Advanced carbon hybrid materials

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2009

Teo, E. H. T. (2009). Advanced carbon hybrid materials. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/14967>

<https://doi.org/10.32657/10356/14967>

ADVANCED CARBON HYBRID MATERIALS

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A thesis submitted to the Nanyang Technological University
in fulfillment of the requirement for the degree of
Doctor of Philosophy

2009

~..~ Dedicated to Dad & Mum ~..~

ACKNOWLEDGMENTS

I am very grateful to my thesis supervisor Prof. Tay Beng Kang, for his constant encouragement and guidance throughout my PhD candidature. His invaluable advices and insights on carbon materials and the Filtered Cathodic Vacuum Arc had been instrumental in the development of the new carbon hybrid materials reported here.

I would also like to express my gratitude to Prof. Daniel Chua and Dr Sheeja for their invaluable guidance during my work on the multilayer amorphous carbon films, Prof. D. G. McCulloch for his insights on the TEM analysis of carbon, Prof. D. R. McKenzie for the discussions on the gradient a-C films and Prof R. Kalish for his invaluable advices on the carbon nanomattress.

I also wish to thank all my colleagues and fellow students in Nanoelectronics laboratory for all the help and support they have rendered me throughout my candidature.

Lastly, I am deeply indebted to the love of my life, Dunlin for her continuing and unconditional moral support. She has been the light that has guided me in the darkest hours of my research.

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LIST OF ABBREVIATIONS

2D on 1D	two dimension on one dimension
3D	three-dimensional
A-C	amorphous carbon
A-C:H	hydrogenated amorphous carbon
AFM	atomic force microscopy
BEA	boundary element analysis
BF	Bright field
BWF	Breit-Wigner-Fano
CAD	computer-aided-design
CCC	carbon-carbon composites
CMP	chemical mechanical polishing
CMC	ceramic matrix composites
CNM	carbon nanomattress
CNT	carbon nanotube
CPMD	Car-Parrinello ab initio molecular dynamics
DC	direct current
DFS	dynamic friction spectra
DLC	diamond-like carbon
DF	dark Field
ECR	electron cyclotron resonance system
EELS	electron energy loss spectroscopy
EDIP	environment-dependent interaction potential

LIST OF ABBREVIATIONS

EDTB	environment-dependent tight-binding
FCVA	filtered cathodic vacuum arc
FEA	finite element analysis
FWHM	full width at half maximum
HMDS	Hexa-Methyl-Di-Silazane
IBAD	ion beam assisted deposition (IBAD)
IC	integrated circuit
IMC	intermetallic composites
MC	Monte Carlo
MD	molecular-dynamics
MMC	metal matrix composites
MSIB	mass-selected ion beam deposition
MWCNT	multiwall carbon nanotube
N/MEMS	nano/microelectromechanical systems
OPBD	off plane double bend
PBS	plasma beam source
PECVD	plasma enhanced chemical vapor deposition
PLD	pulsed laser deposition
PMC	polymer matrix composites
RF	radio frequency
RMS	root mean square
RH	relative humidity
RTA	rapid thermal anneal
SADP	selected area diffraction pattern (SADP)

LIST OF ABBREVIATIONS

SEM	scanning electron microscopy (SEM)
STEM	scanning transmission electron microscopy (STEM)
SW	Stillinger-Weber
TBMD	tight-binding molecular dynamics
TEM	transmission electron microscopy
Ta-C	tetrahedral amorphous carbon

SUMMARY

This thesis reports on the fabrication and evaluation of carbon composites whose constituents are based solely on carbon materials. In particular, three types of carbon composites term multilayer amorphous carbon (a-C) films, gradient a-C films and carbon nanomattress (CNM) are discussed.

Multilayer a-C films are layered composite coatings consisting of high sp^3 content (>70 %) tetrahedral amorphous carbon (ta-C) and intermediate sp^3 content (~50 %) a-C. In order to study how the internal macro-composition affects the properties of the multilayer films, the modulation and relative amount of the two types of constituent material within the composite are systematically varied to create different types of multilayer films. The films are then characterized to determine the differences in properties between them. The properties of interests include intrinsic stress, indentation hardness, reduced elastic modulus, wear resistance, coefficient of friction and surface roughness. From the results, certain trends correlating the internal structuring and material properties of the multilayer films are uncovered and explained in this thesis. Moreover it was also revealed that the highest indentation hardness of the multilayer films measured (41 GPa) is only 20 % lower from those of ta-C films deposited by the same system. This is despite the multilayer film having an intrinsic stress that is 50 % lower than those of ta-C.

The effects of different annealing conditions on the multilayer films were also investigated to determine the most efficient conditions for stress lowering.

The investigation reveals that annealing at 200 °C for 3 min in vacuum is the ideal condition for effective stress reduction without compromising the applicability of the multilayer film in microelectromechanical systems (MEMS). Moreover, using this annealing condition, stress reduction of ~30 % is observed for the films with negligible effects on other mechanical and tribological properties tested. Furthermore, due to the low annealing temperature used, MEMS structures using multilayer a-C films are also successfully fabricated using standard lithography methods. Simulation of the performance of MEMS devices based on multilayer a-C films are also done using IntelliSuiteTM. Significantly, the simulated resonance frequency response of a fabricated microcantilever matches with the actual response measured using a laser vibrometer.

The second carbon composite investigated is the gradient a-C film, which is a graded film with its internal density varying continuously throughout the thickness of the material. One of the most interesting observation on this material is the formation of vertically (with respect to the substrate) self-aligned graphitic sheets within the amorphous matrix of the film. To study how the density profile within the film could affect the self-ordering of the anisotropic graphitic sheets, gradient films with differing density profiles are fabricated and their internal macro and microstructure investigated by transmission electron microscopy and electron energy loss spectroscopy. Furthermore, Raman spectroscopy analysis also revealed that annealing the gradient film at 600 °C for 10 min promotes further alignment within the isotropic regions of the film.

Importantly, these observations open up the possibilities of many engineering applications which are discussed in this thesis as well.

Lastly, this thesis reports on the fabrication process of the CNM, which is a hybrid material system that is both hard with high wear resistance and intrinsic tunable viscoelastic properties. The fabrication process consisted of fusing an a-C layer to the top of a multiwall carbon nanotubes (MWCNTs) film through the formation of carbon nano-spheres which are formed by the direct deposition of a-C onto the tips of the MWCNTs.

CHAPTER 1 USING CARBON IN COMPOSITE MATERIALS

1.1 Introduction

Many great innovations ride on the back of the discoveries of new materials and their properties. Nothing personifies this more than the relationship between the current multi-billion dollar integrated circuit (IC) industry and silicon. It is indeed humbling to know that many of mankind's technological breakthroughs in the last few decades such as the internet, microchips and even Ipods would not have been possible if silicon and its semiconducting properties had not been identified and applied. The need and desire to explore and discover new materials is therefore enormous. This drive is further fueled by the unpretentious assumption that the person or institution who discovers the "next silicon" would likely dominate the future technological scene.

Well-established materials such as metals, ceramics or polymers cannot fulfill many of today's technological needs. As such many researchers have turned towards combining different materials to extract useful properties that were lacking in their original form. This is not to say that this approach is new. History has many examples of the rise and fall of nations due to discoveries of

compositional materials like steel and bronze, and their subsequent applications (usually in military context).[1] For example, blacksmiths for samurais has been carburizing steel through graded blades for toughening swords since feudal times in Japan.[2] Besides artificial materials, nature also has materials build upon the concept of fusing two or more different components to form complex structures.[3, 4] These are usually in the form of inorganic components for structural strength and organic components for bonding between the inorganic parts and soft tissues. Bamboo, bone and nacre are just such examples.[5, 6] As such, taking the cue from nature and learning from the past, current research activities into the engineering of materials through the combination of various separate entities are now done worldwide. This type of materials is generally known as composite materials or composites for short.

1.2 Motivation

1.2.1 Compositional materials

Composite materials make up a very broad and important class of engineering materials. In general, they could be defined as multi-phase materials obtained through the combination of different materials or material phases.[7] The main reasons for the research on compositional materials are for the extraction or engineering of materials with better, strengthen, re-enforced, unique or special properties. As such, it is not surprising that one of

the most prominent and recognizable use of composites is as special structural materials for the airframes of advanced military aircrafts.[8] Besides the use of composites as structural elements, there has also been a lot of work on the development of multi-functional composite materials as well.[9]

As with any broad class of material systems, a standard classification of the various sub-classes of composites would be useful in its study. However, currently there is no universally accepted classification of composites.[3, 4, 7-12] Despite this, two forms of classification scheme based on *Form of Constituents* and *Nature of composites* are commonly accepted. Classification by the *form of the constituents* refers to the scheme where composites are categorized by the structure of their components. Using this method, there are three major groups of composites. The first are particle-reinforced composites such as nano-clusters embedded in thin films and micro-flakes based composites. The second are fibers-reinforced composites consisting of composites with a generally softer matrix strengthen by fibers, wires or tubes. The last are structural (or laminates) composites which are planer composites (usually in the form of a coating) that have multiple layers or laminar constituents.

On the other hand, classification by *nature* refers to the scheme where the composites are classified according to the type of material their components are made of. In this scheme there are 6 major sub-classes grouped by their base material consisting of polymer matrix composites (PMC), metal matrix composites (MMC), ceramic matrix composites (CMC), carbon-carbon

composites (CCC), intermetallic composites (IMC) and hybrid composites. Recently a seventh group termed organic-inorganic hybrid is also increasingly been developed for use as multifunctional and smart materials.[13-18] These hybrid materials are usually fabricated by the incorporation of a functional species into a second structural element which could be in the form of whiskers, fibers, lamellae or mesh.

1.2.2 Carbon based composites

Regardless of their classification, the most important aspects in the design of composites lie with the choice of its constituent components and their structural arrangement within the composite.[19] Currently, the most widely used constituents in composites are carbon-based materials such as graphite and carbon fibers.[9] Many of today's most widely commercialized applications of composites such as automobiles, sports equipment, aviation components, marine accessories...etc have some form of carbon material as at least one of the components in their composition. Even composites based solely on carbon materials are available. An example is CCC which is a sub-class of composites made from highly-ordered graphite fibers embedded in a graphitic matrix.[20] The reason for the popularity of carbon as a constituent material in composites is due to the many remarkable properties of the various forms of carbon. For example, carbon fibers used as a reinforcement material in many advanced ultra light-weight composites is very light, with density at only 1.5 g cm^{-3} but yet have high strength with elastic modulus of 530 GPa. Highly oriented graphite-

based composite used in modern heat sinks is another example. Graphite is used as the primary constituent in the composite because it has a high melting point of 3700 °C and excellent in-plane thermal conductivity of $\sim 2000 \text{ Wm}^{-1}\text{K}^{-1}$. [9, 21]

Besides large structural applications (such as sports rackets, aviation airframes and boat hulls), carbon-based materials are also used in thin film nano-composites. For example, carbon nanotubes (CNTs) reinforced polymer thin films (a type of PMC) are increasingly studied for mechanical strengthening and viscoelastic properties. [22-25] CNTs were chosen as fillers in the PMC because of their high stiffness and low weight. Due to these characteristics of the embedded CNTs, the PMC could have enhanced strength with very little weight penalties. Moreover, because of their high aspect ratio and nanoscale dimensions, which results in large interfacial contact area ($\sim 100 \text{ m}^2 \text{ g}^{-1}$ for multiwall (MW) CNT [26]), very high mechanical damping could be achieved as well. [25] Other carbon-based composite thin films that are actively researched are laminar composites based on amorphous carbon (a-C) thin films. These laminar composites usually consists of a-C layers interspaced between layers of other materials, and are generally designed to improve the adhesion, tribological and mechanical properties of the thin films. [27-32]

1.2.3 Carbon-only Nano-Composites

Besides combining carbon with other materials, nano-composites films with only carbon components have also been investigated recently. A-C coated

CNTs composites for improved field emission,[33] a-C film on CNT film composites for improved toughness,[34] high and low sp^3 content a-C multilayer superlattices for enhanced mechanical performance,[35-37] a-C/carbon nano-ribbons composites for electromagnetic shielding,[38] diamond/a-C composite films for biological applications [39-43] and diamond/carbon flakes hybrid films with special structural features [44] are just such examples.

The primary reason carbon-only nano-composites are possible is due to the fact that carbon exists in a great variety of different forms. Furthermore, along with the various types of carbon are a large range of properties associated with them. Table 1-1 summarized some of their properties for comparison. As can be seen from the table, the properties of different forms of carbons differ drastically. Even a-C with different variation of sp^2/sp^3 content could have big differences in their properties. And it is exactly due to these large properties and structural contrast, that very interesting carbon-only nano-composites could be realized. Not just would this approach create composites with interesting properties, but by using only carbon based components in the material system, synthesizing and integrating them together would be much easier compared to the often more complicated synthesis methods needed to combine composites with different materials. Moreover, the concept of a carbon-only compositional material system presents itself as a very elegant way in fabricating novel material systems.

Table 1-1 Comparison chart of various a-C with reference materials diamond, graphite and C₆₀. [45]

Type	Sp ³ (%)	Density (g cm ⁻³)	Hardness (GPa)	Band Gap (eV)
Diamond	100	3.515	100	55
Graphite	0	2.267	Soft	0
C ₆₀	0	N.A.	N.A.	1.6
Glassy C	0	1.3 – 1.55	3	0.01
Ta-C	80 – 88	3.1	80	2.5
a-C:H	40 -60	1.2 - 2.2	10 – 20	1.1 – 4

This thesis would thus hope to contribute to this field by extending the work on multilayer a-C films and introducing two new carbon-carbon hybrid compositional material systems, termed gradient a-C film and carbon nanomattress. The term carbon-carbon hybrid is used in the context of this thesis to differentiate from CCC which generally refers to graphite/fiber composites.[21]

1.3 Objectives

In this thesis, the primary goal is to fabricate and investigate different types of carbon-carbon hybrid materials (or carbon hybrids for short). Specifically, three types of carbon hybrids will be examined. They are discrete multilayer a-C films, continuous density varying a-C films (gradient a-C films) and a-C/MWCNT hybrid film (carbon nanomattress).

