Novel hybrid carbon materials for nano-electronics

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**Novel Hybrid Carbon Materials for
Nano-Electronics**

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SCHOOL OF ELECTRICAL AND ELECTRONICS ENGINEERING

2013

Novel Hybrid Carbon Materials for Nano-Electronics

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Summary

In this report, detailed studies have been performed on carbon thin films obtained via a filtered cathodic vacuum arc (FCVA). The microstructure of carbon thin film can be modified by applying in-situ techniques (such as thermal and ion energy) or ex-situ techniques (such as laser and electrical pulse). The carbon thin films have been characterized and studied in details with Raman, CAFM, TEM, and IV methods. The improvement in electrical conductivity is due to the formation of nano-crystalline graphitic (NCG) carbon thin film, which served as nano-channels for electrical conduction. The two different in-situ methods of obtaining NCG rich films were compared, and it turns out that the IV characteristic are comparable to one another. The preliminary results for the IV characteristic of carbon films with different thickness from 100 nm to 500 nm have been demonstrated. It has been shown that the IV characteristic remains ohmic as the carbon film thickness increases, which will prove to be interesting for future structural devices that require high electrical conductivity. The in-situ Raman, IV, and TEM have been performed during the post annealing process of the amorphous carbon thin film. The behaviour of the changes from amorphous carbon to NCG has been explored and a hypothesis has been proposed to explain the changes occurring during the conversion of the amorphous carbon to NCG carbon. Two ex-situ techniques for the conversion process, namely laser-induced annealing and electrical pulse induced conversion, have been explored. It is found that there is a compromise between the laser energy and the surface roughness. The optimum laser energy is used to obtain NCG samples, which are being analysed by CAFM, TEM, Raman mapping, and IV metal-carbon-metal (MCM) structures. Overall, the electrical resistivity obtained is higher than the samples obtained via in-situ techniques because the laser energy is limited to ensure a smooth carbon sample surface. It is found that electrical pulse via CAFM or MCM structure can be used to induce NCG carbon films. The IV curves of the conversion progress are shown and discussed. Carbon nanowires have been successfully fabricated via the Langmuir Blodgett (LB) method using polystyrene (PS) balls of diameter 450 nm. Through a series of steps, a carbon nanowire of 500 nm in length and approximately 250 nm in diameter has been successfully produced.

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Chapter 1 : Introduction

The ability of carbon systems to interact with other molecules in the environment has to do with the chemical affinity between the carbon present in organic molecules and pure carbon systems. In fact, this affinity can be exploited in many different ways in biochemistry and pharmacy. There have been recent theoretical proposals suggesting that nano-pores in graphene sheets can be used as highly accurate sensors for DNA sequencing, and experimental demonstrations have shown that graphene can be functionalized in order to trap virus and bacteria in solution. In fact, graphene and nano-diamond are the ultimate biocompatible materials that can be batch loaded with a broad array of therapeutics.

Carbon materials like graphene and carbon nanotubes are currently being explored for use in high speed and molecular/organic large-area deployment electronics. The area of positioning of molecular/polymeric systems associated with solar cell-polymer/fullerene blends shows good efficiency. Large area arrays of transistors and light emitting diodes for both displays and lighting (>100 lumen/W obtained with white OLEDs) are examples of the virtues of carbon electronics. Carbon nanotubes, graphene and diamond are excellent heat conductors. Because sp^2 bonds in carbon are very directional and specific, they are more resilient to extrinsic impurities, and most of the defects found in sp^2 systems do not scatter electrons efficiently. Hence, graphene and carbon nanotubes are among the best electric conductors.

Carbon can be thought of as the ultimate functional material, and companies such as IBM, Intel, Samsung, and Fujitsu, and governmental agencies such as the U.S. Department of Defense, the U.S. Department of Energy, and the United Kingdom Engineering and Physical Sciences Research Council, are investing in the development of carbon-based devices. There is also a clear push in other countries in Asia such as Japan, South Korea, Hong Kong, and China to advance various aspects of carbon systems. Possible applications of carbon-based materials include field effect and high mobility electron transistors, single electron transistors, spin valves and integrated circuits. Other applications include field emitters for plasma displays, electric batteries, spin q-bits, Hall Effect devices, molecular and biochemical sensors, conductive complex composite materials, super-capacitors, optoelectronics, complex coatings for functionality in solar cells and LCD displays. Carbon-based materials can also be used in accurate nano-electromechanical systems for sensing, lab-on-chips, magnetic and resistive memories, highly sensitive pressure, charge injection electrode in light-emitting diodes, charge-collecting electrodes in photovoltaic devices, graphene super-lattices for infrared photon detection (military use), chemically modified graphene for pharmacy, nanotube and graphene mesh for water filtration and desalination.

Integration and devices is a direct consequence of basic measurements and modelling. Semi-conductor devices are the best test-beds for basic measurements that can probe the fundamental issues about electronic structure, and this has led very directly to practical and useful devices that are now being manufactured.

Integrating the theoretical and experimental knowledge of the physical and chemical properties of these new materials enables the development of a carbon-based technology. As the size of traditional copper interconnect decreases in the very large scale integration (VLSI) industry, the resistivity significantly increases due to the effect of surface roughening and grain boundary scattering [1]. As the interconnect decreases to a size smaller than 45 nm, the performance and reliability of copper interconnect is the bottleneck in the VLSI industry. As the line dimensions and grain size become comparable to the bulk mean free path (MFP) of electrons (about 40 nm) [2], the copper (Cu) resistivity increases further. The potential of carbon nanotubes (CNTs) as a replacement for copper interconnects has been recognized. CNTs are well known for their extraordinary electrical, mechanical, and thermal properties and have proven to be able to solve problems in interconnects, chip cooling, etc. in silicon-integrated circuit technology [3-5]. Carbon films have been intensively researched since the first hard, diamond-like amorphous carbon film was deposited in 1971 due to their remarkable properties which is structure-dependent [6]. Amorphous carbon film, with a high fraction of sp^3 hybridized carbons called tetrahedral amorphous carbon (ta-C), has been deposited by filtered cathodic vacuum arc (FCVA) and mass selected ion beams [7-12]. Ta-C is well known for its important application as a protective layer for magnetic hard disk and optical devices. The electrical performance of the amorphous carbon has been studied both experimentally and theoretically by many researchers. However, due to the insulating or semiconducting nature of amorphous carbon films, little function can be exploited.

1.1 Motivations

Carbon technology is an emerging field that has not reached its maturity. Eventually, this technology will be developed into an industrially scalable technology that can be used in devices just like the semiconductor revolution. Furthermore, carbon is bio-compatible, and hence the technology can be used for bio-sensing and monitoring chemical reactions on diamond and graphene surfaces via electronic means. Due to their chemical similarity, the carbon technology can also be incorporated and extended to the current semiconducting industry.

Due to the strength of their chemical bonds, carbon-based structures are the strongest in nature. They can retain their crystallinity down to the molecular scale of a benzene ring and hence address the problem of scalability in modern devices. Another fundamental challenge in the electronics industry is the problem of energy waste due to poor heat and electric conductivity in semiconductors. With the increase in the clock speed and power consumption in modern computers, the amount of heat produced by components has increased exponentially. Hence, there is a big industrial demand for expensive cooling schemes that prevent computers from overheating and malfunctioning. The large number of components requires higher power consumption which leads to more energy wastage. The large heat and electric conduction in carbon materials can help to solve this important problem. Because sp^2 bonds in carbon are very directional and specific, they are more resilient to extrinsic impurities, and most of the defects found in sp^2 systems do not scatter electrons efficiently. Carbon has lower oxygen affinity than silicon, and

hence it is characterized by low oxidation rates. Although from the physical standpoint, crystalline silicon can be considered as having better metallicity than carbon, silicon is more prone to disorder such as dissolved impurities and precipitated metals. In fact, the problem of disorder in silicon is a big industrial problem for the development of electronic components. This huge barrier for electronic applications does not exist in most carbon systems from the start. Hence, carbon-based devices can have a dual impact in modern electronics and in the environment: high speed electronics with low heat generation and low energy consumption, with significant reduction of energy bills, alleviating the environmental impact of greenhouse gas emissions from power generation plants.

Carbon composite can take many different forms. Furthermore, different types of carbon can have very different properties. Take, for example, diamond and graphite: the former is hard and non-electrical conductive, whereas the latter is soft and conducts both heat and electricity well. Such contrasting properties prove to be extremely interesting when it comes to working with hybrid materials. The fusion of two materials with totally contrasting properties will give rise to a whole new hybrid material that is not available in nature. Little has been understood when two materials of highly contrasting behaviour merge. The boundary has always been a key problem; for example, contact resistance between CNT and metal electrodes, stress inducement due to two hard and soft materials, dislocations due to lattice mismatch and the requirements of a contamination-free environment during the deposition to ensure that there is no contaminant that will degrade the performance.

These differences occur when two different materials are deposited separately.

Recently, the discovery of carbon nanotubes and graphene has attracted many researchers due to their excellent properties. However, there are still many issues (cost, ease of fabrication, substrate requirements, etc.) that are limiting their use. This thesis focuses on the usage of an industrially proven and patented FCVA technology to produce different forms of carbon thin films.

In recent years, there has been a particular interest in nano-crystalline graphitic (NCG) carbon that has properties similar and close to graphite/graphene and carbon nanotubes but has the same ease of fabrication as amorphous carbon with FCVA.

As nano-crystalline graphitic carbon is still a new area with few detailed studies, this report conducts a systematic and comprehensive study of the fabrication methods and electrical characteristics. A comparative study will be conducted with the different forms of carbon that can be produced by FCVA technology. The aim is towards configurable carbon technology as shown in Figure 1 (different electrical conductivity of carbon thin films) for future electronics applications.

Figure 1: Configurable Carbon Technology

There are five different methods of obtaining NCG that can be separated into two parts: namely the in-situ method and ex-situ method. The in-situ techniques involve the use of thermal energy and ion energy to produce different forms of carbon thin films, whereas the ex-situ techniques involve post thermal energy, laser energy and electrical pulse to induce the structural changes.

The discovery of nano-crystalline graphitic (NCG) carbon film has opened the window to exploit its remarkable properties for possible novel applications due to its highly anisotropic graphitic planes. One example is the usage of highly oriented graphite and high thermal conductivity carbon coatings for embedded 3D interconnects. As the properties of this material have not been studied in detail, their fundamental properties, such as electrical conductivity, must first be evaluated.

Studies on the fabrication process needed would also be useful to identify the potential for mass production.

1.2 Objectives

The project is divided into three main parts, namely:

1. In-situ annealing of carbon films.
 - Identify the electrical and structural characteristics of different forms of carbon thin films.
 - Optimise two different methods of producing nano-crystalline graphitic carbon via in-situ (during deposition) technique.
 - Synthesis of a library of new carbon structures with tailored properties and functionalities.
2. In-situ characterisation via post-thermal annealing of carbon thin films.
 - Identify the characteristics of the conversion from amorphous carbon to nano-crystalline graphitic carbon.
 - Determine the reason for the changes in electrical properties during the annealing/conversion process.
3. Ex-situ annealing of amorphous carbon films.
 - Identify two different methods of inducing structural changes using laser and electrical pulses to form nano-crystalline graphitic carbon thin films.

4. Applications of carbon thin films.

- Fabrication of carbon nanowires via Langmuir Blodgett method to illustrate the possibility of future expansibility.

Therefore, the main aim of this report is to have a thorough understanding of the influence of nano-crystalline graphitic carbon films obtained via in-situ and ex-situ methods on the electrical characteristics of the carbon films for possible future applications in the electronics industry, such as carbon nanowire arrays or patterned conductive carbon films for future 3D interconnect applications.

1.3 Major contributions

1. The differences in the electrical characteristics of different forms of carbon thin films have been studied in detail. It is found that the electrical characteristics can be manipulated by changing the in-situ deposition parameters.
2. Two different methods of in-situ deposition of nano-crystalline graphitic carbon have been experimentally conducted and studied in detail.
3. In-situ characterisation techniques (Raman, IV and TEM) during the post annealing process have been used to understand and explain the conversion process from amorphous carbon to nano-crystalline graphitic carbon.
4. Localized conversion of amorphous carbon films to nano-crystalline graphitic carbon has been performed and studied in detail. It is found that the electrical

characteristics of carbon thin films can be changed using laser energy or electrical pulses.

5. A cheap and simple way of fabricating large-scale identical carbon nanowire arrays have been successfully performed using the Langmuir Blodgett method.

1.4 Organisation of Report

Chapter 1 provides the background and motivation of this report. The objectives and major contribution have also being discussed.

Chapter 2 will cover on the literature review of the basics of carbon, filter cathodic vacuum arc, and the discovery of nano-crystalline graphitic carbon (NCG) films.

Chapter 3 discusses the fabrication of nano-crystalline graphitic (NCG) carbon thin films using in-situ deposition techniques (thermal energy or ion energy) and their influence on the electrical characteristic due to the change in their structural properties.

Chapter 4 explains the conversion process of amorphous carbon to NCG during the post-thermal annealing process using various in-situ characterisation techniques such as Raman, IV and TEM.

Chapter 5 shows the results obtained from localized NCG inducement using laser pulse or electrical pulse and its influence on the electrical properties.

Chapter 6 concentrates mainly on the feasibility studies and fabrication of the carbon nanowires arrays for possible future applications.

Chapter 7 covers the conclusions and potential future works.

In this thesis, two terms will be constantly used, namely: **In-situ**, which means altering of the process parameter/condition during the carbon thin film deposition process. **Ex-situ** involves the post processing of the already-deposited amorphous carbon thin films.

Chapter 2 Literature Review

2.1 Carbon

Carbon is essential to all known living systems. Without it, life would not exist in the way we know. Crude oil is used by the petrochemical industry to produce useful products; for example, petrol, diesel, liquefied petroleum gas (LPG), kerosene, etc., through a distillation process in refineries. Carbon forms several different allotropes by different kinds of carbon-carbon bonds. A few examples of them are shown in Figure 2.

Figure 2: Different Allotropes of Carbon [13]

The ability of carbon to combine itself with other chemical elements in different ways to form different compounds forms the basis of organic chemistry. A carbon

atom has four valence electrons, which give rise to the possibility of different bonding configurations. Due to its chemical versatility, it has the ability to form a rich diversity of structural forms of solid carbon [14]. The most common forms of crystalline carbon are cubic diamond and hexagonal graphite.

Diamond is commonly used as a gemstone and also as an industrial material [15-17]. It exists in cubic form with each carbon atom linked to four other carbon atoms by sp^3 σ bonds in a strain-free tetrahedral array. Diamond is composed of fully tetrahedral sp^3 -hybridised C-C bonding configurations with four σ bonds at an angle of 109.5° to one another.

Another well-established allotrope of carbon exists in the crystalline form of graphite [18]. Graphite is a fully trigonal sp^2 structure that forms hexagonal six-fold rings of single and double bonds. There are weak van der Waals π bonds between the hexagonal planes. Subsequent studies confirmed the well-known hexagonal crystalline structure of graphite. The basis of graphite is graphene planes arranged like an extended hexagonal array of carbon atoms with sp^2 σ bonds and delocalized π bonding in a stacking sequence [19, 20]. Recent researches have also focused on the unique properties of the single layer of graphene for electronic applications [21-26].

Research on amorphous carbon had been significant [27] since the early fabrication of diamond-like carbon (DLC) in 1971 [6]; it has properties that resembled diamond for scratch-resistant surface coating.

