a decrease in defect content. Defects in structure will cause variation in the atomic spacing and therefore broaden the peaks, upon annealing these variations are likely to be removed resulting in a narrowing of the peak itself.

By contrast, in the case where the carbon is predominately in a carbide phase (floating, earthed and negatively biased samples), heating drives the carbon atoms to diffuse out
of the carbide phase leaving a pure nickel and pure carbon phase. Carbon diffusivity in nickel at 600°C is of the order $1 \times 10^{-10}$ cm$^2$ s$^{-1}$ [170]. This gives a diffusion distance of several microns during an hour of heating time. This is several orders of magnitude greater than the size of the carbide columns, though diffusion across the nickel carbon interface can be much slower [171]. From the XRD results we do not observe any remaining carbide phase and so we can assume that virtually all the carbon has diffused from the carbide leaving a pure metallic fcc phase. While all the carbon has diffused out of the carbide, there is a significant variation in the amount of graphitised carbon which forms, as demonstrated by the varying Raman intensity ratios. However this can potentially be explained by analysing the column sizes. As was seen through TEM analysis, the carbide at large negative biasing forms as large columns, resulting in less grain boundary per unit volume. While the carbon diffused out of the carbide readily, it requires the nickel phase to template and drive graphitisation. In the case of the negatively biased sample there is significantly less nickel boundary available for graphitisation and therefore a large amount of the expelled carbon remains amorphous. Contrast this to the much thinner carbide columns observed for earthed and floating biasing and we see that there is much more interface available for graphitisation to occur at. This may explain why these samples show significantly more graphitisation.

While these results in themselves are not surprising given the metastable nature of the carbide, the controllable size of carbide columns made possible through this deposition method makes it possible to template metallic nickel structures which would not normally be possible to grow directly through film deposition.
8. EFFECT OF HEAT TREATMENTS ON FILMS
Chapter 9

Conclusions and Further Work

9.1 Conclusions

9.1.1 Film growth

i Ni-C thin films (≈ 25 at% Ni) were deposited using a traditional balanced magnetron sputter deposition system with an additional inductively coupled RF plasma. Driven by a copper coil placed between the targets and the substrate, this secondary plasma raised the ionisation fraction of the depositing flux.

ii Films were grown on a number of substrates which were suited to the various characterisation techniques. There was no evidence that substrate type played a role in film structure.

iii The additional control over the energy and flux of the bombarding ions made possible through the application of an electrical substrate bias allows for the growth of structures and phases which previously were produced only through extensive substrate heating.

iv The films consisted of either metallic fcc Ni nanoparticles encapsulated by a series of graphitic shells or of nickel carbide (Ni₃C) columns surrounded by amorphous carbon which become more ordered under ion bombardment. The structure was tunable using a range of deposition parameters but predominantly substrate bias.
9. CONCLUSIONS AND FURTHER WORK

v While the deposition rate increased significantly with the application of the coil, and again for positive biasing, evidence from varying pressure and coil power suggests that this has a negligible effect on the films’ structure.

9.1.2 Plasma properties

i Increasing the RF power raises the floating potential leading to a larger ion flux to the substrate. Since the magnetron power and gas pressure are held constant this implies an increase in ionisation fraction and deposition flux.

ii The ion density was found to be largely uniform for negative biasing as was the plasma potential. This shows that by increasing the value of negative biasing, the energy of the bombarding ions was increased (as the sheath potential increases) but the overall flux of ions was constant.

iii Upon positive biasing of the substrate, mobile electrons were attracted towards the substrate, hence the increase in electron density observed. This led to an increase in plasma density due to more ionising collisions and therefore an increase in ion density was also observed. The plasma potential increased linearly with substrate bias for positive biasing and so the sheath potential remained constant. Therefore upon the application of a positive bias the ion flux increases while the ion energy remains constant.

9.1.3 Film structure

i The columnar structure observed for negative biasing coarsened as the magnitude of the bias was increased. The carbide structure is likely to be the result of low surface mobility of the depositing species which causes the carbon adatoms to form covalent bonds upon deposition and remain in the carbide phase.

ii As the bias is made increasingly negative, the energy of the bombardment increases which causes the carbide columns to coarsen and the amorphous carbon between the columns begins to order into graphitic structures.
iii Switching to a positive bias creates a low energy high flux bombardment. This raises the surface mobility so that the carbon atoms can diffuse to the edge of the nickel particles leaving a pure nickel fcc nanoparticle. At the interface between the nickel and carbon their diffusion rates decrease and they become templated by nickel to form graphitic structures. These graphitic structures limit nickel nanoparticle growth by preventing nickel diffusion into the existing particles. This leads to repeated renucleation giving rise to the observed nanoparticle cluster structure.