Under the investigation of multilayer a-C films, the main emphasis will be on the mechanical properties of thick (1 μm) continuously deposited multilayered films. The mechanical properties of interest are hardness, elastic modulus, wear resistance, frictional characteristics and surface roughness. Specifically, the study is to probe into how the internal macro-composition of multilayer a-C films together with annealing would affect their various mechanical properties. A short study into the applicability of using multilayer a-C films for microelectromechanical systems (MEMS) would also be conducted.

The second carbon hybrid material of interest is the gradient a-C films. This is a new type of graded a-C film where its internal density is continuously varied throughout its thickness following a pre-determined density profile. The aim of the study is to investigate how the varying internal density affects the macro and microstructure of the films. Of most interest in this study is the investigation of how graphitic alignment in the internal structure of the graded films could be realized and controlled. Annealing characteristic of these films together with their potential applications would also be explored.

The last carbon hybrid investigated is the a-C/MWCNT hybrid structure termed carbon nanomattress. This is another unique carbon-only compositional material fabricated through the fusion of an a-C top layer to an underlying vertically aligned MWCNT film. The study would primary focus on the fabrication methodology of this hybrid material.

In all, the investigation of the three types of carbon hybrid materials represented an extension into the study of fabricating carbon-only hybrid

materials. It is hope that this work would help encourage others into creating and investigating other forms of carbon-carbon hybrid materials and their applications.

1.4 Major Contributions of thesis

Under the research topic mentioned above, the major contributions achieved in this thesis are summarized as follows:

1. The influence of internal composition on the mechanical properties of continuously deposited multilayer a-C films fabricated by the off plane double bend filtered cathodic vacuum arc (OPDB-FCVA) in conjunction with substrate bias has been systematically investigated using nano-indentation experiments, pin-on-disk experiments and atomic force microscopy (AFM). Mechanical properties such as stress, hardness, elastic modulus, wear resistance, surface friction and roughness of the multilayer films were extensively evaluated and discussed. Significantly, thick 1 μm multilayer a-C films with relatively low stress (~ 2.4 GPa) and good mechanical properties were successfully fabricated and tested.
2. The effects of annealing on the multilayer a-C films were investigated. Despite having $\sim 30\%$ of stress reduction, the mechanical properties of the multilayer films were found to be mostly unaffected by annealing. Overall, continuously deposited multilayer a-C films together with

annealing showed good potential for applications in coatings as well as structural components for MEMS.

3. Various MEMS structures based on multilayer a-C films were successfully simulated using Intellisuite® and later fabricated using standard lithographic means. Notably, the resonance response of a “T-frame” micro-cantilever was simulated and tested through a laser vibrometer. Both the virtual as well as actual results were comparable showing very good agreement between experimental and simulation results.
4. By intentionally and continuously varying the ion energy during the deposition of a-C, a new carbon composite film with a density grading was fabricated. The internal structure of the gradient a-C films and their annealing characteristic were studied in detail using scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) and Raman spectroscopy. From the investigation of the film, highly oriented graphitic layers were observed within the amorphous matrix of the films. A hypothesis of how the aligned graphitic layers were formed based on deposition temperature effects was also given.
5. It was observed that the aligned graphitic region within the film could be manipulated by controlling the density profile together with annealing. An explanation for the observed inducement of aligned material based on density lowering and energy minimization was given. By having a good control of the aligned graphitic material within the amorphous matrix,

applications ranging from embedded 3-dimensional (3D) interconnects to ultra high conductivity thermal interface could be realized.

6. Using a two dimension on one dimension (2D on 1D) approach, a new form of carbon hybrid composite termed carbon nanomattress was fabricated. This material combines both the viscoelastic properties of CNTs together with the high hardness and wear resistant properties of a-C to form a unique 2 tier material system. Potential for this material system ranges from smart vibration isolation systems to structural materials for MEMS.
7. Ten papers have been published/accepted in journals as listed in the author's publications with another two in preparation/revision. In particular, the initial report on the carbon nanomattress published in Advanced Materials was feature in online nanoscience forum Nanowerk.
8. It is also worthy to mention that a substantial amount of modification on the existing OPDB-FCVA was carried out during the last three years by the author.

1.5 Organization of Thesis

This thesis is organized into 8 chapters. Chapter 1 and 2 are the introductory chapters which gives a general background on the research topic, while Chapter 3 gives the details on the conduct of experiments. CHAPTER 4-

CHAPTER 7 contain the main body of the thesis where most of the results and discussions are presented. These chapters always begin with an introductory segment followed by a short section explaining the scope and objectives of the particular chapter. A short summary would also be presented at the end of every chapter. Chapter 8 is the closing chapter of this thesis.

Chapter 1 provides a general introduction to hybrid materials and presents the case for support for the development of carbon based hybrid materials. In addition, Chapter 2 is devoted to the fundamental background on a-C. Key concepts and theories relating to the formation of sp^3 bonding, micro and macro-structure, stress reduction and deposition methods are presented.

Chapter 3 gives the detailed experimental methodology and characterization techniques. Parameters used on the various characterization systems are elaborated and explained in this chapter. The characterization tools explained includes nano-indentation, atomic force microscopy, micro-tribology, transmission electron microscopy, electron energy loss spectroscopy and Raman spectroscopy.

Chapter 4 focuses on the mechanical properties of multilayered a-C with special emphasis on the effects of macro layering composition and annealing. The first part of the chapter will be on the fabrication methods employed to prepare the a-C multilayer films. The second part will focus on the mechanical aspect of the films followed by surface morphology and tribological properties. Chapter 5 gives an assessment on the viability of using multilayer a-C film as a

structural material in MEMS. To investigate the process capability of multilayer a-C films, a few structural elements were designed, simulated and fabricated.

The main investigations conducted in Chapter 6 are on the micro and macrostructure of density graded a-C films and their annealing effects. Besides studying the as-deposited microstructure of the films, their microstructure changes after annealing are also investigated. The first part of the chapter develops the initial theory on the formation of aligned graphitic material in the graded film. This is followed by the substantiation and verification of the theory by another two different types of graded films. The last part of the chapter elaborates on the potential application arising from this study.

Chapter 7 discussed the fabrication method of synthesizing a two tier carbon hybrid material system by fusing an a-C film with the top of a MWCNT film. Finally, the conclusion and recommendations for future work are given in Chapter 8.

CHAPTER 2 LITERATURE REVIEW

2.1 Introduction

As all three carbon hybrids discussed in this thesis are based on a-C materials, a brief review on the current status of research on a-C in general is thus useful. This chapter would therefore give an overview of the current progress and development of a-C ranging from the debate on the origin of sp^3 bonding in a-C to its deposition systems. This is not meant as a thorough review but a brief outline of the more relevant concepts in the current discussions on properties of a-C. Key theories, specifically those which would be used in the later chapters, would be emphasized.

The key concepts that would be discussed in this chapter are thus the fundamental concepts of sp^3 bonding in a-C, internal structure of a-C, stress reduction principles by annealing as well as deposition methods.

2.1.1 Amorphous carbon

Carbon can form a great variety of crystalline and amorphous structures because its atomic structure can have three hybridization forms, sp , sp^2 and sp^3 . [46, 47] The three main allotropic forms are graphite (threefold coordinated carbon atoms, sp^2), diamond (fourfold coordinated carbon atoms, sp^3) and

buckminster fullerenes (buckyballs and nanotubes).[47] Among these diversities, the most commonly utilized in commercial applications are diamond and graphite, and their amorphous form, termed a-C. However even within a-C there could be further sub-classes. This is because, depending on the relative amount of sp^2 and sp^3 content within the material, a-C could have widely different structural composition, properties and characteristics.

The commercial interest for a-C boom in 1971 when Aisenberg and Chabot[48] produced an ultra hard form of a-C, termed diamond-like carbon (DLC), from the use of energetic species during deposition. From this pioneering work came 3 decades of intense research by others in employing energetic species for the deposition of DLC and their applications.[49] DLC is so termed because of its remarkable similarity in terms of physical properties with diamond without being crystalline (thus diamond-like). DLC has these properties because of its high sp^3 (>40 %) content. Besides the “pure” form of DLC, another common form known as hydrogenated DLC (a-C:H) also exists largely due to the use of hydrocarbon plasmas for DLC deposition.[50] Another form of a-C was also reported by D. R. McKenzie et al [51] with carbon-carbon sp^3 bond content exceeding 90 %. This is termed tetrahedral amorphous carbon (ta-C).

Regardless of the types of a-C, one of the most important aspects of a-C is the relative amount of sp^2 to sp^3 bonding within its amorphous matrix. This is because many of the various remarkable properties (especially mechanical properties) are closely associated with the relative amount of sp^3 content within

the film. As such the mechanisms of sp^3 bond formation in a-C is discussed next.

2.2 Origins of sp^3 formation in amorphous carbon

As mentioned earlier, the relative amount of sp^3 to sp^2 bonding is important in the determination of the properties of a-C. As such good control over the sp^3 to sp^2 ratio within the a-C material is needed in order to create combine forms of them (eg. hybrid multilayered a-C that contains both sp^3 rich and sp^3 poor layers). The understanding of the growth mechanism of a-C is thus crucial. However despite intense efforts, the origin of sp^3 bonding within the amorphous network is still controversial.[45, 49, 51-68]

While Mckenzie and co-workers,[51] proposed a formation of ta-C from the high compressive stress generated by thermal spikes,[67, 69, 70] during film deposition. J. Robertson,[52, 54] maintains that the sp^3 bonding in ta-C arises due to densification of the implanted C^+ ions (into sub-surface sites) from a physical process of subplantation or subsurface growth, which is a modification of the original theory by Y. Lifshitz.[59, 60] This debate was also subsequently extended to discuss the stress relief behaviour of a-C due to annealing as well. Brief reviews on the current status of these on-going discussions are given below.

2.2.1 Compressive-Stress-Induced Formation of Ta-C

Initially, a-C with ultra high (>70 %) sp^3 bonding was thought unlikely to be stable due to bonding constraints imposed on the carbon network although such a structure does exist for amorphous silicon and germanium.[71] McKenzie et al was the first to report on the existence and formation of such a structure which they termed ta-C.[51] Their proposed mechanism for the formation of the high concentration of sp^3 (92 %) content was due to the high compressive stress generated during the filtered vacuum arc deposition process. They based their theory on a molecular-dynamics (MD) study of film growth using a modified Stillinger-Weber (SW) potential.[72] The interaction potential was based on reparametrization of the SW potential for graphite using a Hartree-Fock energy calculation for small tetrahedral coordinated carbon cluster.

In the original theory, for energetic ion-impingement, three distinct energy bands were of importance. The first energy band is for ion energy below 20 eV. For ions within this band, because of the relatively low energy, the incident ions tend to be reflected off the substrate without significant effect on it. In the second energy band of 20-60 eV (intermediate range), the incident ions penetrate the sub-surface layer inducing local compressions. The last energy band is between 80-100 eV where the ions energy is high enough such that the incident ions would push the underlying atoms deeper into the substrate.

Another way to view the collisions of incident ions and surface atoms will be through a thermal spike model. These thermal spikes are induced by energetic collisions and the subsequent transfer of kinetic energy between

incident ions and the underlying atoms (and subsequence quenching). The thermal spikes are thus extremely rapid localized heating and cooling events on the substrate. When these events are small and confined, they form pockets of stress states on the substrate leading to an overall stressful material. However, with increasing ion energy, the impacts would create regions large enough for the excess energy to flow and thus relieve the stress of the material. Therefore a-C films that are built up with high incident ion energies are less stressed compared to a-C films deposited with ion energies in the intermediate range. Further, with enough compressive stress, the effective pressure and temperature inside the film could be driven well inside the diamond stable zone as defined by the Berman-Simon line[73], which is based on thermodynamic grounds, would encourage the phase shift of a-C from a more graphitic like material to one that is more diamond-like. An important prediction by this theory is that since internal stress is the driving force behind the phase change, the surface of the material would therefore be graphitic. This is because the surface of the film is a free surface and is thus stress free. It is now well-established that the surface of all a-C films is graphitic.

The theory centers on the formation of sp^3 bonds due to stress generation by energetic ion bombardment. As such, the mechanism of stress generation by energetic ion bombardment is essential to its validity. A popular model to explain the compressive stress generation by incident ion energy through knock-on implantation and thermal spike was proposed by C. A. Davis[74]. The effects of different ion energies on the substrate was furthered by N. A. Marks et al[66] when they studied how individual ions of differing

energies would affect the substrate by MD simulation using the environment-dependent interaction potential (EDIP). His work showed how single ions would behave during energetic collisions with the substrate. From their simulations, it can be observed that energetic collisions in the range that usually produces high sp^3 content a-C films also produces pockets of tensile and compressive localities with most of these localities being compressive. Since the total stress of the film is a result of the summation of all these localities, the film is naturally under compressive stress. Moreover from their simulation, they noted that the ions do not necessarily penetrate the sub-surface as hypothesized by the subplantation model. They argued that from the simulation results, the densification layer as predicated by the subplantation theory could not have materialized, thus debunking the subplantation process as the mechanism for sp^3 bonding. Therefore, from their work, the stress observed in ta-C is a consequence of ion kinetics and not necessarily via a subplantation process.