Diamond-like carbon or what is sometimes called tetrahedral amorphous carbon (TAC) films have been fabricated by ion-beam deposition [7-9, 28-36], cathodic arc [37], chemical vapour deposition [38], pulsed-laser-deposited [39, 40] and RF/magnetron bias sputtering [41-44]. These films' properties have been studied in detail [45-49].

Carbon is able to form bonds and chains with many other elements to form millions of compounds. Examples of famous carbon structures are buckyballs, carbon nanotubes and carbon nano-fibres. Carbon nano-fibres and nanotubes have a very high strength-to-weight ratio making it very useful for future advance composite materials for structural applications. Carbon is governed by $2s^2 2p_x^1 2p_y^1$, which gives it a unique chemistry property. The tetra valence of carbon is achieved by allowing the excitation of electrons into a higher energy orbital state. The configuration, $2s^1 2p_x^1 2p_y^1 2p_z^1$, has four unpaired electrons in separate orbitals formed due to the shift of the electron from 2s to 2p. These four electrons can pair with another four atoms to form σ bonds, which is a feature of carbon because of the low promotion energy caused by the repulsion relieving electron to electron, which leaves an occupied 2s orbital and fills up the empty 2p orbital [11].

The three types of hybridisation are schematically illustrated in Figure 3.

Figure 3: Schematic illustration of the three possible hybridisations of carbon

Diamond forms σ bonds through the four carbon atom sp^3 hybrid orbitals, whereas graphite uses the three σ bonds via sp^2 hybridisation to form a trigonal plane. The remaining p_z orbital forms a relatively weak π bond that is perpendicular to the triangle. Therefore, graphite materials consist of hexagonal planes which are layered and can slide between the layers. The different bonding states and atomic structures give rise to the diversity of carbon material that is the hardest non-conductive material at one end and at the other end is a conductive soft graphite material.

Stresses in Carbon Films

High internal compressive stress has always been a problem that lies in the deposition of carbon thin films; film stress can be as high as 10Gpa [7, 9, 10, 42, 50-60]. This high stress causes film adhesion problems and therefore different methods have been explored over the years to reduce the compressive stress in carbon thin films. Carbon thin films with high sp^3 content have been commonly annealed at temperatures ranging from 400°C to 700°C [61-82]. Pure carbon thin films with sp^3 content greater than 70% are referred to as tetra-amorphous carbon (ta-C) films, and for sp^3 less than 70% is referred to as diamond-like carbon (DLC)

[83-90]. There is a close and direct relationship between the sp^3 content, intrinsic film stress and density as shown in several studies [83, 87, 91]. Typically, the highest sp^3 content carbon thin films have the best hardness properties but unfortunately also have the highest intrinsic stress, higher than 10GPa. This also results in the limitation in the highest possible thickness of carbon film, hovering between 100 nm to 200 nm [92, 93]. Thermal annealing of these films at temperatures up to 600°C decreases the film stress down to 2GPa without affecting the hardness properties [94-97]. Similar experiments have been conducted on hydrogenated carbon thin films (a-C:H), and it was found that the stress relaxation occurs at temperatures between 400°C and 500°C [94]. It was also discovered that a-C:H films show a higher tendency towards relaxation for carbon thin films deposited at higher bias of -600V as opposed to -40V [98-100]. It was also discovered that there is an irreversible reduction in the H content that results in structural change in the a-C:H carbon film [96, 101, 102]. Molecular dynamics (MD) simulation shows that stress relief occurs at around 1000K (727°C) for high sp^3 (~70%) content carbon thin films [103], which matches closely with the experimental value of ~600°C. Another experiment was conducted by annealing carbon thin films samples varying in sp^2/sp^3 content in air instead of vacuum [104], and it was found that the carbon thin film with high sp^3 content showed no changes in hardness value up to 400°C, and structural changes only occurred after 500°C. Carbon thin films with low sp^3 show significant material loss at temperatures higher than 400°C [104]. High temperature carbon thin films deposition is usually avoided to prevent the deterioration of carbon thin films' properties [105-109]. Simulation studies based on ab initio calculations have been conducted to explain the stability

of high sp^3 ta-C structure during annealing. Generally, ta-C carbon films experience film stress reduction after post-thermal annealing, and the level of sp^3 bonds increases [61, 64, 67, 70, 72-77, 81, 110].

Electronic Properties

The electrical properties of carbon thin film materials can be explained by the electronic structures. For example, the electronics properties of DLC films have been researched extensively. However, the full understanding is difficult due to the presence of both sp^2 and sp^3 content. Various theoretical research works have been conducted on the carbon atomic structure and its vibrational properties [111-114]. For amorphous carbon thin films, the electronic structures of DLC have been previously studied in detail [91, 115, 116]. The theoretical and simulation studies on the electronic structures have also been explored [111-113, 117-120]. The bandgap of carbon thin films is defined as the separation and position between the occupied (π) and unoccupied (π^*) states at the band edges. Energy can be gained by creating π bonds through pairing of sp^2 sites where each of the two hybridized states can be separated into lower or higher energy [121]. In the lower energy state, the total energy is much lower, and therefore π bonded pairs tend to form shorter chains. The occurrences of single sp^2 dangling bonds or atoms are low, and the defect states that are usually associated with geometric anomalies are at the band edges of the sp^3 gap. At the lower energy state where the chains are shorter on the π bonded pairs, there will be a higher electrical conductivity in the carbon thin films. However, few studies have been conducted on the comparison between different forms of amorphous carbon and nano-crystalline graphitic carbon thin films.

2.2 Deposition of DLC

Cathodic Arc Deposition

High energetic carbon ion flux that is related to the target composition is emitted from the cathodic arc. This method has been reported as a suitable process for producing high wear-resistant carbon thin films over a large area [122]. DLC films or doped DLC films can be deposited via this method easily [123, 124]. Figure 4 shows a schematic view of the carbon deposition setup [122]. The cathodic arc utilized a high current but low voltage discharge which induces a very high current density at the cathode causes a spontaneous emission of cathode target material. This emission is then charged and ionized by the intense plasma. The cathode material used is a 99.999% pure graphite target. Hence, carbon ions with a high kinetic energy of about 22eV are emitted [35]. The plasma is self-sustainable in high vacuum and therefore often termed as a vacuum arc system [125].

Figure 4: Cathodic Arc Deposition System

A modified conventional cathodic arc system called filtered cathodic vacuum arc (FCVA) system was used in this work. Figure 5 shows the schematic configuration of the equipment:

- (1) Arc plasma source
- (2) Plasma duct
- (3) Insulator
- (4) Magnet coils
- (5) Magnet coils
- (6) Vacuum chamber
- (7) Insulator
- (8) Collector
- (9) Rectifier
- (10) Bias voltage supply for plasma duct

Figure 5: Filtered Cathodic Vacuum Arc Deposition [126]

During FCVA deposition, the neutrals and macroscopic particles are filtered from the ionized plasma, and only the exact selected charged ions exit the duct and reach the substrate surface. FCVA produced DLC films have properties of high density and hardness [55, 127-132]. It was found that the carbon thin films with sp^3 content as high as 70% have high compressive stress (9-10GPa) and high quality carbon

thin films [105, 123]. FCVA is typically used to produce DLC films. However, in this report, FCVA is used to produce high sp^3 carbon thin films termed ta-C (>70% sp^3), high sp^2 (>80% sp^2) amorphous carbon thin films and most importantly the nano-crystalline graphitic (NCG) carbon thin films through the control of electrical biasing and temperature at the substrate holder.

2.3 Observation of nano-crystalline graphitic (NCG) carbon during carbon deposition

CNTs were a major research breakthrough when they were first discovered in 1991 by Iijima [133]. The second major breakthrough was the discovery of graphene in 2004 [134]. Despite the excellent properties these materials exhibit, there are several issues, such as high temperature process, film uniformity and mass production that requires optimisation, which limit their usability [135-138]. There are two approaches that are being researched: (1) Optimising the material properties by modifying the fabrication process to suit industry mass production capability; and (2) Sourcing for other potential replacement materials [139].

FCVA technology has been widely used in the industry to produce low temperature, highly uniform and conformal diamond-like thin films for hard disk coating and optical devices. It is well known that the microstructural properties of amorphous carbon thin films depend strongly on the sp^2 to sp^3 ratio content. sp^2 hybridised bonds exhibit more graphite-like properties, whereas sp^3 hybridised bonds approach more diamond-like behaviour.[93, 140-142]. This is also reflected in the

microstructural 3-dimensional topology [143]. Ta-C (DLC) exhibits very high mechanical strength and consists of mainly sp^3 bonds and is commonly used for wear-resistant coatings [9, 126, 144-146]. At the other end, amorphous carbon consisting mainly of sp^2 bonds is rarely used, since the material is soft compared to ta-C and exhibits moderate electrical conductivity.

Recently, ongoing research has been concentrating on the modification of nano-structured carbon thin films that contain high sp^2 content [139, 147-151]. The difference between these carbon thin films and amorphous sp^2 films is the appearance of nano-crystalline structures with a preferred orientation. These preferred orientated carbon thin films are observed in a-C films when subjected to post annealing [152], which is different from the typical post annealing of DLC to relieve film stress. A-C films with high sp^2 content are seldom annealed at high temperatures due to the lack of film stability and possible film oxidation. Another recent method involved the manipulation of film intrinsic stress to produce nano-structured carbon thin films [147, 153].

Simulation studies at the atomic level show an abrupt change from amorphous to vertical orientation, which is represented by Figure 6. At the initial film deposition, a preferred orientation is not observed. From simulations conducted, vertical orientated graphitic planes appear in the carbon thin films after 160 carbon atoms have been deposited, and these graphitic planes carry on throughout the film [9, 147, 150].

Figure 6: Atomic Simulation of Graphitic Planes

The sharp transition between disordered carbon and aligned carbon has been explored at high temperatures and pressures [154]. Figure 7 shows that at the critical stress value of 6 ± 1 GPa between the low density sp^2 rich phase and high density sp^3 rich phase, there is a sharp phase transition that is similar to that of graphite and diamond [154]. This intrinsic stress being developed during deposition has been confirmed to be the same as the value measured after deposition [155]; therefore, the stress of the carbon film can be measured after the deposition is completed.

Figure 7: (a) Density versus stress for a-C films (b) Through-film resistance per unit thickness as a function of stress. [147]

It is found that this preferred orientation occurs due to the minimisation of the total energy in turbostratic graphite [156] within a biaxial stress field [157]. The simulation shows that the appearance of the microstructures is thermodynamically driven and not due to dynamic effects such as sputtering or channelling [147, 158].

Compressive stress and activation energy have been found to be the driving force for the conversion from amorphous carbon thin film to nano-crystalline carbon thin films [139]. This report concentrates on the exploration of different fabrication approaches, namely: in-situ and ex-situ of NCG films. NCG films are semi-ordered carbon with graphitic planes aligned perpendicular to the substrate. Such films exhibit high anisotropic properties, and hence high electrical conductivity can be observed in the vertical direction.

Chapter 3 : In-Situ Produced Amorphous and Nano-Crystalline Graphitic Carbon via Thermal Energy

This chapter discusses the formation of nano-crystalline graphitic (NCG) carbon via usage of thermal energy during carbon thin film deposition.

3.1 Introduction

As explained in chapter 2, there are different kinds of carbon. For this project, the emphasis will be placed on nano-crystalline graphitic (NCG) planes in amorphous carbon films, which indicates the appearance of nano-crystals with microstructure similar to that of graphite (graphitic parallel planes) within amorphous carbon matrix. Post annealing of carbon samples have been commonly used for stress relief. In this report, different deposition parameters have been applied during carbon deposition to obtain final sp^2 rich or sp^3 rich carbon thin films.

With the first discovery of the NCG using post-rapid thermal annealing in high vacuum, studies were done to verify if it is possible to obtain NCG by using other means and methods. In this chapter, the in-situ carbon deposition technique that was used to obtain the NCG films will be reported.

This chapter concentrates on the study of the influence of thermal energy (in-situ) during carbon deposition. The effect on the microstructural and electrical properties of the nano-crystalline graphitic carbon (NCG) during deposition will be analysed

and compared. The electrical characteristic for both through-plane and in-plane will be studied.

Modifications were made to the FCVA substrate holder to incorporate a resistive heating element and water cooled piping to enable variation of substrate temperatures. Experiments were conducted with substrate temperature ranging from 10°C to 600°C with varying substrate bias from 0V to 500V. Raman is used as the initial method of identifying changes in the film composition. The results have been separated into two parts, namely: NCG deposition via thermal energy (covered in this chapter) and NCG deposition via ion energy (covered in chapter 4).

In the first section of this chapter, studies will be concentrated on the usage of in-situ thermal energy to alter the substrate temperature to obtain amorphous and NCG carbon thin films.

3.2 Experimental Methods

The carbon thin films were deposited on a p-type silicon (0.01–0.02 Ω cm) with crystal orientation [100] using carbon ions generated from a double-bend FCVA system [159, 160]. The system operates with a 99.999% pure graphite as the target. The FCVA is capable of depositing carbon thin films on silicon substrate of sizes up to 1.5 cm by 1.5 cm. The system comes with a built-in heater that is capable of heating the substrate up to 600 °C and applying negative substrate bias up to -600V. The silicon substrate was first cleaned in ultrasonic isopropanol (IPA) solution to remove organic contaminants. The FCVA chamber was pumped down to a base

pressure below 3×10^{-6} Torr using a turbo molecular pump before the heater power was applied. During deposition, an arc current of 56-60A was applied, and the duct bend current set at 12.5A. One minute of pre-deposition was done with the shield on followed by 1 min of cooling down time. After that, 5 min of deposition was conducted to produce carbon film of thickness 100 nm. The average thickness of the carbon thin film was measured using a TENCOR surface profiler by computing the average thickness over at least five different portions of the sample.

The effects of in-situ thermal energy on the carbon thin film deposition will be explored. Two commonly used substrate biases of -25V and -300V were selected, as these conditions have been used commercially to produce carbon thin films in the industry. Another reason for applying substrate bias is to improve the film adhesion to the substrate to prevent any delamination. The change in substrate bias will result in the change in the carbon ion energy arriving at the substrate and therefore create different composition in the carbon thin film [6, 46, 53, 105]. The substrate temperature is controlled by a custom-made PID controller powered by a variable voltage source capable of current inputs up to 80A. The heater element is made of molybdenum (Mo) for its high thermal stability and placed inside the FCVA system with an isolated substrate holder capable of inputs of up to DC -600V.

A Reinshaw Raman system with a 532 nm laser is used to characterise the deposited carbon thin films. In order for a higher intensity reading and signal to noise ratio, each sample has three accumulation cycles and a cycle duration set at 30 seconds. The output laser power was set at 10% to avoid the annealing effects via laser

irradiation that will occur. Details of laser annealing effects will be further explained in a later chapter.

Two distinct vibration modes known as the D and G modes appear in the Raman spectrum of a disordered form of carbon [161, 162]. G-mode vibration (Figure 8a) occurs between $1500\text{--}1630\text{ cm}^{-1}$ and indicates the zone-centre phonons of E_{2G} symmetry, which has the in-plane bond-stretching motion of pairs of sp^2 bonded carbon atoms. This mode does not require a six-fold ring and hence it can consist of an olefinic chain or aromatic ring-like sp^2 bonds. D-mode vibration (Figure 8b) is related to the breathing mode (disorder mode) of A_{1g} symmetry [163]. This mode strongly depends on the presence of six-fold aromatic rings, which involves phonons near the K-zone boundary [164]. I_D and I_G is the intensity of the D and G peak respectively after curve fitting. The intensity ratio of D and G peak (I_D / I_G ratio) can be used to identify the sp^2/sp^3 content [140, 165].