9.1.4 Film properties

i Films grown at large negative biasing, and therefore consisting mainly of nickel carbide, showed little magnetisation as measured via VSM. Magnetisation increased as metallic nickel content of the films increased with the bias being made more positive.

ii At room temperature all magnetisation curves show paramagnetism, however at low temperatures SQUID measurements showed that a sample grown at a large positive bias was ferromagnetic below 100 K indicating that the paramagnetism was due to a superparamagnetic transition, a result of the small size of the particles.

iii Electronic resistivity measurements showed a negative TCR for all films, indicating no metallic percolation path existed, even in the most positively biased samples. The TCR for the most positively biased samples approached that of pure graphite, suggesting a near complete graphitic network.

iv A large drop in resistivity as the temperature increases was assigned to thermally activated conduction. At low temperatures the conductivity is dependent on tunnelling across small regions of amorphous carbon, while at higher temperatures it is possible to excite the electrons into a conduction band allowing them to conduct more easily.

9.1.5 Heat treatment of films

i Thermal breakdown of the carbide phase was observed when the as-deposited films were heated to 650 °C for an hour. In the case of samples containing the carbide phase, a decomposition to metallic nickel was observed.
9. CONCLUSIONS AND FURTHER WORK

ii Samples grown at large positive or negative biasing showed little change in terms of particle size or graphitic ordering on heating. This is likely due to these films being grown at large energy inputs meaning the carbon was already ordered.

iii Samples grown at intermediate biasing showed a dramatic increase in graphitic ordering. The level of graphitic ordering was related to the amount of nickel surface area, confirming that templating was the main mechanism of graphite formation.

9.1.6 Effect of RF power and pressure

i Samples grown in the absence of a secondary plasma were largely amorphous regardless of deposition pressure.

ii Films grown at low RF power were generally less ordered at any biasing since the ion bombardment effects were reduced due to a lower ionisation fraction.

iii At high RF power there is an increase in ordering at all bias values since there is greater ion bombardment. Additionally the transition to a cubic phase occurs at a smaller positive bias due to there being more ions in the system and so the high flux low energy condition is reached with less bias applied.

iv Films grown at low pressures showed high crystallinity but a carbide structure at all biasing values. This suggests that the condition for cubic nickel growth (high flux bombardment) is never reached due to the low ionisation fraction. The increase in crystalline quality can be attributed to fewer collisions meaning that the ions deposit with higher energy.

v At high pressure the increased number of collisions reduces the energy of the depositing species and so a generally amorphous structure occurs in the absence of any bias. The increase in pressure does however increase the residence time within the secondary plasma and therefore increases the ionisation fraction. At large negative biasing there is sufficient acceleration across the sheath to provide enough energy for the depositing atoms to form as an ordered carbide phase, however a positive bias is required to further increase the ion flux so that the mobility is raised in order to form the cubic metallic nickel phase. Since the ionisation fraction is higher compared to
lower pressures, a smaller positive bias is required to reach the high flux condition and so the cubic phase is observed for lower biasing.

9.2 Further work

The results and findings in this work have shown how ionised magnetron sputtering with an ICP can be used to control the structure of metal carbon nanocomposites. There are however areas where there are still questions to be answered.

The (200) texture observed in carbon-nickel films grown on layers of pure nickel provides an opportunity to further explore the effect of mobility on film growth. By altering the initial diffusion rates of the different species, certain grains appear to grow at a faster rate. TEM analysis on these samples would provide an excellent insight into the role that mobility plays in film growth and also confirm whether a change to a columnar structure had occurred.

The electrical properties showed interesting behaviour, with both small and large resistivity changes with temperature. While a model for this behaviour was proposed, additional experiments would provide further information with which to explain the results. dI/dV versus bias voltage curves can be used to confirm the presence of tunnelling events. Making such measurements in both the high temperature and low temperature regime could confirm that a change in conduction mechanism occurs.

Beyond additional experiments to confirm the findings proposed, extension of the research would also be of value. The work presented here consisted solely of nickel carbon films however the iron group metals (Fe, Co and Ni) have been observed to have similar behaviour with respect to carbon. By extending this work to other metals it might be possible to relate the energy of bombarding atoms to key material properties (such as bond energies) in order to produce a zone model type description of the structures.

It was discussed in the introduction that characteristics such as hardness, wear resistance and catalysis were all potential applications of metal-carbon nanocomposites. Determining how these properties varied with film structure would be of particular interest as this deposition method would provide a simple technique by which to tune the parameters required for specific applications.

The deposition itself is also open to further experiments. Argon was used exclusively
9. CONCLUSIONS AND FURTHER WORK

as the sputtering gas, however both ionisation fraction and ion bombardment would vary if inert gases with different mass were used, such as neon.
References


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