Further evidence of a stress-induced model of sp^3 bond formation is also reported by D. G. McCulloch et al[65] when they used Car-Parrinello ab initio molecular dynamics (CPMD) simulations to study the structure of a-C with different densities. From their work, a strong non-linear dependence of the sp^3 fraction in a-C with stress and in particular a sharp transition point when the stress is at ~4 GPa is observed. Their observation of a general correlation between stress and sp^3 content in a-C films together with the identification of a stress transition point where a sp^2 rich film converts to a sp^3 rich film rapidly are highly indicative that stress is an important determining factor for high sp^3 content in a-C films.

2.2.2 Subplantation model for DLC film growth

The subplantation model of a-C film growth was first proposed by Y. Lifshitz et al[59-61] and subsequently modified by J. Robertson[52, 54]. In the original subplantation theory, Y. Lifshitz et al used a Monte Carlo TRIM[75] program for analysis. They proposed that within the correct incident ion energy range, a sub-surface implantation mechanism would preferentially displace the sp^2 sites in the film causing an accumulation of sp^3 sites leading to an increase in overall sp^3 bonding in the film.

In the original theory by Y. Lifshitz, during the early stages of film growth, energetic ions (termed hyperthermal species in his paper) with enough energy would penetrate into the sub-surface of the substrate. The penetration depth would depend on the energy of the incident ion and the nature of the target substrate. During the penetration of the ions, three mechanisms are responsible for stopping it from driving deeper into the substrate. These are atomic displacement, phonon excitation and electron excitation. The latter two mechanisms can be classified under the kinetic energy transfer model of thermal spikes. The theory further explains that the incident ion could be preferentially trapped (ion channelling) predicting that preferred orientation could be observed due to this effect. These observations of preferred orientation were later verified by many others. This entrapment of the incident ions would increase over time and build up into a dense layer below the surface of the substrate (densification) and with increase ion penetration there would be an upward growth of the material due to the denser layer pushing the top surface up. Although during early stages of growth, the top layer consisted of

the original substrate atoms, these would be sputtered and diluted by ion mixing mechanism with subsequent deposition until only the target material is present.

The structure of the growing film would thus be heavily influenced by two factors. First is the mold effect caused by the host matrix preferentially trapping incident ions in specific orientation and second by the preferential displacement of atoms with lower displacement energies causing, in the case of DLC, higher sp^3 content. In this theory, the stress is a by-product of the film growth and not the cause of higher sp^3 content.

J. Robertson later adopted the subplantation model to explain the high sp^3 content in DLC films.[54] He explained the DLC growth via subplantation-like mechanism using a 2 stage process of penetration (sp^2 to sp^3) and relaxation (sp^3 to sp^2). He later modified this model into a 3 stage model[52] factoring in interstitial sites transition through radiation-enhanced diffusion.[76] The central theme relates the formation of sp^3 bonds with densification of the material during film growth and thus associates the high sp^3 content of ta-C with density and not stress. In his model, the stress build up is caused by ion bombardment and is a by-product of the deposition process. As such, stress is not necessary for the stabilization of the sp^3 bonds. He further argues that the stress-induction model of ta-C growth is not accurate as deposition is not a thermodynamic process and that the phase switch of deposited films at a critical stress level is unlikely because the energy is already quenched.[45]

A. C. Ferrari et al[58, 77] supported J. Robertson's assertions that the stress generated are due to the deposition methods by consolidating various

data on stress versus sp^3 content from various groups. Critically he showed that for a given stress level, sp^3 content ranging from 20 % to 80 % is possible and that no clear trend is observable, refuting proponents of stress-induced ta-C growth who proposed that the sp^3 content is linked to stress level of the film.

Work by P. C. Kelires et al[53, 55-57, 78] on stress relief mechanisms of a-C films also indicates that high stress is not necessary to stabilize the high sp^3 content in DLC films. They based their work on tight-binding molecular dynamics (TBMD) and Monte Carlo (MC) simulations using an environment-dependent tight-binding (EDTB) model developed by Tang et al[79]. From their simulations and earlier atomic stress model[80], they deduced that while the stress at the atomic level can be finite and substantial, the average stress (macro-stress) of ta-C films could be zero. They also proposed that the high stress usually observed in high sp^3 content films are due to non-equilibrium local structures frozen in during deposition. Although they do not disregard the stress-induced model for as-growth film, their results from post annealing does indicate the failure of the stress-induction model to fully explain why stress is inconsequential to the stability of sp^3 sites after deposition.

The brief summaries of both theories are by no means complete but a full description of them would be beyond the scope of this thesis. Moreover the debate is still current with newer experimental results being used as test-beds for both theories. For example, N. A. Marks[81] recently asserted that both models were inconsistent with calculations based on EDIP simulation. In addition, he proposed that another model based on atomic peening[82] more

accurately describes the formation of sp^3 bonding in a-C films. However, this was later refuted by Y. Lifshitz et al[64] based on experimental data using energetic ions at glancing angles for deposition. After this discussion, the next area of review would be on the internal composition of the various types of a-C.

2.3 Micro and Macro-structure of amorphous carbon

In order to understand the properties of a-C, a fundamental understanding of their structure is needed. Because of the importance of understanding the internal micro-structure of a-C, various studies using diffraction,[83] nuclear magnetic resonance,[84] X-ray reflectivity,[85] EELS,[86, 87] electron spectroscopy for chemical analysis,[88] optical spectra,[89] and Raman spectroscopy,[90] were conducted over the past 3 decades. Due to the large variety of a-C and their composites, the structural landscape of a-C is very wide. There are however some area of commonality between them. All forms of a-C can be differentiated by their relative amount of the three types of hybridization within the material. Besides the concentration of the various bonds, how they are arranged or clustered in the amorphous matrix would also determine important properties. Although it seems ironic to discuss ordering in the context of an amorphous material, short term ordering such as clustering and alignment of anisotropic molecules are possible within the long range disarray in a-C.

All three hybridization of carbon can be found in a-C. The sp^3 bonds are commonly associated with hardness and wear resistance. In this configuration, the carbon atoms forms four sp^3 orbitals, making strong σ bonds with its four neighbours. In the sp^2 configuration, the carbon atom forms three sp^2 orbitals with 3 σ bonds and 1 π bond. The π state determines the bandgap because they form filled π valences states and empty π^* conduction states and have a narrower bandgap than the σ bonds.[46] For sp bonds, there are two σ bonds and two π bonds. The sp bonds do not generally contribute much to the properties of a-C and are excluded in this discussion. A diagram of all three hybridization is shown in Figure 2-1.

Figure 2-1 Diagram of all three hybridization of Carbon.

By having differing amount of each type of hybridization and other impurities, different types of a-C could be realized. A common classification of a-C based on sp^2 , sp^3 and H content is illustrated in Figure 2-2.[45, 47] Besides

hydrogenated a-C (a-C:H), various groups have also studied the structure of a-C with other impurities such as metals[91], nitrogen[92], fluorine[93] etc...

Figure 2-2 Ternary phase diagram for carbon-hydrogen alloys.[45, 47]

To complicate matters, a-C is also generally not uniform in its macro-structure. The irregularities could be intentionally build into the material through the manipulation of the ion energy during deposition or unintentionally create by deposition conditions. The most prominent feature of non-uniformity in a-C is in the surface of the material which is always characterized by sp^2 bonds no matter the constitution of the bulk material. The origin of this graphitic surface layer could be explained by both the subplantation as well as the stress induced model. Another source of the non-uniformity is due to the deposition systems used. Laser ablation and cathodic arc discharges methods both tend to create

micro-particles,[45, 94, 95] which if not filtered off, (see section 2.5) could get embedded into the bulk material.

Another cause for non-homogeneity is due to the intrinsic atomic structure of graphite. Single sheets of graphite called graphene[96-101] are highly anisotropic. Across the basal plane (in-plane of graphite), the C-C σ bond is very strong with a very high elastic modulus while perpendicular to it (c-axis), the π bonds are so weak that inter-planes sliding is possible. The macro non-uniformity arises when there are clusters of these graphitic regions in the bulk material orientating to specific directions (parallel and perpendicular to the substrate). These clustering of the sp^2 sites are important as they play a large role in many properties of the films, including optical and electronic properties.[45, 49, 102-104] It has been reported that a-C films from energetic species deposited at temperatures from 150 – 300 °C are graphitic with their basal plane vertical with respect to the substrate [105] while films deposited at even higher temperatures have their basal planes parallel to the substrate. A-C films with preferred orientation of six member sp^2 have also been observed.[63] The orientation effects are usually explained as a combined effect of both a bi-axial stress field generated due to the intrinsic stress of the material as well as the increased mobility introduced by the implanted ions.[106, 107] However, in later work on multilayered a-C, it is shown that graphitic alignment could also occur even in the absence of ion bombardment.[107]

Layered a-C films are also purposefully engineered as superlattices. These macro-layers in the films are usually created by stacking layers of a-C

with varying quantities of sp^2 and sp^3 bonding. These artificial a-C superlattices were first reported by K. K. Chan et al[108] and V. I. Polyakov et al[109]. Their aim was mostly for the realization of fast tunneling devices that utilizes quantum size effects. The effects were subsequently demonstrated by S. Bhattacharyya et al who reported on fast-switching devices based on a-C multilayers based on negative differential resistance.[110]

Besides electronic purposes, the multilayered a-C were also studied for their impact on the mechanical aspect of the film.[35, 36, 111, 112] The most common approach to fabricating the films is to have discrete layers stacked one on top of the other. The author would present in later chapters another structuring method to achieving a different kind of layered compositional film based on a gradient density growth approach.

From the above discussions, it can be seen that there are many different micro and macro-structures configurations available to a-C. This wide variety of internal structure is one of the most important reasons why different types of a-C and carbon in general could form interesting hybrid materials. After the overview on the landscape of the internal structure of a-C the next section would address the stress reduction of a-C through annealing.

2.4 Stress relaxation mechanism by annealing

The stress relaxation mechanism for many amorphous materials could be modeled as a viscous flow characterized by

Equation (2-1),Equation (2-1): $\eta = \tau / \dot{\gamma}$

where η is the viscosity, τ is the shear stress and $\dot{\gamma}$ is the shear strain rate. Then by using Maxwell's model for bi-axial stress conditions for thin films, the strain rate can be calculated by Equation (2-2),[113]

Equation (2-2): $\dot{\epsilon} = \left(\frac{1-\nu}{E} \cdot \dot{\sigma} \right) + \frac{\sigma}{6\eta}$

where $\dot{\epsilon}$, ν , E , $\dot{\sigma}$ and σ are the strain rate, Poisson ratio, elastic modulus, rate of stress change and in-plane film stress respectively. Under conditions of constant strain and a time independent viscosity, the stress decays exponentially with time (t) by Equation (2-3),

Equation (2-3): $\sigma = \sigma_o \cdot \exp\left(-\frac{Et}{6\eta(1-\nu)}\right)$

which is the characteristic of self-relaxation in materials. This form of Maxwell equation unfortunately only works for selected materials and does not adequately describe more complex stress relaxation and thus a time-dependent viscosity is used where the time dependence is characteristic of the kinetics of defect production and annihilation. This improves the model and adequately describes the stress relaxation of amorphous Si and Ge. However, even this complex model could not adequately describe ta-C.[113]

The problem lies in the “deviate” behaviour of a-C in general when compared with other glassy materials.

For glassy materials, the stress relaxation is a function of the material's viscosity. With an increase in temperature, the viscosity is decreased until the glass transition temperature, T_g , is reached (after which the material will enter into a liquid state). Therefore, a material with a lower T_g would be expected to have stress relaxation at a lower annealing temperature. Although there are no firm correlations between T_g and material properties, there are empirical relationships between T_g and melting temperature or Debye temperature of the solid.[114] As such, by comparing the Debye temperature of diamond (the crystalline analog of ta-C) and other amorphous material like SiO_2 (diamond is 2340K while SiO_2 is 500K),[115, 116] it is to be expected that the apparent viscosity of ta-C should be significantly less at the same absolute temperature. However, the low temperatures ($\sim 100^\circ\text{C}$) observed for stress relaxation in ta-C shows that this is not the case.[113] Also, in most amorphous materials, a density increase is usually observed upon annealing. This is due to the minimization of free energy during annealing leading to a more relaxed and dense material. But for ta-C, a slight decrease in density is observed upon annealing and stress release.[107] These apparent contradictions in the annealing and stress relaxation characteristics of ta-C shows clearly that a simple viscous flow model could not explain the stress relaxation behaviour of ta-C and a-C in general.

The problem associated with understanding the stress release mechanism in a-C is made more complex when observations were made that a-C with intermediate sp^3 content actually have an increase in stress after annealing.[117, 118] Many have tried to explain the unusual annealing behaviour of a-C.[55-58, 77, 107, 113, 117, 119, 120] A. C. Ferrari[58, 77] and J. P. Sullivan[113] proposed stress relaxation schemes through the conversion of sp^3 bonds to sp^2 bonds. They explained that although the atomic volume of sp^2 sites exceeds that of sp^3 sites, their in-plane size is less due to shorter bond lengths. Therefore if the basal planes of the graphitic sites (sp^2 sites) are aligned in the plane of compression, the bi-axial stress could be reduced. They further calculated that the strain needed to relieve the stress of ta-C is $\sim 1.2\%$. This corresponded to about 12 % change from sp^3 to sp^2 bonds. However, if the alignment of the sp^2 is taken into account, there is almost no need for any conversion at all as the realignment of the graphitic planes would cause a corresponding decrease in strain. This re-alignment of graphitic planes in a-C is also experimentally observed by them .[103, 121, 122]

Another model proposed by D. G. McCulloch[107] and O. R. Monterio[117] explains the stress release of ta-C and stress increase of intermediate sp^3 content a-C by modeling the total internal energy of the material with respect to density. Based on their model, the total energy of a deposited film can be described by Equation (2-4),

Equation (2-4): $E_{\text{internal}} = E_{\text{bonding}} + \left(\frac{VP^2}{2B}\right)$

where the total energy ($E_{internal}$) of the film is a combination of bonding energy between the atoms ($E_{bonding}$) and elastic strain energy. The strain energy is then expressed in terms of volume (V), pressure (P) and bulk modulus (B).