Figure 8: Mode of Vibration in Carbon (a) G mode (b) D mode

The Raman data will be curve fitted by a skew Lorentzian, which is also known as Breit-Wigner-Fano, BWF line shape for G peak and a Lorentzian for D peak if necessary [166-168].

The BWF curve has an asymmetric line shape due to the coupling of a discrete mode to a continuum [169] and is defined by:

$$I(\omega) = \frac{I_0 [1 + \frac{2(\omega - \omega_0)}{Q\Gamma}]^2}{1 + [\frac{2(\omega - \omega_0)}{\Gamma}]^2}$$

where I_0 is the peak intensity, ω_0 is the peak position, Γ is the full width at half maximum (FWHM) and Q^{-1} is the skewness/coupling coefficient.

With the curve fitted data, the position of the G peak and the I_D / I_G ratio can be determined. Visible Raman consists of photons that excite the π states more than the σ states; therefore, visible Raman is 50-230 times more sensitive to sp^2 than sp^3 bonded carbon [170, 171]. Using the 3 stage model [140], the estimated sp^2/sp^3 content can be obtained. The interesting fact is that the higher sp^2 content exists in the form of nano-crystalline and not just purely amorphous graphitisation as previously shown in the literature [9, 139, 147, 148, 172]. These nano-crystalline structures within the amorphous carbon matrix give rise to very interesting electrical properties that have not been reported in detail before.

Selected samples were studied in depth for electrical properties and microstructures. Carbon films that were chosen represent the few most extreme forms of FCVA deposited carbon samples. They include amorphous **high sp^3** (~80%), amorphous **intermediate sp^2/sp^3** (~50% sp^2 and 50% sp^3), amorphous **high sp^2** (~80%), **intermediate NCG** (mixture of nano-crystalline domains in amorphous carbon matrix), and **high NCG** (continuous nano-crystalline graphitic structures).

This chapter will concentrate on through film and in-plane electrical properties by studying these films' microstructural characteristics to understand the changes in

electrical behaviour. A metal-carbon-metal (MCM) structure, as shown in Figure 9, was fabricated for through film IV electrical measurements. A Keithley probe station was used to measure the current-voltage (IV) characteristics with a voltage sweep from -1V to +1V with a step size of 20mV and a current compliance of 200mA.

The intersection area has a size of $100\mu\text{m}$ by $100\mu\text{m}$, and with a known film thickness of 100 nm, the electrical resistivity can be calculated.

Figure 9: Schematic of carbon film sandwiched between two metal electrodes

The detailed fabrication schematics are shown in Figure 10. A metal shadow mask with a thickness of $100\mu\text{m}$ was used for both metal electrodes and carbon thin film patterning. The reason for choosing a metal shadow mask over standard ultraviolet lithography is due to the ease of fabrication, as the feature size is relatively big, $100\mu\text{m}$ is the smallest size, and most importantly, the high energy carbon ions will be able to penetrate through the photoresist and render the lift-off process ineffective. Another issue is that the temperatures used for carbon deposition far exceed the tolerance of photoresist, which is not more than 120°C .

Figure 10: Metal-carbon-metal fabrication process

The Dimension Icon Atomic Force Microscope (AFM) with a conductive AFM module is used for the CAFM imaging and selective spot IV electrical measurement. The purpose of the CAFM is used to clarify the contribution of the nano-crystalline graphitic planes to the electrical conductivity of carbon film. With the high resolution current sweeping, the CAFM can be used to analyse the conductive domains/channels on the surface, which can possibly give an insight to the in-plane electrical characteristics. IV measurements were conducted on the bright conductive portion to understand the IV characteristics of the samples. The scale of the current graph has been fixed in order to provide comparative studies for all of the samples. The electrical conductivity of the carbon thin film can be readily revealed by using in-situ CAFM observation. A 100mV bias was applied to the sample, and the electrons tunnelling from the sample to the tip were collected.

A JEM 2010 transmission electron microscopy (TEM) operating at an accelerating voltage of 200kV was used to investigate the microstructure of the carbon thin film samples. Two types of TEM characterisations were conducted: namely, the in-plane

TEM and cross-sectional TEM. The in-plane TEM follows the standard TEM sample preparation for planar microstructural analysis. For the cross-sectional TEM, samples need to be specially prepared. The detailed experimental process for TEM sample preparation is shown in Figure 11. The carbon thin film sample was cut into small, equally, sized pieces (2 mm by 2 mm) and glued together with the carbon thin film facing one another. Next, the sample was thinned down using mechanical polishing and finally Ar^+ ion milling. A diffraction ring pattern can also be obtained during the TEM imaging process; this will give a qualitative understanding of the microstructures.

Figure 11: Schematic for cross sectional TEM sample preparation

3.3 Results and Discussion

The deposition rate of the carbon film under different substrate temperatures has been calculated and shown in Table 1 and Figure 12. From the results, there is a general trend of an increasing deposition rate as the deposition temperature increases. Nano-crystalline graphitic (NCG) carbon belongs to the semi-ordered range of carbon [139], which lies between crystalline graphite and amorphous carbon (a-C). NCG carbon mainly consists of nano-crystallites (sp^2 bond) within an amorphous carbon matrix (mixture of sp , sp^2 and sp^3), and hence its density is not

fixed. The density of the NCG carbon film strictly depends on the percentage of sp^2 (a-C and NCG) and sp^3 (a-C) content. NCG carbon film with their aligned graphitic parallel planes has electrical properties (ohmic) closely resembling that of graphite/graphene [172]. As the sp^2 bonding (NCG) increases, the film density decreases due to the decrease in the plasmon energy [110].

With this information, the deposition time has been calibrated and adjusted in order for all carbon films to have a uniform film thickness of 100 nm in all of the experiments.

Table 1: Deposition Rate versus Substrate Temperature

Holder	Deposition Conditions		Film Thickness (nm)	Deposition Rate (nm/s)
	Temp. (°C)	Bias (-V)		
Heater @ -25V	RT (25)	25	126.15	0.97
	200	25	113.3	1.19
	300	25	110	1.22
	400	25	119.2	1.32
	500	25	95.6	1.13
	600	25	115	1.44

Figure 12: Deposition Rate of Carbon Thin Films versus Substrate Temperature

The research in this section will be based on the three-stage model as shown in Figure 13. However, due to the non-linearity of the three-stage model, the film composition (percentage of sp^2 vs sp^3) can only be estimated. Generally, this will give an insight on the possible film composition at different deposition conditions.

The position of the G peak and the intensity ratio of I_D/I_G will be matched with the three-stage model to deduce the estimated film composition. The linear correlation between intensity ratio and film composition at higher intensity ratio tends to imply that higher sp^2 content has been shown in previous work [173-175].

Stage 1 represents carbon thin films with high sp^2 (~100%) content, which is the transformation of single crystal graphite into nano-crystalline structure.

Stage 2 indicates carbon thin films with slightly lower sp^2 (~80%) and that are more amorphous in nature. In this stage, the amount of ordered ring decreases, resulting in the decrease of I_D . The intensity of the G peak does not change as it is only affected by the bond stretching of sp^2 bond pairs.

For stage 3, the sp^2 bonds will change from a ring-like structure to a chain-like structure, resulting in a final structure of sp^2 within a sp^3 matrix [120, 166, 176].

Figure 13: Three-stage model for estimation of carbon thin film composition

The Raman spectra obtained for samples deposited with two substrate bias of 25V and -300V are shown in Figure 14(a) and Figure 14(b), respectively.

Figure 14: Raman spectra with varying temperature and substrate bias

By applying the curve fitting mentioned on page 27, the G peak position and the intensity ratio I_D/I_G can be obtained. Some curves can be deconvoluted into D band and G band using BWF and Lorentzian. This may be due to the formation of nano-crystalline graphitic planes as shown in Figure 15(b). Whereas some spectra of the

samples can only be fitted by a single G band, which suggests that the film is purely amorphous in structure with no sp^2 cluster formed as shown in Figure 15(a).

With the G position and the intensity ratio I_D/I_G obtained, the carbon thin film composition can be obtained and compared based on the three-stage model. Table 2 and Table 3 summarise different parameters obtained from Raman data.

Table 2: Raman data of varying temperature at a substrate bias of -25V

Deposition conditions		G position (cm^{-1})	I_D	I_G	I_D/I_G	Stage
Temp ($^{\circ}\text{C}$)	Bias (V)					
RT	-25V	1553.89	0.59	0.24	0.41	2
200	-25V	1552.41	0.66	0.28	0.43	2
300	-25V	1571.66	0.73	0.48	0.66	2
400	-25V	1562.77	0.60	0.38	0.62	2
500	-25V	1577.58	0.67	0.49	0.73	2
600	-25V	1576.10	0.53	0.35	0.67	2

Table 3: Raman data of varying temperature at a substrate bias of -300V

Deposition conditions		G position (cm ⁻¹)	I _D	I _G	I _D /I _G	Stage
Temp (°C)	Bias (V)					
RT	-300	1570.18	0.35	0.27	0.76	2
200	-300	1556.85	0.43	0.22	0.51	2
300	-300	1567.21	0.41	0.28	0.68	2
400	-300	1580.54	0.26	0.24	0.92	1
500	-300	1583.50	0.52	0.41	0.79	1
600	-300	1592.39	0.69	0.60	0.86	1

A broad G peak with no or a low D peak is typical of amorphous carbon thin films [75] and a narrow G peak for single crystal graphite [162] as shown in Figure 16.

Figure 16: Raman spectrum of (a) amorphous carbon (b) graphite

For the NCG samples deposited at temperatures higher than 400°C, a second D peak (Lorentzian [166, 177]) is required in order for the spectrum to be fitted properly as shown in Figure 15(b). The D peak is an indication of sp² organised graphitic rings due to the zone boundary mode of graphitic clusters [87, 170, 177, 178].

From Tables 2 and 3, it can be observed that the I_D/I_G ratio is lower for samples deposited at -25V bias as compared to the samples deposited at -300V bias. This is because carbon thin films deposited at low bias (<100V) tend to be sp³ rich and those deposited at -300V tend to have a higher sp² content. From the data obtained,

it can be observed that the I_D/I_G ratio seems to have an increasing trend earlier at -300V rather than at -25V. This observation matches with the literature as it is generally more difficult for the conversion of amorphous sp^3 rich films to sp^2 rich NCG films than amorphous sp^2 rich films [50, 150, 152, 168].

Thus, the Raman data provide a preliminary understanding of the types of carbon thin films that can be obtained. Different experimental conditions were selected (as shown in Figure 17) to achieve a better understanding of the different carbon thin films. 150°C was chosen as the lowest point because it is the temperature that most integrated circuit fabrication processes can withstand. 400°C is the initial temperature at which NCG can be obtained, and 600°C is chosen to check if there is any further improvement or change to the structure of the NCG films with an increase in temperature. The substrate bias has also been varied from -25V to -600V.

Figure 17: Experimental Conditions with varying substrate bias and temperature

Through Film Characteristics

CAFM was used to clarify the contribution of the nanoscale graphite sheets to the conductivity of carbon film. The through film CAFM characteristic has been tabulated with the topology, CAFM current graph, and their corresponding IV graph. For qualitative comparison purposes, all images are taken with the same scale bar. First shown in Figure 18 is for the samples deposited at 150°C with substrate bias at -25V, -300V and -600V. It can be observed that at the substrate temperature of 150°C with the substrate bias of -25V and -300V, a very low current density is observed in the current graph.

The corresponding IV curve taken by the CAFM shows a very low current flow, which indicates a very high resistive film, typical of an amorphous carbon thin film. However, there is a change when the substrate bias is increased to -600V. From the topology graph, it can be observed that the carbon thin film has a higher roughness value of 0.392 nm at -600V as opposed to 0.093 nm and 0.076 nm for -25V and -300V, respectively. It is worth noting that the current density graph now shows bright conductive spots on the current graph that indicates some changes in the carbon thin film that resulted in better conductivity. The corresponding IV curve indicates an ohmic behaviour, but a more detailed study needs to be performed as the IV curve saturates too early due to the current limiter in the CAFM equipment.

Figure 18: AFM, CAFM and IV of carbon thin films deposited at 150°C

The Raman data obtained also shows the appearance of the D peak, which indicates nano-crystalline graphitic carbon. Another interesting observation is that the CAFM bright area on the current graph appears as circular domains as opposed to a continuous layer of conductive film. This interesting result will be analysed in detail on page 56 (in-plane characteristic) of this report.

For the samples deposited at 400°C, the results are shown in Figure 19. It can be observed that the surface roughness of the carbon thin film deposited at different

bias values is approximately the same. A similar trend has been observed for the -600V carbon film, which has a slightly higher surface roughness. What is interesting is that at 400°C, the current graph shows bright conductive areas covering almost the whole scan area, which indicates a higher conductivity. The samples deposited at -25V and -300V show similar current graphs that have areas of high conductivity (bright yellow) mixed with areas of low conductivity (dark brown). It appears that at 400°C with -600V bias, the entire current graph is being saturated as compared to the other two current graphs, which indicate higher conductivity than the carbon thin films samples deposited at lower bias. This observation applies to the 150°C -600V samples too. This shows that at very high bias, it is also possible to alter the IV behaviour of the carbon thin films from non-ohmic to ohmic conductor. From the IV curves, it can be observed that the gradient of the IV curve increases with increasing negative bias, and all three curves exhibit ohmic behaviour. However, as before, the IV curve saturates too early to give a good insight of the actual electrical behaviour. Hence, further electrical characterisation needs to be performed.

Figure 19: AFM, CAFM and IV of carbon thin films deposited at 400°C

Figure 20 shows the topology, CAFM current graph and IV for the carbon thin films deposited at 600°C. From the AFM topology graphs, it can be observed that the carbon thin film generally has a low surface roughness at substrate bias of -25V and -300V. The current graph also shows high electrical conductivity almost everywhere on the scanned area. What is interesting to note is that at -600V, the appearance of a circular bright spot is similar to the 150°C -600V samples. This is worth exploring to better understand the reason behind the formation of the circular bright conductive path within the carbon thin film.

Figure 20: AFM, CAFM and IV of carbon thin films deposited at 600°C

To understand the reason behind the higher electrical conductivity, cross-sectional TEM was done on selected samples. The TEM images are shown in Figure 21. It can be observed that at 150°C with -25V and -300V substrate bias, the carbon thin films are purely amorphous without any formation of crystalline structures. This is in good agreement with the Raman data obtained whereby no D peak was observed. The diffraction pattern shows diffused rings, which confirms that the carbon thin film deposited at the two conditions are purely amorphous. However, at 150°C with -600V substrate bias, two clear arcs can be observed on the diffraction ring pattern

that coincide with the (002) graphitic planes. This indicates that there are nano-crystalline graphitic planes present in the carbon thin films.

Figure 21: Cross-Sectional TEM of various carbon thin films
 (Inset: Diffraction Pattern and magnified section)

From the TEM imaging, graphitic planes that run perpendicular to the substrate can be observed, giving it a through film characteristic. As graphite planes are well known for their anisotropic properties, the graphitic planes are responsible for the higher electrical conduction and hence the higher conductivity obtained for the carbon thin film in the CAFM scans. Another point to note is that from the TEM image, it can be clearly seen that the graphitic planes are surrounded by amorphous carbon. This explains why the Raman spectra show twin D and G peaks instead of a

single G peak as it is a mixture of nano-crystalline graphite and amorphous carbon materials.