Thus during annealing, the total internal energy of the film is expected to be reduced either by lowering of the atomic bonding energy or strain energy. Using CPMD liquid quench calculations and subtracting the strain energy term in Equation (2-4), a model of how total internal energy would vary with density is given in Figure 2-3.[107]

Figure 2-3 The energy per atom for a range of 125 atom amorphous carbon networks produced using CPMD liquid quench calculations. The zero energy is chosen to be the energy per atom of crystalline diamond calculated under the same simulation conditions. Also shown is the resulting energy after subtracting the strain energy given by Equation (2-4). [65, 107]

From this model, upon annealing, a film with density at point A (intermediate sp^3 content) would move towards a lower energy state by having more sp^2 bonds and decreasing its density (generating stress in the process due to an increase in volume). Whereas a film with density at point B (high sp^3 content) would move towards total energy minimization by having slightly more sp^3 bonds and increasing the density. This model of annealing behaviour adequately explains the apparent difference in annealing behaviour of a-C with intermediate sp^3 content and ta-C.

After the discussion on the various aspects of a-C, a short introduction on the most common methods to produce them is given in the next section.

2.5 Deposition methods

The last area of review is on the common deposition methods of a-C. There are various methods of depositing a-C materials, but generally they are either performed by thermal or energetic species processes.[45, 49, 76, 94, 123-125] For thermal processes, it is either through a physical vapor deposition or chemical vapor deposition method. Both processes require a source of carbon, either in the form of a pure carbon source or carbon containing compound such as a hydrocarbon gas. In energetic methods, both a target source as well as excitation means are needed. The carbon sources used are usually high purity graphite targets or ionized carbon containing gases. The supply of energy needed for the excitation can be in several forms including,

electrostatic acceleration of C^+ ions, momentum transfer via collision from other energetic species, laser ablation and arc discharge. The most common methods of a-C film deposition are given below. Schematics of the various systems are also shown in Figure 2-4.

Figure 2-4 Schematics of various deposition systems for a-C[45]

The first DLC films were created by ion beam depositions.[48] In a typical ion beam deposition system, the graphite targets are first ionized via energetic

collisions with a neutral gas (sputtering) and then accelerated through a grid by a voltage bias into a high vacuum chamber.[48, 126-129] Alternatively, a hydrocarbon gas (eg. Methane) can be used instead of the graphite target.[130-132] However in either case, the plasma flux induced usually have a low percentage of carbon ions to neutral species ratio. To overcome this, a variant of the ion beam, the cascade arc source, uses a high-pressure source to induce a supersonic expansion which increases the carbon ion density in the plasma.[133]

In order to control the exact energies of the carbon plasma, a mass-selected ion beam deposition (MSIB) is sometimes used in the laboratories.[49, 61, 76, 134] The concept of the MSIB is similar to that of direct ion beam described above with the exception that the ions are accelerated to 5-40 kV and pass through a magnetic filter. This would eliminate any unwanted neutrals and “purifies” the ion beam to contain only ions with the electromagnetic signature of C⁺ ion. After filtering, the beam is decelerated to the required energy level for deposition in an ultra high vacuum chamber ($\sim 10^{-8}$ Torr). The MSIB is generally accepted as the best way to produce pristine ta-C with sp³ content exceeding 90 %. However the drawback of this system is its prohibitive cost and extremely low deposition rate (0.0001 nm s⁻¹). This makes the MSIB an excellent tool for laboratory analytical work but highly unsuitable for industrial adoption.

In contrast to MSIB, sputtering is the most common industrial process for DLC deposition.[135-143] This is largely due to the familiarity of the industry with sputtering methods as it is used for many other industrial coating

applications. Another important reason for its popularity is the ease of scaling up if needed. Both direct current (dc) and radio frequency (rf) sputtering by Ar plasma are commonly employed on graphite targets for depositions. Magnetron sputtering is also commonly used to increase the sputter yield of the deposition by increasing the degree of ionization of the plasma. A technique to increase the sp^3 content of the deposited film is by letting the magnetic field envelope the substrate causing the Ar to bombard the substrate during film growth. Further, by controlling the energy of the Ar ions incident on the substrate, tuning of the quality of the a-C film can be achieved. Alternatively, a dual ion beam system where one ion beam is used for carbon flux generation by Ar sputter and the other for Ar bombardment on as-growth a-C film for densification could also be used. This is termed ion beam assisted deposition (IBAD).[141]

The cathodic arc deposition[51, 86, 94, 144-149] of a-C film is both used by the industry as well as research institution. The cathodic arc is a low-voltage, high current plasma discharge that takes place between two metallic electrodes in vacuum. In the case of a-C deposition, it is semi-metallic as both electrodes (target and striker) are made from carbon. At the cathode of the vacuum arc, the arc current is concentrated at discrete sites termed cathode spots or arc spots. These arc could be run continuously (dc) or in pulse mode by using a capacitor bank to strike the arc or by laser initiation. The arc spots are typically 1 – 10 μm in size and carry a current density of $10^6 - 10^8 \text{ A cm}^{-2}$. These spots are formed by an explosive emission process and have lifetime from about 10 ns to a few micro-seconds.[144] This explosive event creates both plasma and unwanted micro-particles. Due to the unwanted micro-particles, filtering via an

electric-magnetic-field is usually employed together with the cathodic arc. This is termed filtered cathodic vacuum arc (FCVA). The toroidal magnetic filter employed are usually S-bends or double U bends configured in a off-plane fashion, called off-plane double bend (OPDB). As the toroidal currents flows through the bend, a magnetic field is generated along the axis of the filter. As the electrons of the plasma spirals through the filter, an electrostatic field is generated that “pulls” the positively charge carbon ions with it. The plasma mean energy generated by the cathodic arc is dependent on systems setup but is generally between 10-30 eV. In order to vary the ion energy of the incident beam, substrate biasing is common. Both dc and pulse biasing the substrate can be used to accelerate the C⁺ ions.[118, 150, 151]

The advantage of the FCVA is that the plasma it produces is highly ionized with a low ion energy spread and reasonably high deposition rate. Multiple targets can also be used simultaneously to create multilayered films or composite films. The disadvantage is that the micro-particles generated may not all be removed by filtering. (More detail on the FCVA is given in later chapters as all the samples prepared in this thesis were done by this method)

Instead of an arc discharge, very short and intense energy pulses produced by a pulse excimer laser can also be directed at a carbon target to vaporize the material, giving it an intense plasma. This method of plasma generation and deposition is termed pulsed laser deposition (PLD).[112, 152-157] Frequently in this method of a-C deposition, substrate biasing and additional electrodes are introduced to modify the films further. Due to the

similarity of the kinetic energy with plasma energy of MISB and FCVA processes, the a-C films produced by the PLD are similar. As with the FCVA, multiple targets can be used with the PLD through creative use of optical steering of the laser and multi-target setups.

The last deposition method discussed is the plasma enhanced chemical vapor deposition (PECVD).[120, 158-166] It consisted of 2 electrodes of differing sizes with rf power capacitively coupled to the smaller electrode and ground connected to the larger one. The rf power thus produces a plasma between the electrodes and due to the difference in mobility of the ions and electrons, a sheath is created at the electrodes causing the plasma to be positively charged relative to the electrodes. As the sheath acts like diodes, the electrodes acquire dc self bias equal to their peak rf voltage. This self bias is related to the size (area) of the electrodes with the smaller electrode acquiring a larger self bias and thus is negative with respect to the larger electrode. The smaller electrode is made the substrate electrode as the positive C⁺ ions would be accelerated by the negative sheath voltage to cause ion bombardment on the substrate.

A low pressure depositing condition is desirable as this minimizes collision and reduces the ion energy distribution. However, the plasma in the conventional PECVD could not be ignited if the pressure is too low. Another drawback of the simple PECVD setup is the lack of control over the ion energy. Therefore, many advances in the plasma source such as the plasma beam source (PBS), electron, electron cyclotron resonance system (ECR) and

electron cyclotron resonance source[165] are used to increase the ionization efficiency of the plasma. These work either by magnetic plasma confinement or increasing the rf frequency to increase the plasma density. Further, dual power sources in which one for exciting the plasma and the other for biasing the electrode are also used for better control of deposition parameters.

All in all, this last section of the chapter describes the various common deposition techniques of a-C including, ion beam deposition, MSIB, IBAD, sputtering, FCVA, PLD, PECVD and ECR. Among them, MSIB would be most suitable for laboratory research due to its high controllability of the deposition species and their energy levels. While sputtering and PECVD would be better for industrial coatings of DLC since they are very well established systems allowing easy integration into current industrial processes. The FCVA and PLD on the other hand would be best for ta-C mechanical coatings because of their highly ionized plasma with an energetic species.

CHAPTER 3 METHODS & DESIGN OF EXPERIMENTS

3.1 Methodology

Three different types of carbon hybrid material systems are discussed in this thesis. All the carbon films are deposited by OPDB-FCVA systems in conjunction with either a substrate pulsed or dc voltage biased system. Most of the studies will be on their mechanical properties, characteristics and microstructure.

For nano/microelectromechanical systems (N/MEMS), how well it can perform and its durability depends on the strength of the material it is built on. This is especially true for MEMS requiring extensive forced contacts such as micro-gears, actuators and mechanical sensors.[167-173] The strength of a material is usually defined as the highest stress that a material can withstand before it completely fails to perform structurally (with the exception of fracture strength). Stresses induced could be in the form of shear, compression, tension...etc. However for this study, direct testing of the material to failure is not feasible and impractical. As such, an indirect approach to examine the strength of the material is adopted by characterizing the hardness and elastic modulus of the material. Hardness is a measure of the materials resistance to deformation and the elastic modulus is a reflection of the materials elastic behaviour with respect to applied stress. Both of these properties are good

indicators of the material's strength. Moreover, for devices requiring prolonged continuous sliding contacts such as micro gear transmission train,[174] friction, surface roughness and wear resistance are also critical properties.[175-180] Furthermore, these same properties are also crucial to thin film coatings, especially for films employed for surface protection.

Besides mechanical testing, TEM in conjunction with EELS and Raman spectroscopy are also used to probe into the internal microstructure of the materials. The TEM is especially useful in examining the aligned graphite present in an amorphous matrix presented in Chapter 5 and 6.

This chapter would therefore outline the important systems used in the various material syntheses (OPDB-FCVA and PECVD) and characterizing of the materials. Basic operation as well as experimental conditions will be presented.

3.2 Sample preparation and treatment

3.2.1 Amorphous Carbon deposition by OPDB-FCVA

All a-C materials prepared and discussed in this thesis are deposited by the FCVA (see Figure 3-1) utilizing OPDB filtering. Henceforth, the system will be referred as OPDB-FCVA. All the a-C films prepared are non-hydrogenated and were deposited onto silicon substrates (both p and n types). The 60 mm diameter graphite targets used have purity of 99.999%. Typical arc currents

range from 60 A – 100 A, depending on the experiments conducted and the deposition rates needed (0.08 nm/sec to 3.33 nm/sec). For thick (> 500 nm) films, the erosion rate of the targets are very high with craters forming on the surface of the targets over prolonged deposition times. To prevent the need to change targets and exposing the substrates to ambient conditions during the deposition process, the targets used are generally longer (100 mm) with in-situ surface grinding of the targets employed periodically to smoothen the targets during depositions.

Figure 3-1 Schematic of OPDB-FCVA system

Carbon ions are produced via arc discharge between the target (cathode) and the grounded water cooled anode. The arc is ignited by an automatic carbon striker which is brought into contact with the target surface. The plasma stream produced then passed through the OPDB's electric-magnetic-field which effectively filtered out unwanted macro particles.

As the arc moves on the surface of the target, the plasma density would vary with the location of the arc. The change is most drastic if the arc happens to "jump" into a crater caused by excessive uneven erosion of the target. Therefore, although the arc is self sustaining for upwards of 300 sec upon the initial strike, the carbon striker is programmed to automatically re-strike the target every 30 sec. This method of film deposition is found to ensure better uniformity of the plasma density during the deposition and therefore better film thickness control.

A magnetic coil with driving circuitry is employed at the end of the plasma stream to scan the plasma beam onto the substrate plane. This effectively increases the coated surface area of the substrate. The substrate could also be rotated at 15 rpm during the deposition. The plasma scanning together with the substrate rotation was calibrated to ensure excellent uniformity of the coated substrate surface. Typical uniformity of $\pm 1\%$ of the coated area can be achieved with this method. During the deposition, the chamber pressure was typically at $\sim 3 \times 10^{-5}$ Pa.

With an electronically floating substrate (i.e. no bias is applied), the carbon ions reaching the substrate would have their original ion energy.

However, upon negatively biasing the substrate (through the substrate holder), the positive carbon ions could be accelerated within the Debye shielding length when they reach the substrate.[181] Since the degree of sp^2 and sp^3 bonding content in the a-C film is correlated to carbon ion energy,[51, 86, 182-186] the microstructure of the a-C film could be varied by the substrate bias during deposition. Two types of substrate bias are used in this project; one employs a dc power supply while the other employs a voltage pulse generator.