By applying higher thermal energy at 400°C, it can be observed that even at -25V substrate bias, two bright arcs can be observed from the diffraction patterns, which belong to (002) graphitic basal planes. From the TEM image, it can be clearly seen that the graphitic planes appear to have a long range of ordering. By switching to the dark field TEM and focusing on one of the arcs as shown in Figure 22, it can be observed that the nano-crystalline graphitic planes are relatively uniform and are through the film and not split in domains. There are no significant differences in the TEM images between -25V and -600V. However, from the diffraction arcs, it can be observed that the arcs change from a diffused single point to a much sharper arc, which implies that the films contain more nano-crystalline graphitic planes oriented in the same direction at higher substrate bias. At 600°C, the same observation can be seen similar to the 400°C -600V sample. The key point to note is that at higher temperature of 600°C, a low bias of -25V is sufficient to obtain highly uniform nano-crystalline graphitic planes.

At the higher temperatures of 400°C and 600°C, the TEM images confirm that nano-crystalline graphitic planes can be successfully produced via thermal energy. There appears to be no difference in the orientation, and all carbon thin films obtained at temperatures higher than 400°C have graphitic planes oriented perpendicular to the substrate. This vertical orientation occurs throughout the whole

film regardless of the temperature as shown in the dark field TEM image and the schematic in Figure 22.

Figure 22: Dark field TEM image of the nano-crystalline graphitic carbon

As the through plane graphitic planes are aligned perpendicular to the substrate surface and continuous throughout the film, the good electrical conductivity can be expected because of the inherent good electrical transport along the graphitic planes. The in-plane electrical conductivity will be discussed in the next section.

From the CAFM images and I-V curves obtained earlier, it can be observed that there is very little electrical conduction through the amorphous carbon film, whereas there is high conduction in the in-situ annealed carbon at temperatures of 400°C and 600°C. The current density plot shows bright areas, which indicate high current flow through the vertically oriented nano-crystalline graphitic sheets. It is reasonable to propose that these highly conductive nano-crystalline graphitic planes serve as nano-channels for electron transport, which lead to the high conductivity of the carbon film. Hence, it has been shown that highly conductive sp^2 graphitic sheets are aligned perpendicular to the film surface with surrounding amorphous carbon matrix of lower conductivity. In-situ IV measurement was carried out on bright spots of the current density graph. It can be observed that at a temperature of

400°C with substrate bias 300V and below, the dV/dI value is high, whereas once the bias is increased to 600V there is a sign of decrease in dV/dI . Results for 600°C all show low dV/dI . These results, however, were taken with a standard sweep, although the sweep voltage was kept constant to ensure comparable results. It can be observed that the current saturates too quickly, and therefore not much information can be gathered. Cross-sectional TEM has been done, which verified that there are nano-crystalline graphitic planes present. A planar TEM will reveal more information regarding the results given by the CAFM. As can be seen from the AFM topology images, a high substrate bias of -600V created a higher roughness on the carbon thin film surface. This may not be desirable for possible electronics applications in the future. With that in mind, a simple metal-carbon-metal (MCM) sandwich structure using samples produced at -300V was fabricated to measure the electrical conductivity at different deposition temperatures. The initial metal chosen was titanium for its good adhesion to carbon thin films. The schematic of the MCM structure is shown in Figure 23. The first layer of Ti was deposited on SiO_2 wafer followed by the deposition of the carbon thin film. The top layer of Ti was deposited via a shadow mask.

Figure 23: Schematic for metal-carbon-metal structure used for IV measurement

The through film electrical characteristics were conducted on a metal-carbon-metal sandwich structure, and the IV curve is shown in Figure 24.

Figure 24: I-V of carbon deposited at different substrate temperatures (inset: IV curve for a-C)

Several sets of measurements were made on each top electrode pads for each sample. The IV curve shown in Figure 24 is a good representation of the IV

characteristic of the individual films. The IV curve of amorphous carbon (inset of Figure 24) and titanium control sample has been added for comparison. The IV curve of amorphous carbon has been separated from the main graph because of the high electrical resistance of amorphous carbon.

For the amorphous carbon sandwich structure deposited at room temperature, the current-voltage measurement exhibits a non-linear characteristic as shown in Figure 24 inset, which is typical and expected from amorphous carbon. For the carbon sandwich structure of 150°C and 400°C, it can be observed that there is little current flowing through, forming a horizontal line on the graph. The IV measurement obtained at 400°C showed slightly lower electrical resistance than the samples obtained at 150°C. However, in the case of the carbon film deposited at 500°C, the high resistance non-linear current-voltage (I-V) behaviour is replaced by a low resistance linear current-voltage characteristic indicative of a good ohmic behaviour. At the deposition temperature of 600°C, the current-voltage characteristic exhibits even lower resistance than that of 500°C. The striking difference in behaviour is attributed to the microstructural change of the carbon sandwiched between the two metal electrodes. The high conductivity is proposed to come from the carbon film, since the linear I-V curve appears for the Ti control sample.

It has been clearly observed that low electrical resistance appears for the sample deposited at temperatures above 500°C. These IV measurements confirm that the graphitic planes within the amorphous carbon matrix are able to serve as conductive

channels for the transport of electrons. It is possible for the interface between titanium and carbon to intermix due to the high energy of the carbon ions during deposition. It has been reported that titanium intermixing with carbon formed conductive titanium carbide (TiC), which behaves similarly to pyrolytic graphite [179, 180] and hence, such contact is ohmic and not schottky..

In previous studies, it was found that as the sp^2 content increases, sp^2 bonded chains start to cluster into ordered rings, which remain isolated or linked together by olefinic chains [59, 91] resulting in a drop in electrical resistivity [59, 181]. This was later reported by our research group: under certain deposition conditions in the FCVA, semi-ordered NCG carbon with properties resembling graphite was formed within the amorphous carbon matrix [139, 148, 151, 172], and simulation results from another collaborative research group further confirms the findings [9, 110, 147, 150, 158]. The observation from these data shows that as the deposition temperature increases, the electrical conductivity improves due to the increase in the number of nano-crystals in the carbon thin film as shown by the slightly stronger diffraction arc in the diffraction ring pattern. What is interesting to note in this experiment is the ease of obtaining sp^2 -rich NCG carbon thin films at higher substrate bias.

Further analysis will have to be conducted to fully understand the carbon thin films. Therefore, in view of the objective of this report, which is to obtain different forms of carbon thin films with well-defined electrical properties, selective samples were chosen to study the electrical properties and microstructures in depth.

Carbon films that were chosen represent the few most extreme forms of FCVA deposited carbon. Three kinds of amorphous carbon thin films have been explored, namely: amorphous **high sp^3** (~80%), amorphous **intermediate sp^2/sp^3** (~50% sp^2 and 50% sp^3), amorphous **high sp^2** (~80%). Next, two kinds of nano-crystalline graphitic carbon will be studied in detail, namely: **Intermediate NCG** (mixture of nano-crystalline domains in amorphous carbon matrix) and **high NCG** (through film continuous nano-crystalline graphitic structures). The electrical properties of the carbon thin film have been studied using the improved MCM structure with the metal pads deposited using gold as discussed in the experimental methods on page 25.

Figure 25 shows the IV characteristic of different types of amorphous carbon thin films. As expected, the carbon thin film with high sp^3 content has the lowest conductivity, whereas carbon thin film with high sp^2 content conducts much better than the high sp^3 content carbon thin film. The conduction mechanism can be explained by the Poole-Frenkel bulk limited transport mechanism, which involves the hopping of the charge carriers between conductive sp^2 sites [182, 183]. This effect creates a non-linear IV characteristic in the amorphous carbon thin films. It can be observed that the intermediate sp^2/sp^3 amorphous carbon thin films that consist of 50% sp^2 and 50% sp^3 still fair rather closely to the high sp^2 carbon thin films.

Electrical conductivity can be explained by the presence of conductive regions in the form of sp^2 carbon that is not extended over a continuous percolating network. The change in conductivity is a measure of the statistical variation in resistance paths through the carbon film where the net conductivity is determined by the most

resistive element in the current conduction path. Conduction in amorphous carbon is mostly seen through the more conductive threefold bonded regions (sp^2) with fourfold bonded carbon (sp^3) separating the regions [50]. As such, conduction occurs strictly by the hopping mechanism described by Poole-Frenkel transport theory [183, 184] whereby the conduction is proportional to the overlapping of the wave functions localized on each sp^2 hopping site [50, 184] creating non-linear IV graphs.

Figure 25: IV Curve of Amorphous Carbon Thin Films

Figure 26 shows the insertion of a partial crystalline carbon thin film. Intermediate NCG refers to a carbon thin film that consists of non-continuous nano-crystalline graphitic domains embedded within the amorphous sp^3 matrix. There is a tendency for sp^2 domains to convert to NCG more readily than sp^3 domains, which will be explored in detail in Chapter 4. It can be observed that with the appearance of NCG domains within the amorphous carbon matrix, the electrical conductivity increases dramatically due to the fact that electrical conduction through the NCG sites are

ohmic with low resistivity. It is reasonable to propose that with a small appearance of NCG sites within the amorphous carbon matrix, it is possible to fabricate a carbon thin film with varying electrical conductivity. This is done by varying the size of the NCG sites by controlling the deposition temperature between 300°C and 400°C. This is a new discovery since the most conventional ways of varying the electrical conductivity are through complex processes of doping or the insertion of metal particles into the carbon matrix, which are far more complex fabrication processes. The new approach may have the potential of replacing the metal infused carbon resistor by a pure carbon resistor with varying electrical resistivity.

Figure 26: IV Curves of Intermediate NCG vs Amorphous Carbon

Figure 27 shows the IV curves of both intermediate NCG and high NCG carbon thin films. High NCG is defined as a carbon thin film with long-range ordered NCG within the carbon thin films. This was achieved by using a deposition temperature of 600°C. As mentioned earlier, this long range ordered NCG has its graphitic planes perpendicular to the substrate and therefore acts like vertical graphitic planes, which have a higher conductivity and most importantly exhibit an ohmic

behaviour. The results obtained with gold electrodes on carbon thin films show that ohmic behaviour for NCG rich carbon thin films can be fabricated. The calculated electrical resistivity of the NCG rich carbon thin film is $7.5\Omega\text{m}$. The ohmic behaviour also shows that there is no existence of a Poole-Frenkel conduction mechanism (which is common in amorphous carbon) within the NCG rich carbon thin film.

Figure 27: IV Curve of Intermediate NCG vs NCG

The conversion from Poole-Frenkel behaviour typical of amorphous carbon to ohmic behaviour similar to metal film has been demonstrated, and this serves as an interesting finding and provides alternative material for future electronics applications.

Amorphous carbon film is formed from carbon atoms consisting of mainly sp^2 and sp^3 bonding [12]. The percentage of sp^3 bonded atoms within the a-C matrix is one important factor that determines its mechanical properties. On the other hand, electronic properties of a-C films strongly depend on the sp^2 content of the film

including the presence, size and distribution of sp^2 bonded clusters within the sp^3 matrix [115]. For instance, electrical conductivity of a-C films is governed by the hopping of electrons between the conductive sp^2 clusters thereby depending on the microstructure and orientation of sp^2 bonded atoms [185].

The formation and propagation of NCG in the microstructure of the film can be explained by the high internal stress and the anisotropic nature of graphite crystal structure. High intrinsic stress leads to the formation of high strain energy in the system. sp^2 clusters with preferred orientation are shown in Figure 28. The amorphous carbon thin films will convert to NCG to relieve the strain energy and hence the total energy of the system. Graphite has an anisotropic HCP structure. The spacing between carbon atoms in the (002) basal planes is 1.421 Å while the interplanar spacing of (002) planes is 3.354 Å. In the case where any internal or external deviatoric stress field is applied to the structure, the structure tends to reorient in such a way that the basal planes lie perpendicular to the direction of the highest stress component as shown in Figure 28. In the case of a-C film, the intrinsic biaxial stress is in the growth plane (perpendicular to the substrate). Therefore, if sufficient energy is transferred to the system, the (002) planes will reorient in the direction perpendicular to the surface producing conductive nano-channels through the film.

Due to the anisotropic nature of these conductive threads and appearance of these graphite-like structures for deposition temperatures from 400°C to 600°C, the electrical properties and how these conductive threads enhance the electrical properties of carbon films will be examined in detail. If the direction of these

conductive threads can be controlled, the electrical conductivity will become directional and can be used for future applications. The ability to grow NCG films by controlling the deposition temperature leads to an important application. The graphitic sheet is the strongest two dimensional structure known and has very high in-plane electrical conductivity. For this reason, arrays of aligned carbon nanotubes with their axes normal to the plane of the array have been proposed in electronics as electrical interconnects. Fully oriented graphitic planes in NCG have the possible advantages shown by carbon nanotubes without the limitations of the need for catalysts and special requirements for substrates.

Figure 28: Formation of graphitic-like sp^2 structure

In summary, it has been demonstrated that the synthesis and high conductivity of a nano-crystalline graphitic carbon thin film with vertical oriented graphitic plane can be fabricated via thermal energy. The TEM images of the in-situ annealed carbon thin films are revealed to be graphite-like planes embedded in amorphous carbon matrix. The graphite-like planes aligned normally to the film surface forming vertically oriented nano-crystalline graphitic carbon thin films, providing the effective electron transport channels, which is the origin of the extremely high

conductivity of carbon film. It is reasonable to propose that these highly conductive graphitic sheets serve as nano-channels for electron transport, which lead to the high conductivity of the carbon film.

In-Plane Characteristic

With some of the interesting results obtained from the earlier section, the in-plane characteristics will be examined in detail to reveal some of the reasons for its unique behaviour. The interesting aspect is the appearance of circular bright spots in the CAFM current graph at high bias deposition conditions as shown in Figure 29.

Figure 29: CAFM at -600V bias (a) 150°C (b) 400°C (c) 600°C

It has been shown in the previous section that the appearance of the circular conductive spots is not due to the topology of the carbon thin films. As the graphitic planes have very anisotropic behaviour and these planes are aligned perpendicularly to the substrate surface, it will be interesting to observe and understand the planar TEM images of the samples in order to identify its properties. Therefore, the in-plane TEM is performed on the carbon thin films samples. From the TEM images in Figure 30, it can be observed that for the carbon thin films deposited at 150°C -25V and -300V, the film is purely amorphous, which tallies with the results obtained from the cross-sectional TEM in the earlier section. At higher temperatures (400°C

and 600°C), NCG planes can be observed in all of the other TEM images. What is interesting is the unique change in the structure of the NCG at high substrate bias of -600V. It can be observed that most of the NCG exhibits circular and tubular characteristics. This can be clearly seen and explained from the CAFM current graph that shows circular bright spots instead of a continuous current graph for the NCG films. This shows that only the circular NCG are conductive, and these NCG domains are enclosed within an amorphous carbon matrix explaining the darker areas in the current graph. But, for lower substrate bias deposition, it can be observed that the graphitic planes are more parallel in nature, and very little twirling of the NCG planes can be observed. It appears that the parallel planes conduct more uniformly from the CAFM current graph shown earlier.

Figure 30: Plan View TEM of Various Carbon Thin Films

The in-plane electrical conductivity was measured by depositing equal distance metal pads on top of the carbon thin films as shown in Figure 31. The carbon thin film was deposited on thermally prepared SiO₂ wafers.

Figure 31: Schematic of In-Plane IV measurement of Carbon Thin Film

Electrical measurement was being conducted by measuring between two adjacent metal pads, and therefore the distance between the two metal pads was kept constant while different areas of the sample were measured. The IV curves obtained are shown in Figure 32. For comparison purpose, in-plane IV measurement was conducted on two highly conductive samples at 600°C with -300V and -600V substrate bias. The IV measurement results show that the electrical conductivity for both the carbon thin films is comparable. However, for the sample deposited at -300V, there seems to be a split into two groups of IV characteristics with one having lower conductivity.

*Figure 32: In Plane IV measurements for Carbon Thin Films Deposited at 600°C
(a) -300V and (b) -600V*

With the results obtained, it is reasonable to propose that the IV curves are separated into two regions as shown in Figure 33d. This is due to the parallel planes on the sample deposited at -300V as shown by TEM image in Figure 33a. This is

different from the circular and twirling of the NCG planes in the -600V samples as shown in Figure 33b, whereby there are good electrical contacts between each set of NCG domains. From the TEM image in Figure 33a, it can be observed that the sample deposited at -300V consist mainly of graphite-like planes where samples deposited at -600V (Figure 33b) give crisscross and twirling structures. There are two possible hypotheses being proposed here.

First, it is hypothesized that the carbon samples produced at -300V does not have sufficient energy for the complete transformation of amorphous carbon film to NCG. There may be areas whereby NCG exist in lesser quantity resulting in a lower conductivity as opposed to NCG rich area which exhibit higher conductivity (Figure 33c). The total activation energy required for conversion is the combination of thermal energy (600°C) and thermal spike due to ion energy (-300V) which in this case is lesser than the samples deposited at 600°C, -600V which has a higher overall activation energy.

Second, it is hypothesized that if the IV measurements are conducted along the graphitic planes of the NCG (Figure 33d), the high in-plane conductivity results in a direct low resistance path. Due to the anisotropic nature of these graphitic planes, if the gold contact pads are positioned perpendicular to the graphitic planes (Figure 33e), the electrical conduction will involve the conduction across multiple NCG planes resulting in a higher resistance path. For the samples at -600V, due to the intersecting and twirling structures, most of the graphitic planes are interconnected and exhibit isotropic behaviour hence provide a lower resistive path for electrical conduction.

Figure 33: In-plane TEM for samples deposited at 600°C (a) -300V (b) -600V (c) IV curves for 600°C -300V (d) In-plane (e) Off-plane

Samples deposited at -300V consist mostly of parallel graphitic planes with no inter-twirling as shown in Figure 33a. For the samples deposited at -600V, the planar TEM reveals structures that are circular and crisscross graphitic planes, and therefore IV is less directional and conduction is omnidirectional.

High temperature thermal spikes in the vicinity of the impinging high energy carbon ions induce a local annealing element on the carbon film [186]. One of the recent pieces of data by our research group's simulation studies has shown the formation of different carbon nanostructures. The simulation studies were conducted using density functional Frauenheim's tight binding molecular dynamics (MD) [187, 188] utilising the code for Linear-combination of Atomic orbitals (PLATO) [189]. In the process of heating up to temperature of 3500K, high density (3-3.5 g/cc) sp^3 carbon decreases due to the rearranging to form intersecting curved graphitic stripes and planes. The simulation data shows that if the density and temperature are low (2500K), these graphitic planes straighten into parallel graphitic planes (Figure

34a), whereas if the density and temperature are high (3500K), these graphitic planes fold into carbon nanotubes (Figure 34b). Both of these structures consist mainly of sp^2 carbon and formed highly defective pentagons and heptagons.

Figure 34: Transformation of a-C to (a) graphitic planes (2500K) (b) carbon nanotubes (3500K)

These simulation data show the mechanism for the formation of plate-like (graphitic planes) and circular/twirling (carbon nanotubes) nanostructures. This is in good agreement with the experimental results. At high deposition bias, a high temperature thermal spike occurs due to the bombardment of the impinging carbon

ions during deposition leading to a formation of circular nanostructures. At lower substrate bias, a lower spike temperature results in the formation of plate-like graphitic planes nanostructures [148].

3.4 Chapter Summary

In this chapter, we have seen that the microstructures of carbon thin films have been successfully modified from amorphous carbon to nano-crystalline graphitic (NCG) carbon using thermal energy during the film deposition. Raman spectroscopy has been used as a quick method to identify interesting film transition points from amorphous to NCG carbon. Carbon thin films were deposited at two commonly used substrate bias of -25V and -300V. It was observed that NCG occurs at temperatures higher than 400°C as observed from the change in Raman characteristics. The deposition parameters were selected carefully and in-depth studies using CAFM, IV and TEM were utilized to explore the through-plane and in-plane electrical characteristics of the carbon thin films. It was found that the electrical conductivity strongly depends on the formation of NCG (observed in TEM) within the carbon thin films. These NCG serves as conductive nano-channels for the electrical conduction through the carbon thin films and exhibit ohmic behaviour. The in-plane electrical IV and TEM also showed interesting results due to the differing structures at different substrate bias. It was found that parallel planes occur at substrate bias lower than -300V and at a high -600V; circular planar structures are more prominent. The in-plane electrical IV results show that circular planar structures have a more uniform IV characteristic than the parallel plane structures.

Chapter 4 In-Situ Produced Nano-Crystalline Carbon via

High Ion Energy

This chapter discusses the formation of nano-crystalline graphitic (NCG) carbon via usage of high carbon ion energy during carbon thin film deposition.

4.1 Introduction

In the previous chapter (3), it has been shown that it is possible to obtain nano-crystalline graphitic (NCG) carbon thin films by applying high bias of -600V at 150°C. In this chapter, this effect will be explored by fabricating NCG carbon thin films via the usage of high bias, which is equivalent to high ion energy. The substrate bias is approximated as the ion energy as the substrate bias of -100V is equivalent to an ion energy of ~110eV. In this study, the substrate bias was varied from 0V to -600V. As it is common for the substrate temperature to rise at high bias, a specialized stage with cooling by chilled water to maintain the substrate at 10°C was used. The purpose is to confirm that the formation of NCG is purely due to the high ion energy and not due to the increase in substrate temperature via high bias. The studies have been done for two values of substrate temperatures: room temperature and forced cooling at 10°C. Similar to Chapter 3, Raman analysis has been conducted at all the experimental conditions. Selected samples were chosen for cross-sectional and planar TEM and MCM IV measurements. Another thing to note is the improvement in the adhesion of the carbon thin film at higher bias and low temperature. Hence in this section, the effect of varying the thickness of the carbon films on the IV curve will be explored.

4.2 Experimental Method

The carbon thin films are being deposited using the same conditions as stated in section 3.2. As this section studies the influence of carbon ion density, the carbon thin film sample was placed on a specially designed cooling stage and placed near the filter duct. By placing the substrate holder nearer to the filter duct, it has the effect of increasing the carbon ion density by five times, as proven by another separate study [148]. For the room temperature samples, the samples were deposited with the substrate at room temperature without any form of active cooling. For the samples deposited at 10°C, the substrate holder was force-cooled down by chilling water to the temperature of 10°C throughout the deposition cycle to prevent any form of heating that would arise from the substrate biasing condition. It is noted that due to the design of the cooler stage, there is a limitation of the allowable substrate bias capped at -500V because at -600V, a short circuit was found between the substrate bias stage and the cooler stage. Two min of deposition was conducted to produce carbon film of thickness 100 nm. For thicker samples, the deposition time was doubled for 200 nm and tripled for 300 nm, etc. The maximum thickness of the carbon film achieved was 500 nm due to the limitation of the design of the FCVA and cooler stage.

The effects of in-situ high ion energy on the carbon thin film deposition have been explored. The change in substrate bias may result in the change in the carbon ion energy arriving at the substrate, and therefore different composition may be created within the carbon thin film.

Selected samples were chosen to study electrical properties and microstructures in depth. Only the sample with **high NCG** (through film continuous nano-crystalline graphitic structures) will be analysed in greater detail and compared with the high NCG obtained via thermal approach.

4.3 Results and Discussions

As before, the substrate bias was varied from 0V to -600V at RT and 10°C. Figure 35 shows the Raman spectra obtained for the two different substrate temperatures of 10°C and RT, respectively. For the 10°C results, the -600V bias was not used as mentioned earlier due to the limitation of the cooler stage. Another reason was because of the frequent electrical arcing at high bias resulting in a rough sample surface than that obtained at -500V. Therefore, for the detailed studies, only the sample deposited at -500V will be used. Initial observation shows that from 0V to -200V, there is no significant difference between the Raman spectra for the 10°C and RT.

Figure 35: Raman spectroscopy of samples deposited at various substrate bias at 10°C and RT

However, for the sample deposited at -300V, it can be observed that there is some difference in the Raman spectra. The Raman spectra were curve fitted with the BWF line shape for G peak and Lorentzian for D peak. It can be observed that for the sample deposited at room temperature, there is an appearance of the D peak, which, as mentioned in the earlier sections, can be used to imply the change in the sp^2 to sp^3 ratio. The I_D/I_G ratio will be examined in detail.

Figure 36: Raman Spectra for sample obtained at -300V substrate bias

The various I_D/I_G ratio calculated and the corresponding stage according to the three stage model are tabulated in Table 4 and Table 5

Table 5. It can be observed that there is a sudden change at -300V for the RT sample with the I_D/I_G ratio changing from 0.31 to 0.76. For the 10°C sample, the I_D/I_G ratio changes from 0.23 to 0.54. It can be observed at -500V that the I_D/I_G ratio is approximately the same and the G peak is at the same position. It is therefore concluded that the formation of the high NCG sample is due to the high energy of the carbon ions and not due to the substrate heating effect (thermal energy). At lower substrate bias of -300V, there may be a slight influence and the RT sample starts to show changes in the I_D/I_G ratio. However, at higher bias of -500V, there is little difference in the I_D/I_G ratio and therefore the high ion energy sample studied

was deposited at -500V RT. This is because during the RT deposition, the carbon ions striking on the substrate holder result in a temperature spike and hence a different final deposition temperature due to the slower quenching [53, 190-192] as compared to a forced cooled substrate holder.

Table 4: Raman for samples deposited at 10°C with varying substrate bias

Deposition conditions		G peak position (cm ⁻¹)	I _D	I _G	$\frac{I_D}{I_G}$	Stage
Temp (°C)	Bias (-V)					
10	0	1553.89	0.58	0.20	0.35	2
10	50	1570.28	0.43	0.09	0.22	3
10	100	1574.62	0.31	0.08	0.25	3
10	200	1565.84	0.43	0.10	0.23	3
10	300	1567.21	0.41	0.22	0.54	2
10	400	1567.32	0.46	0.34	0.74	2
10	500	1570.18	0.52	0.34	0.65	2

Table 5: Raman for samples deposited at RT with varying substrate bias

Deposition conditions		G peak position (cm ⁻¹)	I _D	I _G	$\frac{I_D}{I_G}$	Stage
Temp (°C)	Bias (-V)					
RT	0	1553.89	0.59	0.24	0.41	2
RT	50	1586.46	0.28	0.12	0.41	2
RT	100	1573.14	0.37	0.07	0.19	3
RT	200	1570.60	0.46	0.14	0.31	2
RT	300	1570.18	0.35	0.27	0.76	2
RT	400	1558.33	0.42	0.30	0.71	2
RT	500	1570.18	0.45	0.32	0.71	2
RT	600	1567.32	0.51	0.35	0.68	2

Figure 37 shows the cross sectional TEM of the samples deposited at room temperature with varying substrate bias. The TEM results for the carbon thin film samples obtained below -200V are purely amorphous and therefore not shown in the results. It can be observed from the TEM image that for the sample deposited at -300V, there is an appearance of the NCG domain. This result is different from the

previous studies since the cooler stage was placed nearer to the filter duct than the heater stage, which has the effect of increasing the carbon ion density by five times. Therefore, it is possible to obtain NCG domains at a lower substrate bias of -300V. From the TEM images for all three different substrate biases, there is no visible difference. All three TEM images show long-range ordering of NCG domains, which should exhibit good electrical characteristics. However, due to the scope of this study, only the sample deposited at -500V bias is studied in detail because of the higher possibility of better electrical properties. Thermal spikes occur due to the impinging of the high ion energy caused by the high substrate biasing (-500V). The temperature of the thermal spike is directly proportional to the kinetic energy of the impinging carbon ions during the deposition [46, 53, 148, 190-193]. The formation of NCG is analogous to high temperature deposition in Chapter 3 because the NCG carbon formed depends on the thermal spike temperature which is related to the carbon ion energy and substrate bias [3, 46].

Figure 37: Cross Sectional TEM of Carbon Film deposited at RT with various bias

Figure 38 shows the plane view TEM of the samples deposited at various substrate bias values. As mentioned earlier, the samples deposited below -200V are purely amorphous and will not be shown here. What is interesting to note from this set of

results is that at lower bias of -300V, the planar structure consists mostly of parallel graphitic planes. These observations are similar to the results obtained by high temperature carbon thin film deposited at the same -300V but at higher substrate temperatures of 400°C to 600°C. This result shows that the planar structure of the NCG films obtained seem to be consistent regardless of the deposition temperature used. For the carbon thin film sample obtained at higher bias, both the planar TEM obtained for sample deposited via thermal energy and ion energy show that the structure approaches that of circular / tubular shape. This result again shows that this planar structure for NCG can be obtained regardless of the deposition temperature. But, the key point is that these structures will only appear when the deposition conditions favour the formation of NCG. Once the deposition condition favours the growth of NCG structures, the planar structure will follow that of the substrate bias used. The low substrate bias tends to produce parallel planes and high substrate bias more towards circular / tubular structures.

Figure 38: Plane View TEM of Carbon Thin Film deposited at RT with various bias

Figure 39 shows the IV curves measured by using the MCM structure. The IV curves of two samples with one deposited at 10°C and the other deposited at room temperature are compared. From the result, it can be observed that there is a

difference of 51.3% for the dV/dI obtained at 1V, with the sample obtained at room temperature showing a better electrical property. The sample deposited by thermal energy is done at a substrate bias of -300V, whereas the sample deposited by ion energy is done at a substrate bias of -500V. The carbon composition of the interface strongly depends on the impinging ion energy [8, 139, 197, 198]. At -500V, due to the high ion energy, there is enough energy for stress relaxation formation of semi-crystalline carbon at the interface. However at -300V, a thick layer of amorphous carbon is formed due to the lower impinging ion energy [139, 148].

Figure 39: IV Curve of NCG obtained via Ion energy at RT and 10°C.

Next, the IV curves as shown in Figure 40 obtained for both the NCG deposited via thermal energy and ion energy are compared. The result shows that the dV/dI at 1V shows a difference of 20.4%. It seems that the NCG obtained by ion energy has a higher electrical conductivity than the NCG obtained via thermal energy.

Figure 40: IV Comparison between NCG obtained via Ion energy and Thermal energy

In order to understand the improvement in the electrical conductivity, the carbon/substrate interface was studied as the cross sectional TEM obtained for the carbon thin films are similar. From Figure 41, it can be observed that there is a thin layer of amorphous carbon at the interface for the sample deposited via thermal energy, whereas for the sample deposited via ion energy, the interface is thinner and still consists of small semi-crystalline structure domains instead of a thin layer of amorphous carbon. As mentioned earlier, electrical conduction through amorphous carbon is not as good as the conduction through NCG. However, as this layer of amorphous carbon is very thin, it does not influence the NCG's electrical conductivity enough to create a non-linear IV characteristic, although the electrical conductivity is slightly lower than the sample deposited via ion energy. As the interfacial studies are complex, it would be recommended in future work to further explore its effects on electrical properties.