In order to determine the film thickness, the films were marked with a gel based marker before deposition and cleared off by acetone after the deposition. The marked spot act as a mask during the deposition and upon clearing leaves an area that is not coated with carbon. Then by using a surface profiler to scan through the marked spot together with the coated region, the difference in height between the two areas would indicate the thickness of the film. The deposition rate could then be estimated by using Equation (3-1).

Equation (3-1): *Deposition rate = Thickness of film/ time of deposition*

How the different types of films are produced is further elaborated at their respective chapters since their synthesis technique and deposition conditions vary considerably.

3.2.2 PECVD growth of Aligned Carbon Nanotubes

All the MWCNTs were growth on Si substrates using Ni as the catalyst. A complete PECVD system by Nanoinstruments Pte Ltd was used for the aligned MWCNTs growth. The system consisted of a 4-inch diameter isolated substrate

heater with a maximum temperature of 800°C. Supported gases include NH_3 and C_2H_2 , with mass flow controllers controlling the flow of gases up to maximum flow of 500 sccm for each of the 2 process gases. Pressure sensor consists of a micro-pirani, allowing the reading of base pressure and piezo which allows gas independent pressure reading during processing. The heater control consisted of a fully programmable ramp segment. The plasma generator used a dc power supply.

Prior to the MWCNTs growth, 10 – 120 nm of Ni catalyst is sputtered onto the substrate using magnetron sputtering. This Ni layer is used as the catalyst-support layer. The substrates were then transported to the growth chamber of the PECVD system. The catalyst layer was then sintered at 800 °C for 2 min with the NH_3 gas flowing at 240 sccm (no plasma ignition). The chamber pressure was maintained at 13 mbar throughout the growth process. After the sintering, the feed gas, C_2H_2 (20 %) was introduced via a flow controller and the dc discharge is initiated. To vertically align the MWCNTs (perpendicular to the substrate) a 500 V bias voltage is maintained throughout the growth. The total deposition time was varied between 30 – 120 min. [187]

3.2.3 Annealing

For annealing purposes, both a rapid thermal anneal (RTA) system (Jipelec/Jetstar) and tube furnace (Lindberg/Blue M) was used. Vacuum levels during annealing were 10^{-6} Pa and 10^{-3} Pa for the RTA and tube furnace respectively. For all samples the ramp up and cool down periods are not considered in the annealing time. Multiple samples are annealed simultaneously

so as to keep the annealing conditions between samples as close as possible.

Nitrogen is used as the purging gas during cooling down.

3.3 Material Mechanical Properties

3.3.1 Intrinsic Stress, Indentation Hardness & Reduced Modulus

The substrate the a-C films were prepared on is crucial in the determination of some of the mechanical properties of the film. This is especially so for stress measurements. This is because the mechanical compressive stress on the film is largely dependent on the material properties of the substrate such as surface properties (surface energy, adhesion characteristics with the film, roughness ...etc) and elastic modulus. Moreover for properties calculated from indentation experiments the measurements may be inaccurate due to the yielding of the substrate before that of the film. This is especially important for hard films on softer substrate. However, since all the substrate used in this thesis were standardized (Si wafers), the problem associated with the use of multiple types of substrate is eliminated. This section thus continues with the description of the measurement techniques used to determine the mechanical properties of the film including special precautions when needed.

By measuring the wafer curvature before and after deposition of the films, the internal stress, σ_s of the a-C films could be calculated using Stoney's equation [188] given by,

Equation (3-2):
$$\sigma_s = \left(\frac{E_s t_s^2}{6(1-\nu_s)t_c} \right) \cdot \left(\frac{1}{R} - \frac{1}{R_o} \right)$$

where E_s , ν_s , t_s and t_c are the Young's modulus, Poisson ratio, thickness of the substrate and of the film, respectively. R_o and R are the radii of curvature of the bare and coated substrate, respectively. The films were all measured at three separately marked points and the results averaged. The scan length used is at least 10 mm. The results obtained have an error rate lower than ± 0.5 GPa.

Nanoindentation experiments, using a Hysitron triboscope with a Berkovich diamond tip were used to investigate the indentation hardness, H_{indent} , and reduced modulus, E_r . The H_{indent} is a measurement of material hardness derived through indentation experiments while the E_r is the combined moduli of the indenter and the tested sample. The E_r is different from the elastic modulus or Young's modulus in that it takes into account the effects of the elastic deformation of the indenter (due to non-rigidity of the indenter). This is especially important for indentation experiments on hard materials as the indenter itself may deform slightly upon loading. The E_r is related to Young's modulus of both the specimen tested and indenter by Equation (3-3),

Equation (3-3):
$$\frac{1}{E_r} = \left(\frac{1-\nu^2}{E} \right)_{specimen} + \left(\frac{1-\nu^2}{E} \right)_{indenter}$$

where ν and E are the Poisson's ratio and Young's modulus respectively. Although the Young's modulus of the tested sample can be derived from Equation (3-3), ($E_{indenter} = 1144$ GPa and $\nu_{indenter} = 0.07$) it would require an estimate of the ν of the tested sample. As most of the samples being tested are

compositional in nature, an accurate estimate is difficult and thus E_r would be used instead.

As some of the samples tested have high hardness, repeated indentations would wear down the diamond tip, causing the area function to vary with usage of the tip. As such, calibration of the diamond tip was done using a fused silica standard periodically throughout all the indentations experiments.[189, 190] Creep and drift were also minimized by keeping the loading rate and temperature (26 °C) constant throughout all the indentations.

The nanoindentations experiments were all carried out using the same protocol made by first indenting at a constant rate (100 $\mu\text{N}/\text{sec}$) followed by unloading with the same rate. The maximum applied load was varied from 50 to 12000 μN depending on indentation depth required for the various films. Generally the indentations depth ranges from less than 1 % to about 10 % of the film for each sample. This is done to minimize substrate effects.[191]

In order to extract the elastic and hardness properties of the samples, the software attached to the instrument, digitally records the load-displacement characteristic of the indentations and fits the unloading points by a power law relation. The E_r of the indented film then can be inferred [189] from the measured initial unloading contact stiffness, S (the slope of the initial portion of the unloading curve) from;

Equation (3-4):
$$S = \frac{dF}{dH_c}$$

Equation (3-5): $\frac{1}{S} = \left(\frac{\pi^{1/2}}{2}\right) \cdot \left(\frac{1}{A^{1/2}}\right) \cdot \frac{1}{E_r}$

Equation (3-6): $E_r = \frac{1}{\frac{1-\nu^2}{E} + \frac{1-\nu_i^2}{E_i}}$

Where E and ν are the Young's modulus and Poisson's ratio for the sample respectively, and E_i and ν_i are the same parameters for the indenter (here $E_i = 1141$ GPa and $\nu_i = 0.07$) and h_c is the contact depth. F is the load applied and A is the area in contact calculated based on the area function after calibration.

Although indentation experiments to examine the hardness of materials have been going on for about 100 years, the exact definition of material H_{indent} , is still being discussed.[192-197] For this thesis, the simplest and most commonly used definition of H_{indent} is adopted. The H_{indent} is defined as the mean pressure (as defined by contact area under load) exerted by the indenter at maximum load (see Equation (3-7))

Equation (3-7): $H = \frac{F}{A_c}$

Where F is the applied load and A_c is the contact area. A crucial point to note about this definition of hardness is that since the mean pressure is defined by the contact area during loading and not the indented impression after loading, the results could vary significantly from those obtained using the latter method. This is especially significant for materials with small Young's modulus over hardness ratios such as ta-C ($E/H \sim 0.1$).

3.3.2 Tribology

To investigate the tribological properties of the films, a pin-on-disk tribometer (CSEM), was employed to measure the circular sliding resistance of the various films. The software included in the system recorded the coefficient of friction versus the wear cycles as the dynamic friction spectra. The coefficient of friction was extracted from the steady value of the spectra. The tests were all conducted under a controlled environment under ambient air with relative humidity (RH) ~50 % and temperature at 26 °C. The static friction partner used was sapphire (diameter, 6 mm). The tests parameters were set at a constant load of 2 N, linear speed of 0.1 m/s and wear track of 2 mm for repeated cycles. The standard notation for friction coefficient is μ .

Equation (3-8): $\mu = F/W$

where F is the lateral force and W is the vertical load.

The wear rate was then calculated from Equation (3-9) using the cross-sectional area of the wear track which was measured using a surface profiler.

Equation (3-9): $\text{Wear rate} = \frac{V}{(WS)}$

where V is the wear volume calculated from the cross-section of the wear track and radius of wear cycle, W is the applied load and S is the sliding distance. To ensure better accuracy of the calculations, 4 different points taken 90° apart on the wear track were used to find an average.

Lastly, a commercial AFM (Digital Instruments) in tapping mode was used to determine the root mean square (*r.m.s.*) surface roughness of the samples. The roughness, R is defined as

Equation (3-10):
$$R = \left[\sum \frac{(h_i - h_{ave})^2}{N} \right]^{1/2}$$

Where h_i is the film height, h_{ave} is the average of the height values in a given area and N is the number of points. Each image consists of 512 line scans. The R values were computed after flattening procedures by the software attached. The flattening is done to account for the macroscopic tilt with respect to horizontal scan directions which is inherent in all AFM scans. This would only have significant effects for samples with roughness exceeding the scan size. The evaluation is done on an area of 1 μm by 1 μm .

3.4 Material internal microstructure

3.4.1 Transmission electron microscopy

Samples were prepared for TEM by initial mechanical polishing using a tripod polisher, followed by further thinning to electron transparency using a GATAN dual ion mill model 600 ion beam thinner and Gatan precision ion polishing system model 691. The samples were analyzed using a Jeol 2010 TEM operating at 200 kV equipped with a Gatan imaging filter (GIF2000).

3.4.2 Electron Energy Loss Spectroscopy by Scanning Electron Transmission

EELS were performed using a GATAN imaging filter. EELS linescans through the films were performed by the TEM in scanning mode (STEM). The low-loss spectrum containing the plasmon and the zero-loss electrons were deconvoluted by the Fourier logarithm ratio with the spectra of the electron beam passing through vacuum.[87] All spectra are collected at a convergence angle of 7.4 mrad and an acceptance angle of 7 mrad, for the 200 keV electrons.

The low loss spectrum in the EELS is proportional to the energy loss function, $\text{Im}(-1/\epsilon)$ and in the free electron limit, the complex dielectric function, $\epsilon(E)$, is given by the Drude model,[87] defined in Equation (3-11),

Equation (3-11):
$$\epsilon(E) = 1 - \frac{E_p^2}{E^2 + iE\Gamma}$$

and therefore

Equation (3-12):
$$\text{Im}\left(-\frac{1}{\epsilon(E)}\right) = \frac{E_p^2 E \Gamma}{(E^2 - E_p^2)^2 + (E\Gamma)^2}$$

where E and Γ is the energy lost and the full width at half maximum (FWHM) of the loss peak respectively. E_p is the plasmon energy defined by Equation (3-13),

Equation (3-13):
$$E_p = \hbar \left(\frac{n_e e^2}{\epsilon_o m^*} \right)^{1/2}$$

where ϵ_0 , m^* and $\hbar$ is the vacuum dielectric function, electron effective mass and Planck's constant respectively. n_e is the valence electron density defined by Equation (3-14) by assuming carbon has four valence electrons and is free from hydrogen and nitrogen.

Equation (3-14):
$$n_e = 4 \frac{\rho N_A}{M_C}$$

where N_A is the Avogadro number and M_C is the molar mass of carbon. Thus by combining Equation (3-13) and Equation (3-14), the mass density, ρ , could be derived by Equation (3-15),

Equation (3-15):
$$\rho = \frac{\epsilon_0}{4\hbar^2 N_A e^2} M_C m^* E_p^2$$

using $m^* = 0.87m$, where m is the free electron mass.[121]

3.4.3 Raman Spectroscopy

The visible Raman spectra of a-C are usually dominated by features of graphitic carbon. This is because visible Raman is 50 to 230 times more sensitive to sp^2 sites than sp^3 sites.[198] In fact the Raman spectra of all disordered carbon are dominated by the relative shape G and D features of the sp^2 sites. The G mode is due to the in-plane bond stretching motion of pairs of carbon sp^2 atoms and is present regardless of the bond arrangements (olefinic chains or aromatic rings). It lies around $1500 - 1630 \text{ cm}^{-1}$. [199] The D mode around 1355 cm^{-1} , is an A_{1g} breathing vibration of a 6-fold aromatic ring which is active in the presence of disorder.[200]

Generally the exact sp^2/sp^3 content of a-C could not be accurately calculated from visible Raman spectroscopy.[63, 201] However some characteristic of a-C could be inferred from the shift of the G peak, $I(D)/I(G)$ ratios and coupling factor. Specifically, the relative amount of graphitic ordering in different types of a-C configurations could be deduced.[201]

For this study, the Raman spectra were collected from the films using a Renishaw (Ramascope) system operated with an Ar^+ laser with excitation wavelength of 514.5 nm (visible range). To reduce the noise signature during spectra collection, multiple scans (typically 30 scans with collection time at ~60 sec) were conducted. Si samples were used for calibration prior to all test.

The spectra were fitted by a Breit-Wigner-Fano (BWF) lineshape (with a linear background) for the G peak and a lorentzian for the D peak if necessary.[202-204] The BWF line has an asymmetric line shape which arise from the coupling of a discrete mode to a continuum,[205] and is given by

Equation (3-16):
$$I(\omega) = \frac{I_o [1 + 2(\omega - \omega_o)/Q\Gamma]^2}{1 + [2(\omega - \omega_o)/\Gamma]^2}$$

Where $I(\omega)_o$ is the intensity as a function of frequency, I_o is the maximum peak intensity, ω_o and Γ are the peak position and full width at FWHM respectively and Q is the BWF coupling coefficient.

CHAPTER 4 MULTILAYER AMORPHOUS CARBON FILMS

4.1 Introduction

4.1.1 Multilayer films

For composite thin films, the most common structural composites are those whose internal composition varies across the thickness of the film. These are commonly known as graded films. For artificial graded films, their compositional depth variance could be unintentional, usually caused by material preparation conditions such as sub-species atomic diffusion during deposition, oxidation during annealing and clustering of atomic species. Or they could be intentionally engineered into the material for the purpose of enhancing the property of the films.[6, 206-213] These enhancements are usually in the form of improved mechanical performance such as higher hardness, elastic modulus, wear resistance and lighter weight.

For graded thin films, two forms of depth variance in the film are common;

- i) Periodic layering with discrete steps having sharp interfaces between layer boundaries [35, 36, 111, 214, 215] and

- ii) gradually graded films with highly diffused interfaces or with no boundaries at all since individual layers could not be effectively defined.[212, 213, 216-218]

This chapter would only focus on compositional a-C films prepared by the first approach (see section 4.2). A-C films prepared and studied using the second approach will be presented in CHAPTER 6.

For periodic layering, sometimes referred as multilayering, multiple materials (not necessarily different materials) could be deposited or grown one on top of another to achieve a stacked up effect. These films with multiple sandwich layers are sometimes also known as laminates or simply multilayer films. A schematic (see Figure 4-1) is given below to illustrate the principle of multilayering. This could be contrasted with the gradual grading approach illustrated in Figure 6-1 of CHAPTER 6.

Figure 4-1 Example of multilayering with two materials termed “Hard” and “Soft” layer. The characteristic of multilayered films are a stacked up effect and sharp interfaces between layers.

The periodic layering technique has several advantages, including better control of stress and inelastic deformation (material damage) and improving the adhesion between the material and substrate. Commonly, multilayering is also used in conjunction with annealing for further enhancement of physical properties.

Although the need to stack a material layer by layer is costly in terms of fabrication complexity, the benefits gained from the approach generally offsets this disadvantage. One good example is as-grown ta-C which has intrinsic stress exceeding 9 GPa at a film thickness of only ~100 nm.[58, 219] Due to the high stress and subsequent delamination of the ta-C film from the substrate at even moderate thickness, multilayering was used to improve adhesion and lower the stress of the material.

4.1.2 Multilayer Amorphous Carbon films

Although as-grown ta-C films have remarkable mechanical properties, its high intrinsic compressive stress limits its uses to applications that restrict the film thickness to below 100 nm and are tolerant of substrate curvature. These restrictions heavily limit the application of ta-C in many areas of surface coatings. In order to circumvent the problems associated with high stress, various methods including annealing,[77, 107, 113, 119] and substrate biasing,[118, 151, 220-223] were investigated. Both methods are useful in that they both successfully lowered the intrinsic stress of ta-C, and in the case of annealing, did not reduce the sp^3 content of the film.[77, 119]

A remarkable demonstration of the stress lowering approach via annealing was demonstrated by T. A. Friedmann et al,[119] when they deposited a 1.2 μm thick ta-C film on Si using a PLD technique. They managed to deposit such a thick film by repeatedly growing a 150-200 nm film followed by annealing at 600 °C for 120 sec. This cyclic method of ta-C growth could potentially produce stress free ta-C with an unlimited thickness. However this approach does present an added problem. Although useful in lowering stress, the practicality of this approach is undermined by the need to do multiple annealing cycles. For example, in order to produce films of 1 μm thickness, 7 cycles of annealing are needed. These necessary annealing cycles complicates the film fabrication process and adds heavily towards fabrication cost in terms of resources and time.

Substrate biasing on the other hand is a straight off approach in film growth. It is a continuous process enabling the entire film to be deposited in a single step. Two methods of substrate biasing are possible. One uses a direct dc voltage supply while the other uses a pulse voltage supply. Both essentially work by changing the ion energy of the carbon plasma during deposition which in turns alters the stress (and quality) of the a-C film deposited.[51, 86, 182-186] Although substrate biasing could produce a-C films with significantly lower stress, the disadvantage of the approach is the loss of sp^3 content in the deposited film,[224] which could translate into reductions in their mechanical properties. For example, pulse biasing during deposition by FCVA at -3 kV have been reported to reduce the H_{indent} of a-C from 86 GPa (ta-C) to 26 GPa.[151]

Multilayering[35-37] followed by annealing was thus introduced as a compromise between the above two methods. This approach has been shown to improve the adhesion of the film onto the substrate as well as to lower the overall stress of the film. Critically, some of the mechanical properties of the multilayer a-C films would be affected, but overall their mechanical properties were still better when compared with the drastically lower sp^3 a-C films deposited with just substrate biasing. Further, thick films ($>1\ \mu\text{m}$) could be prepared in a single process step without the need of a cyclic annealing process. Multilayering of a-C thus gives a good compromise between fabrication complexity and film quality.

4.2 Experiment objective and Scope

Many studies on the internal microstructure and annealing of multilayer a-C films produced by the FCVA technique have been conducted using various tools such as Raman spectroscopy,[225] electron transmission/energy loss spectroscopy,[226] X-ray reflectivity[37] etc... by others. However, besides the microstructure, the macro composition will also greatly affect the overall material properties of multilayer a-C films. Therefore a comprehensive knowledge of how the macro composition will affect the properties of the films is useful. In addition, since annealing has been identified as a good process to lower the stress further in the film, a good understanding of their thermal characteristic is also crucial. However, studies into the effect of both periodicity and annealing of the multilayer a-C films have not been conducted before. As such, a systematic study into the annealing characteristics and internal macro composition of the multilayer a-C films with respect to their various mechanical properties should be conducted.

This chapter will thus focus on the mechanical properties of multilayered a-C films produced by the OPDB-FCVA with special emphasis on the effects of macro level layering and annealing. The first part of the chapter will be on the fabrication methods employed to prepare the a-C multilayer films. The second part of this chapter will focus on the mechanical aspect of the films such as stress, hardness and elastic modulus. This would be followed by studies on the surface morphology and tribological properties such as friction and wear

resistance. A brief overview of the results will be also given in the last section of this chapter.

4.3 Multilayer Film fabrication

All the films produced in this study were produced by a modified commercial OPDB-FCVA operating with an arc current of 80 A. The deposited multilayer a-C films consist of two kinds of sub layers. The first type termed “hard sub-layer” was produced by the OPDB-FCVA operating in the absence of substrate biasing. This corresponded to the C plasma having a peak ion energy of 28 eV (ion energy distribution of 18 eV based on the full width at half maximum) and therefore produced essentially a typical ta-C film (~80 % sp^3 fraction).[181] The second type termed “soft sub-layer” was produced by the OPDB-FCVA operating in conjunction with a negative high voltage pulse generator. The substrate biasing parameters used for depositing the soft sub-layers were -3000 V at a frequency of 600 Hz and pulse width of 25 μ s. This produced a-C films (intermediate sp^3 of ~50 %),[226] that were generally lower in stress and hardness than typical ta-C.[118, 227] All the 1 μ m multilayer a-C films prepared in this study were done by alternately turning the negative high voltage substrate pulse bias on (soft layer) and off (hard layer). Using this method, sub-layers below 10 nm could be produced. A cross-sectional TEM micrograph of a 500 nm test sample with sub-layer size at ~10 nm is shown in

Figure 4-2. From the figure, the periodic layering can be seen and the hard (dark bands) and soft (brighter bands) sub-layer could be distinguished easily.

Figure 4-2 TEM micrographs of a 500 nm a-C multilayer film prepared with sub-layers thickness at ~10 nm. **A.** Full cross section of the film showing uniform layering. **B.** Close up on the sub-layers. The two sub-layers are clearly distinguishable.

In this study, all the films were deposited continuously without stoppage to simulate a realistic industrial adoption scheme where coatings are produced as fast as possible. The thickness of the individual sub-layer was approximated by varying the deposition time. All the films were prepared with the first layer (in contact with the Si) as the soft sub-layer and the top most layer as the hard sub-layer. The various types of films examined in this study were summarized in Table 4-1. Samples 8 and 7 were the reference specimens in this study and were used as control samples. Sample 8 is a thick 1 μm single layer film

prepared using the same parameters as the soft sub-layers in the multilayer films and sample 7 is a 100 nm ta-C film deposited without substrate bias.

Table 4-1 Internal composite of various DLC multilayer films

Sample no.	Soft sub-layer thickness (nm)	Hard sub-layer thickness (nm)	Total no. of sub-layers	Ratio of soft to hard sub-layer thickness
1	50	50	20	1 : 1
2	25	25	40	1 : 1
3	16.6	16.6	60	1 : 1
4	12.5	12.5	80	1 : 1
5	75	25	20	3 : 1
6	25	75	20	1 : 3
7	-	100	-	-
8	1000	-	-	-

4.4 Intrinsic compressive Stress

Stress evolution in multilayer a-C were examined by S. Logothetidis et al, both experimentally using rf magnetron sputtering[228, 229] and theoretically using MC simulation.[230] In their study, it was shown that the soft sub-layers in the a-C multilayer films acted as a sort of stress “absorber”, buffering the higher stress of the hard sub-layer and lowering the overall stress of the entire film. Their studies also indicated that the overall stress of the multilayer a-C films is a combination of contributions from the various sub-layers and the interactions of their interface. The intrinsic stress in the multilayer a-C films prepared in this study was thus expected to be affected by their internal compositions as well.

Table 4-2 summarizes the compressive stress, H_{indent} and E_r for all the test samples. A Si <100> wafer was also used as a control sample in some of the tests. The highest stress observed was the 100 nm ta-C (sample 7) measured at 7.8 GPa and the lowest was the single layer a-C film (sample 8) at 0.5 GPa. These results for the single layer films are consistent with prevailing literature.[151, 181, 220, 227] From Table 4-2, the stress variation between the multilayer samples was not significant and they averaged at ~2.4 GPa. The only exception was sample 6 which had the highest hard sub-layer content (75%) and compressive stress of 4.2 GPa. This is consistent with results from D. G. McCulloch et al[226] who measured the stress of multilayer a-C films produced by the FCVA with a ratio of 2 : 1 (hard to soft layer ratio) at 4.3 GPa.

CHAPTER 4 MULTILAYER AMORPHOUS CARBON FILMS

Table 4-2 Indentation Hardness, Reduced Modulus and intrinsic stress of different a-C films

Sample no.	Film type	Indentation Hardness (GPa) (± 2)	Reduced Modulus (GPa) (± 50)	Stress (compressive) (GPa) (± 0.5)
1	Multilayer a-C	36	280	2.7
2	Multilayer a-C	28	260	2.4
3	Multilayer a-C	25	260	2.2
4	Multilayer a-C	24	280	2.8
5	Multilayer a-C	33	280	2.4
6	Multilayer a-C	41	280	4.2
7	Single layer Hard-ta-C	52	340	7.8
8	Single layer soft-a-C	25	270	0.5
-	Si	12	170	-

It is interesting to note here that the results indicated that below a critical number of hard sub-layers, the modulation of the internal composition did not significantly affect the total stress of the films. In fact, their stress values are lower than expected for the relative amount of hard to soft sub-layers. This was also observed by J. W. Ager et al[231] who had used the same technique as this study to deposit multilayer a-C films, although no explanation was given.

A possible cause for this observation could be due to the deposition condition of the films; specifically the temperature during deposition. During the deposition, the substrate would heat up more rapidly if it was biased due to the

more energetic C^+ ions. In the case of the samples produced in this study, the substrate heating effects would be even more prominent as the samples were prepared continuously without any rest periods. Unfortunately, direct measurements of the substrate temperature during deposition were not possible due to constraints on the deposition system. However, temperature measurement on the substrate holder taken 4 min after the deposition of sample 8 (1000 nm single layer a-C) measured at $\sim 80^\circ\text{C}$. During deposition, the substrate temperature is estimated to be at least another 100°C hotter.[226] Therefore during the entire deposition process, the temperature on the substrate holder would be fluctuating with the on/off sequence of the bias voltage. Two mechanisms for the unintentional stress reduction by incidental substrate heating are possible.

The first mechanism is due to the intrinsic deposition process. This means that the a-C films were deposited with intrinsically lower stress due to the elevated deposition temperatures. M. Chhowalla et al[122, 232] observed that the stress, sp^3 content and Young's modulus of a-C films are substantially lower if the substrate temperature is high during deposition. This is observed when the substrate temperature exceeds $\sim 140 - 250^\circ\text{C}$, depending on the incident ion energy. This process therefore could be responsible for a generally lower stress (and lower sp^3 content) film. It should be noted that this effect is different from the general stress relief mechanism due to ex-situ annealing.