*Figure 41: Cross-sectional TEM of interface between carbon and Si substrate
(Inset: Magnified section)*

The IV curves obtained for different carbon film thickness is shown in Figure 42. It is interesting to note that there is little difference in the IV characteristics between carbon films with the thickness of 100 nm and 200 nm. However, for the films with thickness 300 nm and above, there is a large difference in the IV characteristics.

Figure 42: IV Curve for various thicknesses of carbon films obtained via Ion energy

To have a better understanding, dV/dI at 1V was plotted for all the samples and shown in Figure 43. It can be observed that there is little change in the dV/dI for the sample thickness of 100 nm and 200 nm. However, the dV/dI starts to increase linearly when the thickness is increased to 500 nm. As the results obtained are preliminary, a detailed study in the future may explore the cross-sectional TEM of the various carbon films for film continuity throughout the whole layer of carbon film.

Figure 43: dV/dI at 1V obtained for different carbon film thickness

4.4 Chapter Summary

In this chapter, the detailed studies performed on carbon thin films obtained by controlling ion energy and characterised using Raman, CAFM, TEM and IV characteristics have been reported. The improvement in electrical conductivity is due to the formation of nano-crystalline graphitic (NCG) carbon thin film that served as nano-channels for electrical conduction. Another observation is that instead of thermal energy, NCG can also be obtained by using suitable carbon ion energy. The effects of ion energy have been explored and studied in detail. The electrical characteristics also show ohmic behaviour, which is interesting for future

electronic applications. The two different methods of obtaining NCG-rich films were compared, and their IV characteristics were found to be comparable. The preliminary results for the IV characteristics of carbon films with different thicknesses from 100 nm to 500 nm have been reported. It has been shown that the IV characteristic remains ohmic as the carbon film thickness are increased, which proves to be interesting for future structural devices (MEMS actuators, sensors cantilever, etc.) that require high electrical conductivity.

Chapter 5 Post-Thermal Annealing of a-C with In-Situ

Characterisation

This chapter focuses on the in-situ Raman, IV and TEM characterisation processes during post annealing of the amorphous carbon thin films to convert into nano-crystalline graphitic carbon.

5.1 Introduction

It has been shown in chapter 3 that it is possible to obtain nano-crystalline graphitic (NCG) carbon thin films via thermal energy. However, there are no studies that have been conducted on the understanding of the behaviour of the changes from amorphous carbon to NCG. In order to fully understand this behaviour, a post-annealing method has been adopted with in-situ monitoring. It may be the first time that such a study has been conducted. The starting carbon thin film used was the intermediate sp^2/sp^3 in the ratio of 50:50. During the post-annealing process, in-situ Raman, IV and TEM have been performed.

5.2 Experimental Methods

The carbon thin films are being deposited using the same conditions as stated in section 3.2. The deposition time was calibrated such that carbon film of thickness 100 nm was produced. Raman system with a 532 nm laser was used to characterise the samples. The sample stage consists of a Linkam heater substrate holder that is capable of heating the sample from room temperature up to 700°C with a step size

of 10°C. The sample stage can attain vacuum levels in the range of 2×10^{-2} Torr. Raman analysis was being performed at progressive annealing temperature step size where the Raman laser is being focused through a small transparent aperture on top of the heater stage onto the carbon thin film sample. The in-situ Raman spectra was taken with 3 accumulation cycles with a cycle duration of 30 seconds for higher intensity reading and most importantly higher signal to noise ratio while holding the annealing temperature. The output laser power is set at 10% of the maximum power to avoid the annealing effects via laser irradiation.

During the post annealing process, the temperature was held at each step while in-situ TEM imaging using a TITANS transmission electron microscopy (TEM) operated at an accelerating voltage of 200kV with a built-in annealing stage to investigate the microstructure of the samples. Firstly, the carbon sample is cut into small pieces of size 1 mm by 1 mm and glued together face to face with two layers of carbon in contact. The sample thinning down was done using mechanical polishing followed by Ar^+ ion milling to electron transparency. The resulting sample was placed onto a copper grid and glued using high temperature resistance epoxy. In-situ HRTEM was performed on these specially prepared samples while heat was applied from room temperature to 700°C with a step size of 100°C.

The temperature was held at each step size while the in-situ electrical property of the deposited carbon film was measured using an electrical test structure. Firstly, 1µm thick of silicon oxide as insulating layer was grown on silicon using the low temperature oxidation process. Next, 5/50 nm of Ti/Au layer was deposited using

Denton Electron Beam Vapor Deposition as the bottom electrode with a shadow mask. Another shadow mask was used during the deposition of the carbon thin film with thickness 100 nm at a constant DC substrate bias of -300V using FCVA. Following that, a shadow mask was placed on top of the carbon film, and another 5/50 nm of Ti/Au layer was deposited on top of the carbon film by evaporation as top electrode. The metal pads were bonded with high temperature silver paste with gold wires connected to a feed through on the Linkam heater stage to a Cascade 300 mm Probe Station. A Keithly 4200series Semiconductor Measurement System (shown in Figure 44) was used to measure the in-situ I-V characteristic of the metal-carbon-metal sandwiched films while heat was being applied through a Linkam heater stage from room temperature to 700°C under vacuum.

Figure 44: Schematic of in-situ IV measurement during post-thermal annealing

5.3 Results and Discussion

A MCM structure was placed inside the Linkam stage. The annealing temperature was set at a ramp rate of 20°C/minute, and I-V was performed at each 10°C step

size from room temperature to 700°C. Due to the large change in electrical conductivity during the conversion from amorphous carbon to NCG, a linear y axis may not be able to show any meaningful results. Therefore, the corresponding I-V was plotted with a $\log_{10}$ y-axis (current – A) and linear x-axis (voltage – V) for a clearer illustration as shown in Figure 45. It can be seen that there is a significant increase (two orders of magnitude) in the current from 160°C to 180°C.

Figure 45: In-situ annealing I-V Curve plotted on a current log scale

The dV/dI at -1V is plotted against annealing temperature and shown in Figure 46. It can be observed that the change is abrupt, with the dV/dI value dropping by two orders of magnitude from 160°C to 180°C, indicating abrupt change in the electrical conductivity. Therefore, it is highly likely that there are some changes to the microstructure of the carbon thin film when the temperature increases from 160°C to 180°C.

Figure 46: Plot of dV/dI at $-1V$ vs Temperature

In order to have a clear picture of the changes, the individual IV curve for 160°C to 180°C was extracted and plotted in Figure 47. The first observation is that there is an increase in the conduction current by approximately two orders of magnitude. The second observation is that the IV characteristic still resembles that of a non-linear amorphous carbon thin film. This is interesting as the sudden drop in resistivity has been hypothesized to be due to the conversion of amorphous carbon to NCG carbon. In this situation, the IV behaviour resembles more of amorphous carbon than NCG carbon because the IV property of NCG carbon is ohmic. However, it is worth noting that the IV curve characteristic starts to ‘straighten’ towards ohmic behaviour.

Figure 47: IV Curve at Annealing Temperature (a) 160°C (b) 170°C (c) 180°C

In-situ Raman and in-situ IV measurements were performed and the results are shown in Figure 48 and Figure 49, respectively. The Raman curve at room temperature and 100°C are the same. Hence, only one of it is shown here. The in-situ TEM done during the annealing process is shown in Figure 50. The TEM could not be obtained for temperature of 100°C due to some technical issues. The Raman spectrum (Figure 48a) is curve fitted with a single BWF line shape (G peak). It is possible to fit the Raman spectra with Lorentzian and BWF as shown in Figure 48b, but it is not commonly done due to the extremely low D peak and a high fitting error. When the post-annealing temperature increased from 100°C to 200°C, the IV curve shows a current change of three orders in magnitudes, but there is no change in the Raman spectrum. Raman spectrum are used mainly to determine the ratio between sp^2 and sp^3 content in carbon thin films. Visible Raman are sensitive to the formation of sp^2 clustering [181]. Only a very small fraction of sp^2 sites within a sp^3 phase are formed without any increase in sp^2 clustering. Therefore, the Raman spectrum is not able to differentiate between NCG and sp^2 content, and therefore it has been hypothesized that the first drop in electrical resistivity is due to the conversion of amorphous sp^2 to NCG carbon. It has been known that sp^2 requires a lower energy (lower temperature) to convert into NCG carbon [148, 199] in the post-annealing process than sp^3 -rich carbon thin films. In the past, it has been a common practice for the annealing of sp^3 -rich ta-C at high temperature to relieve the high stress in the carbon thin film, and therefore the thermal stability of sp^3 is a known fact [50, 75, 200]. From the TEM in Figure 50a, it can be observed that there are some small NCG crystals formed all over the carbon thin film samples, but these NCG crystals are still being surrounded by the amorphous carbon matrix.

Therefore, it is reasonable to propose that, from the temperature of 100°C to 200°C, the amorphous sp^2 carbon is converted into NCG carbon, which causes the sudden drop in the electrical resistivity. These NCG carbon nano-particles are embedded within the amorphous sp^3 carbon matrix, exhibiting a non-linear IV characteristic due to the electrical conduction by the Poole-Frenkel hopping mechanism [50, 182, 184]. At 300°C, the number of NCG crystals increases with a decrease in the amount of amorphous carbon, as no significant change can be observed in the Raman spectrum. From the TEM image in Figure 50b, it can be observed that these NCG crystals are scattered all over without the NCG domains aligned to one another. However, the NCG crystals are uniformly distributed throughout the carbon thin film. At 400°C, it can be seen that the NCG crystals are almost covering the whole carbon thin films, and these NCG domains are starting to align in a particular orientation. This can be observed in the IV measurement whereby the IV curve is starting to change from a non-linear characteristic to a more linear characteristic. This argument seems valid because when the annealing temperature was increased from 400°C to 500°C, there is an appearance of the D peak in the Raman spectrum and show an increased in I_D/I_G ratio. The IV curve changed from almost linear at 400°C to perfectly linear behaviour at 500°C. For the sample at 400 °C, the Raman spectrum has been attempted to be fitted with BWF and Lorentzian (Figure 48d), and it can be observed that the D peak is much lower than the Raman spectrum at 500 °C and almost identical with the a-C sample. For the sample at 500°C, the spectrum cannot be resolved with a single BWF line shape. The spectrum requires a BWF line shape to fit the G peak and Lorentzian for the D peak (Figure 48e) [161-163]. At 500°C, there is an increase in sp^2 content where sp^2

bonded chains start to cluster into ordered rings that remain isolated or linked together by olefinic chains [59, 91], resulting in a drop in electrical resistivity [59, 181]. These sp^2 clusters rapidly combine promoting aromatic sp^2 clusters [201]. This causes the Raman spectra to shift and the D peak that corresponds to the breathing mode (disorder mode) of A_{1g} symmetry [163]. This mode strongly depends on the presence of six-fold aromatic rings (graphitic carbon) that involves phonons near the K zone boundary [164]. At 500°C, it can be observed from TEM that the NCG carbon is aligned in a preferred direction, and the surrounding amorphous carbon has transformed NCG carbon. This occurs because the remaining amorphous sp^3 carbon has gained enough activation energy to convert into sp^2 NCG carbon. It was reported that a conductivity increase of 450 times corresponds to ~6% increase in sp^2 [50, 182, 184]. From 600°C onwards, long-range ordering of NCG carbon can be observed. This has been hypothesised as the conversion of the remaining sp^3 content to NCG carbon resulting in a through film with continuous conductive channels, resulting in the IV curve becoming ohmic. This result matches with the Raman and IV data as it has been shown that the appearance of the NCG crystals vastly improves the electrical conductivity. With the reduction in the amorphous carbon and the alignment of the NCG crystals, the carbon thin film gains nano-channels, which it is able to conduct freely with less restriction, and hence the ohmic characteristics as observed for all NCG rich samples.

Figure 48: In-situ Raman at Various Annealing Temperatures
 (a) Room Temperature (b) 200°C (c) 300°C (d) 400°C (e) 500°C (f) 600°C
 (g) 700°C

*Figure 49: IV Curve at Different Annealing Temperature
(a) 100°C (b) 200°C (c) 300°C (d) 400°C (e) 500°C (f) 600°C (g) 700°C
(RED: Reference Line)*

Figure 50: In-situ TEM at Various Annealing Temperatures
(a) 200°C (b) 300°C (c) 400°C (d) 500°C (e) 600°C (f) 700°C

5.4 Chapter Summary

The in-situ Raman, IV and TEM have been performed during the post-annealing process of the amorphous carbon thin film. The behaviour of the changes from amorphous carbon to NCG has been explored, and it has been proposed that at an annealing temperature of 200°C, the amorphous sp^2 carbon converts into NCG carbon surrounded by amorphous sp^3 carbon, explaining its conductive nature but with non-linear IV. At the high annealing temperature of 500°C, the remaining amorphous sp^3 converts into NCG carbon with the appearance of a D peak in the Raman spectrum and the IV characteristic changes to linear behaviour. It is the first time that such a study has been conducted whereby in-situ monitoring has been performed during the post-annealing process for the conversion of amorphous carbon to NCG carbon.

Chapter 6 : Ex-Situ Conversion of Amorphous Carbon to Nano-Crystalline Graphitic Carbon

This chapter focuses on the conversion of deposited amorphous carbon thin films to nano-crystalline graphitic carbon by the usage of either external laser pulse or electrical voltage pulse.

6.1 Introduction

In chapter 3 and 4, the in-situ formation of nano-crystalline graphitic (NCG) carbon was discussed. While Raman was being performed on those samples, it was discovered that if the laser power of the Raman system was set too high, the amorphous carbon thin film would show properties change similar to the NCG carbon. Another observation is that during the electrical probing process, it was discovered that if the voltage range exceeded a certain level, the amorphous carbon would convert to exhibit NCG-like IV characteristics. This brings the possibility of the usage of an external excitation method to obtain NCG from amorphous carbon thin films. This has the advantage to induce localized conductive NCG on an insulating amorphous carbon thin film. In this chapter, the ex-situ method used to produce NCG is discussed. A 100 nm layer of amorphous carbon thin film was deposited on Si substrate, and a selective area of the film was subjected to ex-situ treatment, namely the laser annealing and electrical pulse. The advantage of the ex-situ method is the ability to localize the place and position where the NCG will be formed. The electrical properties of the carbon films before and after conversion

have been studied. The electrical pulse technique has also been attempted to enhance the electrical properties of NCG films produced via other techniques. This chapter will present some initial data and showcase the possibility of the usage of laser or voltage pulse for the conversion of amorphous carbon into NCG carbon.

6.2 Experimental Methods

The carbon thin films are being deposited using the same conditions as stated in section 3.2. A substrate bias of -300V was applied to the sample holder. A KrF Excimer-laser with a wavelength of 248 nm working at a pulse width of 23 nsec and a laser spot size set at 3 by 3 mm was used. The schematic of the process is shown in Figure 51. The carbon thin film sample was irradiated by a single pulse laser and the laser energy varied from 95 to 605mJ/cm². Visible changes in the texture can be observed on the surface of the carbon film at laser energy of 405mJ/cm². JEM 2010 transmission electron microscopy (TEM) operated at an accelerating voltage of 200kV was used to investigate the microstructure of the ex-situ laser annealed samples. Cross-sectional TEM was conducted on the laser annealed spot. Conducting Atomic Force Microscope (CAFM) was used to obtain IV measurements from the annealed and non-annealed portion of the samples. CAFM was also done on the boundary to study the effects of the laser on the edge.