The second mechanism is an extrinsic stress relief process due to the increase in temperature as the film is deposited. This means that the a-C film

was deposited with intrinsically high stress but was subsequently lowered during the deposition by self-annealing. Therefore, in contrast to the first mechanism, this is the general stress relief observed when ta-C is annealed after deposition. (See section 2.4) As the multilayered films in this study are thick, the deposition time needed per sample is between 15 – 20 min. Therefore during the deposition processes, if the substrate temperatures get high enough, the films could be “incidentally” annealed lowering the stress. B. K. Tay et al.,[118] had reported a stress reduction of ~80 % of ta-C from annealing at 200 °C for just 2 min indicating that very high temperatures are not needed for stress relief. Another aspect of this mechanism is that the sp^3 content of the film would be hardly changed. This is in contrast to the first mechanism which predicts a reduction of ~ 50 % of the sp^3 fraction. Significantly, both mechanism explained here occurs at temperature much lower than 1100 °C, which is the temperature that ta-C is known to be stable (not much change in sp^3 content) in vacuum.[77]

It is expected that for both mechanisms, the substrate heating effects would be most prominent on the samples prepared with the longest duration of bias voltage being turned on. Samples 1 – 5 have between 50 to 75 % soft sub-layers. This meant that during their growth processes they are exposed to additional heating of the substrate at least 50 % of the time. Sample 6 had only 25 % soft sub-layers and correspondingly would experience the least amount of substrate heating. This could therefore explain the relatively lower stress levels of samples 1 – 5 when compared with sample 6. Using the data from M. Chhowalla and B. K. Tay, the estimated drop of stress of the hard sub-layers is

approximated to be from 8 to 4 GPa. Using this value, the total stress calculated by averaging the stresses of the various sub-layers is ~2.3 GPa. This fits well with the average experimental value of 2.4 GPa. At this stage, it is difficult to determine accurately which mechanism is responsible for the stress lowering. However, it is likely that both mechanisms are affecting the films simultaneously and it is also possible that only partial portions of the hard sub-layer had its microstructure changed by the deposition temperature.

It is widely accepted that ta-C films could have maximum stress relief in less than 10 min by annealing at 600 °C. This can be achieved with no major micro-structural change, thus enabling the film to retain its remarkable properties. Unfortunately, this annealing temperature is not acceptable for many temperature sensitive applications. This is especially so for device fabrication using standard lithography (patterning using photoresist) where high temperatures (> 200 °C) are usually not tolerated. Arguably the most common negative photoresist used by MEMS engineers for high aspect ratio patterning is SU-8.[233] SU-8 is stable to slightly more than 200 °C. At 300 °C in an inert environment, shrinkage of the photoresist structure is apparent and at temperatures exceeding 400 °C, massive structural damages would be observed after just a few minutes. Although process steps can be designed to circumvent the temperature sensitivity, this usually requires more complicated process designs (eg. Hard mask deposition, reactive ion etching of a-C...etc). Therefore if annealing was to be used for stress reduction in multilayer a-C films, the annealing time and temperature should be kept to the minimum level for it to be an applicable material in devices requiring patterning such as MEMS.

The issue of annealing time and temperature is further complicated by the very different annealing behaviour of the hard and soft sub-layers (see section 2.4). A compromise is thus needed to balance the amount of stress reduction with acceptable process temperature and duration.

In order to determine the optimized and balanced annealing conditions, a set of test specimens, using the same deposition conditions as sample 6 were prepared. The specimens were prepared this way because sample 6 had the highest stress value and thus any changes in stress after annealing would be more prominent. These test specimens were annealed at various test conditions. Annealing in both ambient air and vacuum (10^{-3} Pa) was done and reflected in Figure 4-3 and Figure 4-4.

Figure 4-3 Multilayer a-C (sample 6) stress reduction as a function of annealing time in both vacuum and ambient air at 200 °C.

Figure 4-3 shows the percentage of stress reduction with respect to annealing time for the test specimens in both ambient air and under vacuum. The temperature was maintained at 200 °C and the specimens were periodically checked for both thinning (due to oxidation) and stress relief. No significant thinning of the films was observed throughout the tests. A tube furnace was used in this study as the RTA could not support the long annealing duration needed. The specimens were allowed to cool for 30 min before stress measurements were conducted. As the graph adopts a logarithmic time scale, the initial zero point (corresponding to 0 % stress relief) was set at 0.1 min for ease of presentation.

The annealing behaviour can be described generally as having a rapid stress reduction ($\sim 0.7 \text{ GPa min}^{-1}$) in the first few minutes followed by a much slower rate ($\sim 0.008 \text{ GPa min}^{-1}$) of stress relief after that. There is also no discernible difference between annealing in air and vacuum. This is expected since the surface of the multilayer a-C films were essentially ta-C which is not expected to oxidize in ambient air below 400 °C.[234] No literature is available on the long term annealing of multilayer a-C so a direct comparison is not possible. However the short term ($<10 \text{ min}$) annealing on multilayer a-C at 200 °C was reported to have a sharp drop in the first 2 min ($\sim 0.8 \text{ GPa min}^{-1}$) followed by a slower stress relief rate ($0.02 \text{ GPa min}^{-1}$).[107] This is in good agreement with the current results. The same trend is also generally observed for pure ta-C[77, 117] and a-C multilayer films annealed at 600 °C.[226] The

test results obtained here, therefore indicated that an annealing time of less than 5 min is more than sufficient for stress relief of multilayer a-C films in general. As such an annealing time of 3 min was used for all subsequent experiments on multilayer a-C films.

Figure 4-4 Multilayer a-C (sample 6) stress reduction as a function of annealing temperature in both vacuum and ambient air. The time of annealing is fixed at 3 min.

Figure 4-4 summarized the stress relief behaviour of the test specimens in relation to different temperatures in both air and vacuum. Annealing at 100 °C is not conducted since this temperature is already exceeded during deposition. All annealing are done in the RTA. After 3 min of annealing, the films were cool down in the RTA in a N₂ environment via a N₂ purge. The films annealed under vacuum did not show any signs of oxidation at all for the entire test range. However the films annealed in air shows considerable oxidation at 400 °C.

Beyond 400 °C, only partial traces of the film was found on the Si substrate. These observations are consistent with current literature on the thermal stability of a-C and ta-C in different environments.

The annealing characteristics for both the air and vacuum environments parallel each other until 350 °C when their similarity deviates. For the film annealed at 400 °C in air, ~15% of the total film thickness is lost to oxidation. (The stress calculation took into account this change in film thickness) Graphitization is also possible at this temperature in air.[234] From the results, the rate of stress relief increases with annealing temperature as expected. Moreover, the difference between annealing at 200 °C and 600 °C is an additional of 25% reduction in stress. This is a significant difference and thus for applications of multilayer a-C that is insensitive to temperature and requires extremely low stress, (eg. protective coating for certain optics and high wear mechanical components) annealing at high temperatures in a vacuum environment would be recommended. However as mentioned earlier, many fabrication processes are very sensitive to high temperatures. As such, even though the stress in the multilayer film is not completely removed due to lower annealing temperatures, the advantage of having more applications could potentially outweigh this disadvantage. Further, the results also indicated that with low annealing temperatures, annealing in air for stress reduction is a possibility. This would further reduce the need for vacuum furnaces and therefore reduce the complexity of any device fabrication using multilayer a-C films.

After examining the relative performance of annealing the multilayer films in various conditions, a compromise parameter is established for all annealing of multilayer a-C films in this study. All annealing experiments discussed further in this chapter will use the RTA for annealing at 200 °C for 3 min.

To understand the annealing behaviour of multilayer a-C films, an understanding of how the individual sub-layers behave during annealing is crucial. Therefore sample 7 and 8 were also annealed at the same conditions as the other multilayer films. Their stresses after the annealing were ~2 GPa for both films. These values are very close to the results reported by B. K. Tay for a-C films annealed in vacuum at 200 °C (2 GPa for ta-C and 1.8 GPa for intermediate a-C).[118] It should be noted that sample 7 and 8 are only rough indicators of the annealing/stress characteristics of the sub-layers within the multilayer films. The actual thermal behaviour of single layer films could be different from the sandwiched sub-layers within the multilayer matrix. Furthermore, as explained earlier regarding the deposition process, the sub-layers themselves could have different micro-structural properties when compared to their single layer counterparts due to substrate heating. (Sample 7 was only 100 nm thick and prepared without any substrate bias at all.)

However, from the measured stress of the single layer films, it would seem that the lowest stress achievable by the multilayer films would be ~2 GPa. Interestingly most of the multilayer films are already close to this stress level even before annealing indicating that incidental substrate heating could have reduced the stress during deposition to an already low level.

To understand further how the composition of the internal layering would affect the overall stress of the multilayer films, the films were divided into two sub-groups. The first group consisted of multilayer films with different ratios of soft to hard sub-layers (Sample 1, 5 and 6). These films had the same number of modulation (20 layers) but different sub-layers compositions. The annealing characteristics of the first group are presented in Figure 4-5. The second group consisted of multilayer films with a fixed soft to hard sub-layer ratio (1:1) but differs in the amount of the films modulation (Sample 1-4). The annealing characteristics of the second group are presented in Figure 4-6.

Both Figure 4-5 and Figure 4-6 show a clear trend in the decline of the stress level after annealing. The average reduction in stress for the films was 30%. This is comparable with multilayer a-C:H films annealed at 250 °C.[35] The lowest stress recorded was at 1.5 GPa.

From Figure 4-5, the largest decrease of stress was for sample 6. This was the sample least affected by substrate heating during deposition. However, its stress level is still relatively high compared with the rest of the multilayer samples. Sample 1 and 5 with lower hard sub-layer content had reduced their stresses to the estimated lowest level of 2 GPa.

Figure 4-5 Compressive stress before and after annealing for multilayer films of different soft to hard sub-layer ratio. All samples display a clear decrease in stress level (~30 %) after annealing.

Figure 4-6 tabulates how the modulation of the multilayer films would affect the overall stress. The results generally indicated that the films had all lowered their stresses to the expected lowest level. No clear trend in how the modulation could affect the initial stress is observed. However there is a weak correlation between the number of sub-layers and total stress relief. Sample 3 and 4 have slightly better stress relief characteristics compared to sample 1 and 2 despite the similarity in their hard to soft sub-layer content. This could be due to the higher number of interfaces in sample 1 and 2 when compared with sample 3 and 4. Work by McCulloch et al[107] indicated that rapid stress reduction is present at the interfaces between the hard and soft sub-layers after annealing at ~600 °C due to the material's intrinsic resolve to lower its total

energy. A consequence of this stress reduction is an observation of preferential alignment in graphitic planes within the bulk of the film. This is also observed by D. R. McKenzie et al[36] in pre-annealed multilayer a-C prepared by another method. They also reported that these regions of alignment are maximized at the interface of the multilayer a-C. As such, a similar energy minimization principle and thus stress lowering mechanism could be present at the interfaces (albeit weaker) for the multilayer a-C films prepared by this study. This effect would also be expected to be more prominent in samples with more interfaces, explaining the slightly better stress reduction observed for sample 3 and 4.

Figure 4-6 Compressive stress before and after annealing for multilayer films of different modulation. Decrease in stress level is evident for all samples. The lowest stress observed is 1.5 GPa.

4.5 Indentation Hardness and Reduced Modulus

The hardness of a-C films in general is more dependent on their sp^3 than sp^2 bonding sites as the former contributes more rigidity to the material network.[57] This is not to say that the sp^2 sites are totally negligible in their contribution towards the hardness of all forms of a-C. For example for low hardness a-C:H films, the sp^2 sites do actually contribute some rigidity in the material network.[235] However, for most a-C films, the relative significance of the sp^3 bonding far outweighs those of sp^2 bonding to the extent that in high sp^3 content a-C such as ta-C, the sp^2 sites actually softens the material.

As the multilayer films were not uniform across their thickness, the depth of penetration of the indents would be expected to have an effect on the H_{indent} measurements. As such, it would not be meaningful to specify an absolute H_{indent} value for any particular multilayer film. But for the ease of comparison between the various samples, an arbitrary indentation depth of 50 nm was chosen as the reference depth and the H_{indent} measurements obtained from there were used as an “average” hardness for the samples. The H_{indent} values shown in Table 4-2 were based on this penetration depth (with the exception of sample 7 which had an indentation depth of 10 nm).

From Table 4-2, the H_{indent} of the single layer ta-C at an indentation depth of 10 nm was 52 GPa while the H_{indent} of the single layer a-C film taken at 50 nm was 25 GPa. As the H_{indent} of the films was related to their sp^3 fraction, these values were reasonable considering the difference in sp^3 fraction between them.

The multilayer films were expected to have hardness values between those of the hard and soft sub-layers. Comparatively, the H_{indent} of the Si control sample indented at 50 nm was only 12 GPa.

Also from Table 4-2, two trends were apparent; first, the H_{indent} increased with the amount of hard sub-layer within the film which was expected. The second was that H_{indent} decreased with an increase in the total number of sub-layers or interfaces (see Figure 4-7). This hardness lowering effect due to increased modulation was so pronounced that it actually superseded the gain from adding more hard sub-layer content as can be observed when comparing sample 4 (50% hard sub-layer, 24 GPa) and 5 (25% hard sub-layer, 33 GPa). This softening effect observed could be due to the intermixing effects of the interfaces. P. Patsalas et al[37] had used X-ray techniques to probe into the interfaces between the sub-layers of multilayer a-C and found that the transition within the interfaces may not be sharp. The interfaces could in fact consist of a totally unique layer form by the intermixing of the two sub-layers as one sub-layer is deposited on the other causing a decrease in hardness of the material. Similar effects on the softening of multilayer superlattices due to the formation of diffused interfaces were also reported for metal-based multilayer films when amorphous alloy regions (due to intermixing of the two sub-layers) were formed between the sub-layers.[236-242]

Figure 4-7 Indentation hardness as a function of number of sub-layers

The result from Figure 4-7 could also be interpreted as a lowering of H_{indent} as the sub-layers got thinner. However, as explained earlier, the softening was a consequence of the increase in modulation and not a decrease in the sub-layer thickness. This point is brought up because some others[228-230, 243] have observed the opposite effect. They reported that a-C multilayer films with thinner sub-layers are harder compared to those with thicker sub-layers. They also commonly explain their observations based on models developed by J. S. Koehler[244] and S. L. Lehoczky[245, 246] who were pioneers in superlattices based on different metals. The theory behind the strengthening of the multilayer films from their experiments in multilayer metal composite was based on repulsive dislocation-images forces. Specifically they explained that the hardening of the composites was highly dependent on the

difference between the dislocation-line energy of both metals making up the superlattice. As the dislocations (damage) requires a large amount of stress to move from a lower elastic modulus layer into a higher elastic modulus layer, the interface between the two metals would result in an elastic repulsion of any induced dislocations and thereby increase the composite's resistance to deformation. The higher the difference in elastic modulus, the more prominent is the strengthening effect.