Figure 51: Schematic of Laser Annealed Samples

The second section of this chapter will report some preliminary results obtained by the CAFM equipment on carbon thin film sample and the Keithley IV probe station on the MCM structure. In CAFM, the tip was placed stationary on a single point on the amorphous carbon thin film in contact mode while a voltage pulse was pumped through the CAFM tip. The IV curve during the process was recorded and shown in this report. For the technique via the Keithley IV probe station, a MCM structure, which was previously used to measure the electrical characteristics of carbon thin films were used. The voltage was increased progressively and once the change occurred, the IV curve was recorded.

6.3 Ex-Situ Laser Annealed a-C: Results and Discussions

The laser energy used for annealing of the amorphous carbon thin film varied from the minimum power to 605mJ/cm^2 . The optical image of the sample is shown in Figure 52 below. The laser energy was increased gradually from left to right in the different rows with the lower laser energies in row 1 and the higher laser energies in row 2. Visible changes can be observed at a low energy of 405mJ/cm^2 : there are some changes in the colour and texture of the carbon thin film.

Figure 52: Optical Image of Laser Annealed Sample

The topologies of the laser spot exposed at 405mJ/cm^2 and 605mJ/cm^2 are shown in Figure 53(a) and (b) respectively. The roughness values obtained are 0.197 nm and 7.674 nm , respectively.

Figure 53: AFM Topology of laser-annealed sample at (a) 405mJ/cm^2 (b) 605mJ/cm^2

From the TEM images as shown in Figure 54, at the laser energy of 405 mJ/cm^2 , the diffraction patterns show the presence of film alignment after a single pulse laser irradiation. At higher laser energy of 605mJ/cm^2 , the TEM image clearly shows fringes and the diffraction patterns are more prominent. This results show that the presence of NCG carbon is more pronounced in the high energy laser irradiated film. This has clearly demonstrated that laser irradiation energy of as low as 405mJ/cm^2 can induce NCG carbon in amorphous carbon film. Although higher laser energy produced more NCG, the down side is that the surface of the carbon film becomes very rough, as shown in Figure 53. NCG carbon films are mainly produced by stress-induced preferred-orientation [139]. By control the deposition

condition (e.g., Bias), the carbon ion energy can be altered (unique feature of filtered cathodic vacuum arc deposition system), leading to an introduction of compressive stress (~ 4.5 - 7.5 GPa [150]) in the carbon film. Therefore, two crucial factors for the transformation from amorphous carbon to NCG carbon are: biaxial compressive stress as the driving force; and a source of energy to overcome the activation energy. When laser of sufficient energy (405 mJ/cm^2) is being applied on the sample, both factors are fulfilled, leading to the formation of NCG carbon [139, 148]. The cross-sectional TEM, is shown in Figure 54; the inset shows an enlarged section that clearly shows the graphitic planes. From the diffraction patterns, two arcs can be observed that belong to (002) graphitic basal planes; this clearly shows the semi-ordered graphitic planes typical of NCG [139, 148, 172]. These NCG carbon consist of sp^2 -rich graphitic planes, have very high in-plane electrical conductivity and serve as conduction path for electrons similar to graphite and graphene [172].

*Figure 54: Cross-Sectional TEM for different laser energy
 (a) 405 mJ/cm^2 (b) 462 mJ/cm^2 (c) 605 mJ/cm^2*

With the initial successful demonstration of NCG induced by excimer laser, further experiments were conducted on films produced using different substrate biases and

laser energies. Samples were produced at 60A arc current, 50V duct voltage, 0V substrate bias and room temperature. The samples were laser annealed at $387.5\text{mJ}/\text{cm}^2$. Surface topography scans were performed, and the results are shown in Figure 55. From the surface topography image, it can be seen that the surface of the sample before and after the annealing is the same, thereby eliminating the rough surface caused earlier by high laser energy.

Figure 55: AFM surface topography (a) non annealed (b) annealed at $387.5\text{mJ}/\text{cm}^2$

The current image scan was obtained and shown in Figure 56. From the current image, it can be clearly observed that after the laser annealing, the film becomes highly conductive as compared to the film before laser annealing. However, there are still several non-conductive spots in the film. Hence, detailed studies are needed using Raman imaging scan and planar TEM analysis. An IV scan from -100mV to 100mV was performed on the bright spot of the current image, and the IV curve obtained is shown in Figure 57. It can be confirmed that the carbon thin film has become electrically conductive.

Figure 56: Current Image (a) non annealed (b) annealed at 387.5mJ/cm²

Figure 57: IV Curve (a) non annealed (b) annealed at 387.5mJ/cm²

An 80 μm scan was performed over the boundary between the annealed and non-annealed area. The current graph image obtained is shown in Figure 58. An electrical current sectioning was performed to determine the electrical current available at each point. From the current graph, it can be observed that there is no direct transition from conductive to non-conductive, but rather a gradual decrease. This is, however, not a conclusive study, and detailed interfacial studies are recommended under the future works.

Figure 58: Cross-Sectional Current Scanning Across Boundary

A 50 x 50 μm scan was performed on the boundary with both the surface topography and current image, and the results are shown in Figure 59. The topography edge was mapped onto the current image. From the image, it can be seen that there is a large spread similar to a diffusion effect on the conductive areas. The second observation is that there is a trench-like surface on the edge between the annealed and non-annealed portions. Little can be understood from the CAFM images, and hence cross-sectional TEM was performed in order to deduce the microstructure.

Figure 59: Laser-Annealed Samples Boundary (a) Topography (b) Current Image

A series of lower laser power was attempted and each sample was analysed using CAFM. The reason for doing this is to try to reduce the spread. Hence, after some experiments, $250\text{mJ}/\text{cm}^2$ power was chosen where the sample conductivity increase can be observed from the current image scan as shown in Figure 60. It can be observed that the IV curve is almost identical to the higher laser energy sample due to the low current saturation of the CAFM. When the laser energy used to anneal the carbon thin film sample was lower than $250\text{mJ}/\text{cm}^2$, there was no observable change in electrical conductivity, and the resultant IV curve looked identical to the non-annealed sample.

Figure 60: IV Curve (a) Before Annealing (b) $250\text{mJ}/\text{cm}^2$ laser annealed

From the surface topography and current image shown in Figure 61, it can be observed that the spread has improved although the trench still appears; but the spread is much less.

Figure 61: Refined Laser Annealed Boundary (a) Topography (b) Current Image

Laser energy (as low as $250\text{mJ}/\text{cm}^2$) has been successfully used to induce alignment in 100 nm thick amorphous carbon film. Cross-sectional TEM confirmed that at higher laser energy, the more prominent is the alignment fringes. However, at higher laser energy, the surface roughness increased due to the surface etching effect of the strong laser power. The boundary of the annealed and non-annealed areas has been studied using the CAFM, which shows the reduction in spread when the laser energy is reduced. However, the transition is still not a direct and prominent shift. This may be due to the Gaussian spread of the laser or thermal spread of the heat from the laser.

A commercial laser writing machine was also employed to induce the same NCG conversion process because of the possibility of future laser writing of selective areas on the amorphous carbon thin film. The optical image at the laser power of 10% is shown in Figure 62(a) and at the laser power of 0.3% as shown in Figure 62(b). It can be observed that at the laser power of 10%, there is severe damage to the sample. The laser power was reduced such that there was no visible damage on the film surface.

Figure 62: Optical Image of Laser-Annealed Sample (a) 10% power (b) 0.3%

However, from a close zoom-in on the sample surface, it can be observed that there are circular, laser-annealed spots as shown in Figure 63.

Figure 63: Zoom-in on the Laser-Annealed Spot

A Raman mapping conducted on the circular, laser-annealed spot is shown in Figure 64. Since the yellow portion on the Raman mapping belongs to the D peak positioning, it can be understood that the annealed spot has been converted successfully from amorphous carbon into NCG carbon.

Figure 64: Raman of Laser-Annealed Spot (a) Optical Image (b) Raman Mapping

The IV curve measured using a MCM structure is shown in Figure 65 below. It can be observed that the IV curve is linear in nature, which is similar to those obtained earlier via in-situ annealed techniques. The electrical resistivity value obtained is $16.4\Omega\text{m}$, which is higher than the samples obtained via the in-situ method. The reason for the higher resistivity value is the compromise between surface roughness

and NCG conversion. If the laser energy is higher, more amorphous carbon would be converted to NCG but the surface roughness would increase drastically.

Figure 65: IV Curve of Laser Annealed Sample

6.4 Ex-Situ Voltage Pulse Induced NCG: Results and Discussions

The CAFM tip and MCM structure were used for the first and second part, respectively, for the inducement of NCG from amorphous carbon. The sample used for the CAFM inducement is 100 nm amorphous carbon (-300V substrate bias, room temperature) deposited on a highly doped Si wafer. The second part involves the fabrication of the MCM structure with 100 nm of amorphous carbon (-300V substrate bias and room temperature) sandwiched between the two metal electrodes.

Conversion from Amorphous Carbon to NCG via CAFM

A standard IV scan was performed from -200mV to +200mV with an incremental step size of 100mV. The initial IV measurement from the CAFM is shown in Figure 66(a). It can be observed that there is very little current flowing through the sample

since the initial carbon thin film is amorphous and highly resistive. The scanning range was then increased to -300mV to +300mV, etc. At the scanning from -1300mV to +1300mV, as shown in Figure 66(b), it appears that there was a sudden increase in the electrical conductivity. At the scanning range of -1400mV to +1400mV as shown in Figure 66(c), the IV curve resembles that of a NCG IV obtained in chapter 3. A further scan at low voltage of -100mV to 100mV also revealed the same IV curve.

Figure 66: Conversion via CAFM (a) 200mV (b) 1300mV (c) 1400mV

Conversion from Amorphous Carbon to NCG via MCM

The experiment was repeated this time with the MCM structure which has a larger contact area of 100 μ m by 100 μ m as opposed to the CAFM tip, which is a point voltage source. The voltage sweep was increased from 0V to 10V, and the result is shown in Figure 67. It can be observed that there is a sudden increase of the current with a magnitude of two orders (which was similar to the results obtained in chapter 4) at 7.84V.

Figure 67: IV Sweep from 0V to 10V on MCM structure

The IV curves before and after the conversion processes are shown in Figure 68. It can be observed that the initial IV curve reveals characteristics similar to an amorphous carbon thin film, and the IV curve after the conversion process is similar to that obtained by NCG carbon film.

Figure 68: Conversion via Electrical Pulse (a) before conversion (b) after conversion

The resistivity value obtained from the MCM is $4.97\Omega\text{m}$, which was the best NCG sample obtained. It was also confirmed that the increase in conductivity was not due to a short circuit between the two metal electrodes because of the much higher resistivity as compared to if the electrodes were shorted.

To support the experimental observation, there are reports of two separate simulation studies conducted using molecular dynamics (MD) and Extended-Huckel-Theory-based Non Equilibrium Green's Function (EHT-NEGF) methods. Both simulation data show that a voltage pulse gives atoms enough kinetic energy to convert from amorphous insulating carbon to conductive carbon with an increase in electrical conductivity by several orders of magnitude under certain bias condition [202, 203]. This modification of the carbon film is due to the thermal annealing effect caused by Joule heating [200, 204]. Conductive filaments (NCG) are being formed within the insulating carbon rather than a full conversion of the whole carbon film into NCG as shown in Figure 69.

Figure 69: (a) Schematic of simulated structure (b) Conversion from amorphous to NCG

In a studies conducted by our research group, an SPM has been successfully used to inject electrons on amorphous carbon to form conductive channels due to the growth of aligned graphitic planes (NCG) [205]. The possible reason for the better electrical conductivity compared to the rest of the technique is because of the direct conversion of the whole carbon thin film into NCG, including the interface between

the carbon and metal. However, this will need to be verified in the future via TEM for in-depth interfacial studies.

6.5 Chapter Summary

In this chapter, it has been shown that it is possible for amorphous carbon thin film to be converted into nano-crystalline graphitic (NCG) carbon. This study utilises two techniques for the conversion process, namely: Laser-induced annealing and electrical pulsed induced conversion.

For the laser-induced annealing method, different laser energies were employed for the annealing process, and it has been found that there is a compromise between the laser energy and the surface roughness. The optimum laser energy was used to obtain NCG samples and was analysed by CAFM, TEM, Raman mapping and IV MCM structures. Optimum laser energy has been found for a sharper edge definition between annealed and non-annealed spot. Overall, the electrical resistivity obtained is higher than that for the samples obtained via in-situ techniques, because the laser energy was limited to ensure a smooth carbon sample surface.

For the electrical pulsed induced conversion, two different approaches were used. The first approach uses the CAFM tip to induce a voltage on the amorphous carbon to trigger the conversion process to NCG. The IV curves of the conversion progress were shown and discussed. The second approach uses the metal-carbon-metal (MCM) sandwich structure. Voltage sweeping was from 0V to 10V. It has been

observed that at 7.84V, there is a sudden increase in electrical current flow. The IV curves before and after conversions have been shown and discussed. Currently, this technique produces the highest electrical conductivity of NCG as compared to the other techniques.

Chapter 7 : Carbon Nanowire Fabrication

This chapter demonstrates the possibility of micro-fabrication of nanowires from carbon films using the Langmuir Blodgett method.

7.1 Introduction

In this chapter, the methods for the fabrication of carbon nanowires will be discussed. Carbon nanowires were fabricated by using a top-down approach, which gives the advantage of a more uniform height and identical nanowires with the same properties. This is a competitive advantage over CNTs, which have these issues. This chapter will also demonstrate the feasibility of future large-scale fabrication of carbon nanowires using FCVA-deposited carbon films.

7.2 Experimental Methods

Carbon nanowires were fabricated by the Langmuir Blodgett (LB) method as shown in Figure 70. First, a p-type silicon wafer was plasma-treated with $\text{CF}_4:\text{O}_2$ (80:20) to remove all native oxide to promote adhesion between the deposited carbon and silicon. A thick layer of amorphous carbon ($\sim 1\ \mu\text{m}$) was deposited on the prepared silicon wafer using FCVA with 300V substrate bias, 60A arc current and 50V filter voltage to further enhance adhesion. Next, a thin layer ($\sim 100\ \text{nm}$) of silicon oxide (SiO_2) to serve as a hard mask was deposited using PECVD in a low-temperature process to prevent any oxidation of the carbon film. Following that, the surface of the SiO_2 was treated with oxygen plasma to convert the surface from hydrophobic

to hydrophilic to ensure an even coating of monolayer polystyrene (PS) balls. Approximately 20-40 μ L of suspended (~5%) PS ball in (95%) alcohol solution was deposited onto the SiO₂ surface using a pipette as the initial masking for the preparation of the hard mask. The PS balls with an initial diameter of 450 nm shrunk to approximately 150 nm after being exposed for 600 seconds to 30W argon (Ar) plasma. A calibrated etching process consisting of CF₄:Ar (80:5) was introduced to etch the SiO₂ layer without affecting the size of the PS balls very much. Finally, 10-20mins of 100W 20sccm O₂ plasma was used to etch the carbon with the SiO₂ as the hard mask to produce carbon nanowires.

Figure 70: Schematic of Carbon Nanowires Fabrication Process

7.3 Feasibility Studies

Deposition of thick a-C film

Initial deposition of thick amorphous carbon samples proved to be difficult due to the high stress involved, and delamination was very common. A solution to this

problem is to pre-treat the silicon wafer with $\text{CF}_4:\text{O}_2$ in the ratio of 80:20 sccm to remove all of the native oxide. Another technique used was the application of 300V DC substrate bias to the wafer during deposition to increase the effectiveness and depth of the ion bombardment on the substrate, thereby improving the adhesion. Deposition rate has been calibrated at approximately 50 nm/min at an arc current of 60A. A 30-minute cooling break was introduced between 5 minutes of deposition time to prevent heating of the substrate due to the high substrate bias and ion bombardment.

Verification of anisotropic etching of carbon via RIE

One important factor during the fabrication of nanowire via the top-down approach is the anisotropic nature of the material to the etching process. In view of this particular concern, dry etching using the reactive ion etcher (RIE) is favoured over conventional wet etching. A small piece of small silicon wafer acting like a hard mask was placed over 1 μm thick amorphous carbon and placed inside the RIE. Oxygen plasma was chosen for its most likely chemical reaction of $\text{C} + 2\text{O}^+ \rightarrow \text{CO}_2$. The plasma power applied was 100W for 30 minutes. Visual inspection showed signs of carbon being etched off. The sample was observed under the JEOL scanning electron microscope (SEM); the resulted image is shown in Figure 71.

Figure 71: SEM Image of cross-sectional view of etched carbon

From the SEM image, it can be clearly observed that the edge of the carbon is nearly vertical, although there are some signs of roughness on the sides. It may be possible to fine tune the etching parameters to obtain a smooth side wall. The etch rate was calibrated by using a hard mask to selectively shield a portion of the carbon samples, as shown in Figure 72. Taking the average of the various etch rates, the etch rate obtained is approximately 55 nm/min with 20sccm O_2 flow at 100W plasma power at a pressure of 168mTorr.

Figure 72: Etch rate of carbon using 100W plasma power, 20 sccm O_2

Treatment of SiO_2 surface from hydrophobic to hydrophilic

One requirement of LB by the lift-off method is that the surface needs to be hydrophilic. A contact angle check was performed on the PECVD SiO_2 layer, and the results revealed that the surface was hydrophobic with a contact angle of 83.15°

as shown in Figure 73(a). This makes the surface rather unsuitable for the monolayer formation of PS balls using the LB method. A short low-power O_2 plasma treatment with a power of 60W and 20 sccm O_2 was performed for 15 seconds, and the contact angle was rechecked. The value was now lowered to 25.3° as shown in Figure 73(b), which was suitable for the LB process.

Figure 73: Contact angle measurement for (a) before treatment (b) after treatment

Etch Selectivity between PECVD growth SiO_2 , C and PS balls

One important factor in the whole fabrication process is the etch selectivity between the PS balls, SiO_2 and C. Carbon can be etched away by oxygen plasma, whereas SiO_2 has relatively high resistance to oxygen plasma with an etch selectivity ratio of 1:225. The standard etching recipe for SiO_2 at 100W is $CF_4:O_2$ in the ratio of 80:20. However, it was not used due to the etching of O_2 on PS balls. This is because PS is a kind of polymer that is highly susceptible to oxygen plasma. The etching recipe was changed to $CF_4:Ar$ with the ratio 80:5; a small amount of Ar is required for the plasma creation of CF_4 . The etch rate of this new recipe was tested on SiO_2 , and an

etch rate of approximately 25 nm/min was achieved. This new recipe was then tested on PS balls, and the results are shown as SEM images in Figure 74.

Figure 74: SEM Images of (a) before etch (b) 1 min (c) 2 mins (d) 4 mins etching

With the etching for SiO₂ previously obtained, the total time required for etching of 100 nm thick SiO₂ of hard mask is about 4 minutes. Using this known etching time for SiO₂, a time trial of 1, 2 and 4 mins of etching was done on PS balls to check the influence of the Ar plasma. Polymers are known to be highly resistant to CF₄ etchant, but Ar produces a mild physical etching effect on the PS balls. From the SEM images, it can be observed that the gap between the PS balls has increased by approximately 20 nm. This mild size reduction was noted and added to the size-

shrinking process of the PS ball so that an accurate diameter of carbon nanowire could be obtained.

7.4 Carbon Nanowires: Results and Discussions

Shrinking of PS ball

The PS ball can be easily shrunk by applying 30W, 20 sccm Ar. Two different times were tried, and the corresponding SEM images are shown in Figure 75. Sizes of approximately 250 nm can be obtained for 300 seconds of Ar etching. Longer timing is not recommended due to the reduction in the height of the PS ball, thereby reducing the resistance of the PS ball to CF_4 :Ar plasma. Another reason is that if the PS balls are reduced for too long, the physical shape of the PS balls will alter too much, creating a non-round feature. If size reduction is required, the correct method is to start with a smaller-sized PS ball. With this limitation, the spacing between the individual PS balls is determined by the maximum etching time allowed and the PS ball size.

Figure 75: SEM Images of shrinking process for (a) 200 secs (b) 300 secs

Annealing of PS ball

The PS balls were annealed at 110°C for 11 minutes to change the structure of the polymer and to improve the adhesion of the PS ball to the surface. Prior experiments done without the annealing have shown that the PS balls are not very resistant to the CF₄ etchant after the Ar shrink treatment. Hence, the PS balls did not successfully act as a mask for the SiO₂ etching. It may be possible that the PS balls, after going through the Ar plasma, are much less resistant than when initially tested. After annealing, there appears to be some change in the PS balls, but not much information can be gathered from the top view as shown in Figure 76(a) and (b). However, when the SEM cross-sectional view was taken, it can be observed that the PS ball has a change in the shape as shown in Figure 76(c) and (d), from the initial circular to rectangular shape. The rectangular-shaped PS ball has more surface area contacting the substrate, thereby providing a better etch mask protection for the SiO₂.

Figure 76 SEM Images of PS balls (a) before annealing (b) after annealing – Cross-sectional view (c) before annealing (d) after annealing

SiO₂ hard mask etching

After successfully ensuring that the PS balls can safely withstand the CF₄ etchant after the annealing process and with the enhanced adhesion level, the samples were taken for CF₄:Ar etching for four minutes to etch away the 100 nm SiO₂ layer. Those areas that were under the PS balls were protected due to the anisotropic etching nature of RIE. An experimental trial was also conducted using a total of six minutes of etching time; the results are not that ideal, as there are signs of the PS balls being reduced. After exposing these samples to O₂ etching, there are no traces of carbon nanowires, possibly due to the failed etching of the SiO₂ hard mask, as

the PS balls are significantly weakened by the long six minutes of etching. From the SEM images in Figure 77, it can be observed that there is little change in the diameter of the PS balls after the SiO_2 etching process.

Figure 77: SEM Images of PS balls after SiO_2 etch for (a) 200 secs and (b) 300 secs

Oxygen Plasma Etching of Carbon Films

The samples were subjected to 100W 20sccm O_2 for 10 minutes. SEM images were taken as shown in Figure 78. There are two SEM images, which correspond to two different shrinking times for the PS balls namely, (a) 200 seconds and (b) 300 seconds. The top view shows some differences from the previous images, and it appears that there is slight etching on the top of the carbon nanowire; the unshielded areas are rather rough.

Figure 78: SEM Images O_2 etch for 10 minutes for (a) 200 secs and (b) 300 secs
 As the top view does not yield much information, the SEM sample stage was tilted to an angle of 30° to reveal a slanted view of the samples. The SEM images obtained are shown in Figure 79. It can be clearly observed that carbon nanowires with smooth sidewalls can be obtained by using the top-down approach.

Figure 79: Tilted 30° SEM Images O_2 etch for (a) 10 mins and (b) 20 mins

7.5 Chapter Summary

Thick a-C films (500 nm to 1 μm) have been successfully deposited after the treatment on the silicon. Without the treatment, there was clear sign of delamination of the carbon film from the silicon substrate. By treatment of the silicon using RIE with etchant gas $\text{CF}_4:\text{O}_2$, the native oxide on the silicon wafer was etched away,

creating a surface that is highly conductive. The effect of etching also made the silicon surface rougher, which could promote adhesion of the carbon film.

The anisotropic etching of carbon using RIE has been verified, giving near vertical sidewalls. The sidewalls appear rough initially, but the process can be improved by introducing breaks in between etching and using lower RF power during etching.

The LB method for depositing monolayer requires a hydrophilic surface. Plasma treatment was performed on the silicon oxide hard mask to reduce the surface energy, thereby changing the surface from hydrophobic to hydrophilic.

PS balls that were deposited by the LB method have one disadvantage, which is the adhesion of the PS ball to the silicon oxide surface. This adhesion was improved by subjecting the PS ball to annealing that changed the shape and increased the contact area between the PS balls and the silicon oxide surface.

As carbon and PS balls are vulnerable to oxygen plasma, a modified recipe of CF_4 :Ar was used to etch the silicon oxide hard mask. There was very little chemical reaction of the CF_4 on carbon and PS ball. As the flow of argon was very small, its main purpose was to initiate the plasma cloud to dissociate the CF_4 gas and react with the silicon oxide.

Carbon nanowires were successfully obtained after the oxygen plasma etching process. After the CF_4 gas etching, the residues of the silicon oxide hard mask and the micro particles at the bottom of the substrate were removed, producing ordered arrays of nanowires with exact height, diameter and composition.

Chapter 8 : Conclusions and Future Works

This project started with the intention of having a thorough understanding of the influence of carbon film alignment obtained via in-situ and ex-situ methods on the electrical characteristic of the carbon film in order to produce uniform conductive and non-conductive carbon nanowire arrays and patterned carbon films for possible future electronic applications.

Three co-related portions of this project have been discussed in this report, including in-situ annealed carbon films, ex-situ induced carbon films and fabrication of carbon nanowires. The investigation of these techniques is based solely on carbon-based materials. Different techniques to produce these carbon materials have been discussed in this report.

Under the in-situ annealed carbon deposition, it has been demonstrated that nano-crystalline graphitic carbon (NCG) films have been successfully fabricated at temperatures above 400°C. The successful fabrication of NCG films is verified by Raman, transmission electron microscope (TEM) and diffraction patterns. From the conductive atomic force (CAFM) microscope measurements, it is observed that the electrical resistivity is lower at higher temperatures (600°C). It has been observed through the CAFM current graph that at high bias of -600V, there is formation of NCG even at the low temperature of 150°C. The detailed studies on the influence of carbon deposited with high ion energy are performed. Different thicknesses of NCG have been fabricated and characterised. The results show that the long-range

ordering seems to be limited to film thickness of not more than 200 nm. The increase in the film thickness (from 300-500 nm) shows a linear relationship between film thickness and resistivity. What is interesting is the ohmic behaviour of NCG films, which still persists with thicker films.

The in-situ Raman, TEM and IV have been conducted on post-annealed amorphous carbon thin film samples. This experiment gives insight on the conversion process of the carbon thin film from the amorphous to the nano-crystalline state. This is the first time such a study has been conducted experimentally and explored in detail. It is found that the amorphous sp^2 carbon content has the tendency to convert to NCG at a lower temperature of 200°C. With the appearance of NCG, the electrical resistivity drops by two orders of magnitude but still exhibits non-linear IV characteristic due to the presence of amorphous carbon matrix. At higher temperatures, the appearance of the D peak in the Raman spectrum can be observed which is a tell-tale sign that the sp^3 content has reduced and the matrix has converted to NCG carbon. The resulting IV characteristic shows an ohmic behaviour, which is typical of all NCG carbon thin films characterised in this report. Ex-situ induced NCG, namely the laser-annealing and electrical pulsed inducement, has been performed on amorphous carbon: NCG films can be obtained from amorphous carbon via external means other than thermal annealing. Selective areas have been subjected to laser treatment, and CAFM measurements show high contrast in electrical resistance. TEM studies further confirm the presence of NCG films. It is observed that NCG is more prominent at higher laser energy. However, at higher laser energy, surface roughness has been observed to increase drastically. Minimisation of laser energy has enabled a decrease in the thermal spread between

the annealed and non-annealed carbon films. The electrical pulsed inducement has been conducted by using CAFM and MCM structure. It is possible to induce changes from amorphous carbon to NCG by the usage of electrical pulse voltage. The change in electrical conductivity is abrupt, and the film conductivity is the highest of all other techniques. Figure 80 shows the combined IV results of NCG obtained via the various techniques. It is found that the electrical pulsed method produces the highest electrical conductivity but requires the existence of external metal electrodes for inducement. The most convenient method is via laser-induced annealing, but there is a compromise between film surface roughness and electrical conductivity. The in-situ method provides a moderate IV characteristic should the situation allow the deposition of carbon thin film under electrical bias and/or temperatures.

Figure 80: Overall IV Curve of NCG obtained via various techniques

Carbon nanowires of length of 500 nm to 1 μm with a diameter of 250 nm have been successfully fabricated. The fabrication process involves the understanding of the surface energy on the silicon oxide layer that was used as a hard mask. The

adhesion strength of the polystyrene (PS) balls on the silicon oxide, which was deposited by the Langmuir Blodgett (LB) method, has also been studied. Heat treatment on the PS balls was found to improve the adhesion strength on the silicon oxide layer. A short oxygen plasma treatment on the hydrophobic silicon oxide has successfully changed its properties to hydrophilic enabling the LB method to be applied.

This study serves as a stepping stone for future experimenting and direction with the usage of pure carbon thin films deposited via FCVA techniques for possible future electrical and electronic applications.

Future Works

1. One of the possible future works could involve the exploration of increasing the in-situ deposition temperature and bias to an even higher level, which could not be done in this report due to the equipment limitation. It has been shown that at higher bias, there are some changes to the planar structures, and it would be interesting to further explore the behaviour of the carbon thin films under higher temperature and bias.
2. Metal strips could be deposited on top of the amorphous carbon thin film as shown in Figure 81 before the laser-annealing process. These metal thin strips will shield off the laser power, and this would be interesting and more practical for cross-sectional TEM analysis of the interface between the annealed and non-annealed carbon sample.

Figure 81: Experimental flow for metal strips fabrication

3. If the electrical pulse could be reversed or executed in very short pulses, it may be possible to reverse the changes back from NCG to amorphous carbon. This will be interesting for applications in RAM and flash memory.
4. Future works for the nanowires can be concentrated on expanding the inter-spacing between the nanowires. This can be done by using PS balls of larger diameters as shown in Figure 82. Inter-spacing between each carbon nanowire can be changed by using different sizes of PS balls.

Figure 82: Proposed Concept 942 nm PS before (d) after

5. The carbon nanowires could be subjected to laser irradiation as shown in Figure 83. These carbon nanowires could be useful for the purpose of nano-antenna in the field of GHz, which requires highly conductive carbon pillars with widespread uniform electrical properties, length and diameter that is a common problem for CNTs' nano-antenna.

Figure 83: Schematic of proposed idea (a) before (b) after laser annealing

List of Publications

Journal Papers

- [1] **Tan, C.W.**, Tay, B.K., “Carbon nanowires fabrications via top down approach”, *Journal of Nanoscience and Nanotechnology*, vol 12 (1), pp. 707-713, 2012.
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Conference Paper

- [7] Li, F., Shakerzadeh, M., **Tan, C.**, Yu, H., Tay, B., “Highly conductive aligned carbon film for interconnect application”, *INEC 2010 - 2010 3rd International Nanoelectronics Conference, Proceedings*, art. no. 5424560, pp. 730-731, 2010.
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