Critically, there are two important points regarding Lehoczky and Koehler's model with regards to the discussion on hardening of a-C multilayer films. First the original model is based on crystalline materials as lattice mismatch at the interfaces are crucial to the hardening effects, although the concept could also be applied if only one of the layer is crystalline while the other is amorphous. The second is the importance of the sub-layer thickness. Both Lehoczky and Koehler emphasized the importance of thin (<100 atomic layers) sub-layers for the hardening to be significant. Not surprisingly, much of the work showing an increase in hardness through reducing the sub-layer thickness are for relatively thin films with thin sub-layers. For example, multilayer a-C films studied by S. Logothetidis,[143, 229, 230, 243] have shown an increase in hardness following a decrease in the sub-layer thickness were only ~ 100 nm thick with sub-layers thickness at ~ 10 nm. Comparing with multilayer a-C films with thicker sub-layers (>20 nm) the hardening effects became rather inconclusive[36, 231]. W. Zhang et al[111] even reported that the hardness of multilayer a-C films were positively correlated to sub-layer thickness, similar to the trend reported in Figure 4-7. As such, the hardening

effects of a-C multilayers films may not be substantiated if the sub-layers are too thick and obviously not all a-C multilayer films would experience hardening with decreasing sub-layer thickness.

In order to study the H_{indent} of the films with respect to the indentation depth without the influence of the interfaces between each layer, the hardness of samples 6, 5 and 1 (representing multilayer films with different soft to hard sub layer ratio) versus indentation depth is shown in

Figure 4-8. All the films have the same number of interfaces since the number of sub-layers is the same. All three films showed a decrease in H_{indent} as the indentation depth increased. This trend is typical of thin films deposited on relatively less stiff substrates. For example, the hardness of SiC film on Si substrate was reported to decrease with indentation depths as well.[247] Several models based on soft substrate influence had been proposed to account for this trend.[191, 247-252] However none of these models can fully explain the trends seen here since the yielding from the substrate was insignificant considering none of the indents were more than 10% of the total film thickness and therefore unlikely to cause the downward trend observed. As such, an alternative explanation based on the structure of the multilayer film is thus proposed and explained below.

Figure 4-8 Indentation hardness as a function of indentation depth for multilayer films with different soft to hard sub-layer ratio.

Not considering the sp^2 rich mono-layer present on all a-C film surfaces, the hard ta-C sub-layer was always the surface layer of the multilayer a-C films prepared in this study. As such, for shallow indents the hardness values would be largely dependent on the ta-C sub-layer which was a lot harder than the soft sub-layers. But as the indentation depth increased, the bottom soft sub-layers would start to yield (before any yielding of the Si base) and influence the H_{indent} measurements. This model would predict that the effect would be more prominent for multilayer films with thinner top hard sub-layer as the bottom soft layers would yield much earlier. From

Figure 4-8, the rate of decrease of the hardness with depth was higher as the thickness of the hard sub-layer decreased confirming the prediction by the proposed model.

After the H_{indent} measurements of the as-deposited samples, the annealed samples were reviewed next. The results from the annealed samples were contrasted to the as-deposited samples in Figure 4-9. As mentioned earlier, the hardness of the multilayer films depends largely on the sp^3 to sp^2 ratio of the various sub-layers. This has important implications for the multilayer a-C films since the two types of sub-layers behaved differently under thermal excitations as well.

Figure 4-9 A. Hardness before and after annealing for multilayer films of different soft to hard sub-layer ratio. B. Hardness before and after annealing for multilayer films of different modulation.

For the hard sub-layers, it is expected that its internal structure remains largely unchanged after annealing.[77] This was confirmed by the measured

H_{indent} of the annealed single layer ta-C at 52 GPa which is the same as the as-deposited case. However, for the soft sub-layers, its sp^2 fraction would have increased,[107] and the hardness would be expected to decrease after annealing.[118] The measured H_{indent} for the single layer a-C was at 22 GPa, which is lower than the as-deposited case. As such, thermal induced hardness variation, if any, of the multilayer a-C films would be due mostly to the soft sub-layers. This means that after annealing, the largest change (decrease) in H_{indent} should be observed in multilayer films with the highest soft sub-layer content. This is observed in Figure 4-9, where multilayer a-C films with higher soft sub-layer content shows a larger decrease in H_{indent} compared with those of lower soft sub-layer content. From Figure 4-9 B, the modulation had very little effect on the H_{indent} of the material after annealing. Despite these, the actual variation in the H_{indent} of the various multilayer films after annealing were relatively small (5 - 8 %) compared with the much higher decrease in residual stress of ~30 %.

Figure 4-10 shows the E_r as a function of indentation depth for multilayer films with different soft to hard sub-layer ratio. As expected, the same decreasing trend (with respect to depth) observed for the H_{indent} was also observed for the E_r . The figure also shows that the E_r for all the 3 samples converges and stabilizes at about 280 GPa. This is in fact observed for all the multilayer samples. The values of E_r for all the samples were thus taken from this plateau region.

Since the sub-layers were in an isostrain condition, the E_r could be modeled by a simple rule-of-mixtures. The reduced modulus and volume

fraction of the hard sub-layer, $E_{r,hard}$, V_{hard} , and soft sub-layer, $E_{r,soft}$, V_{soft} , were known. The weighted average E_r of the multilayer films was then given by Equation (4-1),

$$\text{Equation (4-1): } E_{r,multilayer} = E_{r,hard}V_{hard} + E_{r,soft}V_{soft}$$

Using Equation (4-1), the $E_{r,multilayer}$ would be 305 GPa for samples 1 to 4, 288 GPa for sample 5 and 323 GPa for sample 6. From Table 4-2 the actual values were close to the calculated results and were just slightly lower by ~10 % which is within error bars. Furthermore, the E_r of the multilayer films seems stable with annealing as no significant change was observed. This is consistent with the marginal hardness variation observed after annealing.

Figure 4-10 Reduced modulus as a function of indentation depth for multilayer films with different soft to hard sub-layer ratio

4.6 Surface Morphology and Tribology

One of the most remarkable features of a-C and especially ta-C is its ultra smoothness (~ 0.1 nm *r.m.s.*) as deposited. The mechanism for this deposition smoothness was proposed by C. Casiraghi et al[253-255]. They explained the process as a dynamic smoothening by the incident ions as they dissipate their kinetic energy upon impinging with the growing substrate. The energy dissipated (this could be interpreted as thermal spikes. see page 17) then acts to flatten the surface due to energy minimization principles. This process could also explain the smoothening of an originally rough substrate surface during ta-C deposition.[254, 256, 257] As such, for multilayer films, the main factor determining the surface roughness is the top hard sub-layer. Since all the top surfaces of the multilayer films prepared are essentially deposited at the same conditions, their roughness should not differ by much. Table 4-3 summarizes the roughness, $R_{r.m.s.}$, of the various films together with their coefficient of friction and wear rate.

During the surface roughness measurements, different areas of the samples were probed. It was found that there were subtle differences in the roughness from point to point. The differences average at $\sim \pm 0.1$ nm. (The AFM's specification states that the noise in the vertical direction is 0.05 nm) There was no correlation between roughness and regions on the samples and thus the variation of the roughness could be assumed to be random across the sample's surface. The difference may be small, but considering that the samples of a-C are extremely smooth, this variation is important.

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The single layer control specimens were smooth, with the ta-C and a-C samples having average $R_{r.m.s.}$ of 0.1 nm and 0.15 nm respectively. The multilayer films all exhibited a slightly higher average $R_{r.m.s.}$ that ranges from 0.12 -0.23 nm. The values reflected in Table 4-3 are the average of 6 points on the samples. Considering the vertical resolution of the AFM and the variation in roughness across the individual sample's surfaces the $R_{r.m.s.}$ values of all the multilayer samples are comparable. Both the ratio of soft to hard sub-layers as well as modulation has no observable effect on the roughness. Moreover, these values of $R_{r.m.s.}$ were generally good for most tribological applications. There were also no $R_{r.m.s.}$ changes after annealing. Typical 3D AFM topographic images of the multilayer films are shown in Figure 4-11 while their respective topographic images after annealing are shown in Figure 4-12.

Table 4-3 Coefficient of friction, wear rate and surface roughness of the films

Sample no.	Film type	Coefficient of Friction (± 0.02)	Wear rate (10^{-8} mm ³ /N.m) (± 1.0)	Surface roughness ($R_{R.M.S.}$) (nm) (± 0.1)
1	Multilayer DLC	0.09	2.1	0.17
2	Multilayer DLC	0.09	1.9	0.16
3	Multilayer DLC	0.09	2	0.15
4	Multilayer DLC	0.1	1.9	0.15
5	Multilayer DLC	0.1	3	0.12
6	Multilayer DLC	0.09	1.6	0.15
7	Single layer hard-DLC (ta-C)	0.11	1.2	0.1
8	Single layer soft-DLC	0.09	3.8	0.15

Figure 4-11 3D surface topographic images of $1\ \mu\text{m}^2$ cell taken before annealing of the multilayer samples. The *r.m.s.* roughness shows no correlation to compositional changes within the multilayer films.

Figure 4-12 3D surface topographic images of $1\ \mu\text{m}^2$ cell taken after annealing of the multilayer samples. No significant changes were observed.

Tribology of materials relates primary to frictional and wear characteristics. Friction is a measure of the dissipation of energy as two surfaces move across each other,[258, 259] and wear is the removal of material during the movement.[258] The primary means to determine both properties is direct sliding (very often circular sliding) of the flat material of interest against a smaller circular counterpart (sliding partner). This is sometimes referred to as the pin-on-disk test. These tests are very sensitive to test conditions[260-265] such as:

- i) The type (sapphire, iron, polymer...etc) of counterpart used.
- ii) The magnitude of the contact load (Hertzian pressure) used to apply pressure during the test.
- iii) The sliding velocity of the test sample relative to the sliding partner.
- iv) The test environment (humidity, temperature, gases present (air, N₂, vacuum...etc) and ambient conditions during the test.
- v) The use of any other artificial lubricant during testing.

As such, it is not surprising that compilations of the friction coefficient of a-C films showed that they span a large range of values, from $\mu = 0.002 - 0.4$ for vacuum environments to $\mu = 0.05 - 1.00$ in ambient air with relative humidity of 20 – 60 %.[47, 266] The tribological behaviour of a-C and a-C:H is also very different in different test environments.[267, 268] Due to these complications, it is crucial to state the test conditions of all tribological tests.

The tests carried out in this study were done to minimize the differences in test conditions between different samples. The sliding partners used were always fresh (either by using a new partner or rotating the contact surface to a new unused area) and the test environment was sealed during experimentation. Only one condition was used for all experiments (as specified in CHAPTER 3). This is sufficient for the purpose of testing the differences in the tribological behaviour of the various multilayer a-C films with respect to layer composition and annealing.

After the films had completed their 30,000 test cycles, surface profile scans revealed that the wear tracks for all the films have exceeded at least 60 nm in depth. (See Figure 4-13) This meant that except for sample 6, the wear for the multilayer films had gone through at least the first sub-layer. Therefore, the tests carried out in this study would give a good assessment of the tribological behaviour of the films as the wear would have progress through different layers in the multilayer films.

Figure 4-13 Wear profile of sample 6 after sliding for 30000 cycles with a constant load of 2 N at a linear speed of 0.1 m/s and wear track of 2 mm.

From Table 4-3, the coefficient of friction of the single layer films were similar at ~ 0.1 for both samples. This is expected since the frictional characteristics of a-C prepared by the FCVA were not expected to vary between samples prepared with or without substrate pulse bias up to -7 kV.[220, 227] The dynamic friction spectra (DFS) of the multilayer films are shown in Figure 4-15 and Figure 4-16. The noise of the reading was approximately 0.02 for all the multilayer films. The red line represented the DFS after smoothening of the noise. From the DFS, all the films exhibited 2 stages of friction evolution. (See Figure 4-14)

The frictional characteristic of a-C is governed largely by surface chemistry of both a-C and the sliding partner. As the chemistry of the sliding surfaces changes during different stages of the test period, the frictional

characteristics as recorded by the DFS would also change correspondingly. The different stages of the DFS could be explained as follows:

The initial stage (stage 1) or startup period involved the formation of transfer layers.[269, 270] These transfer layers were formed through a friction-induced transformation of the top layer of the a-C film into graphitic layers. These layers are generally lubricating in high humidity environments (such as the environment in this test) since intercalation of water between the graphite layers lowers the coefficient of friction. In the case of this study, the transfer layer would consist of graphite layers from the a-C top surface as well as alumina from the sliding partner. (i.e. alumina would be transferred to the a-C surface and carbonaceous material transferred to the sliding partner forming two distinct surfaces)[271] These transfer layers largely determine the coefficient of friction for most a-C surfaces. This is because once the transfer layers are fully formed, the original two surfaces (a-C and sliding partner) would no longer be in contact and the resultant shear strength during sliding is that of the transfer layers sliding against each other.

The second stage (stage 2) was the equilibrium stage where the transfer layer was fully formed and the frictional characteristic is stable. This is the value of the coefficient of friction reflected in Table 4-3. A third stage where further reduction of friction was reported by others (due friction-induced annealing) was not observed in the time period of this experiment.[269]. Illustration of both stages are given in Figure 4-14.

From Figure 4-15, the comparison of the frictional characteristics with respect to modulation could be examined. The stable (stage 2) frictional characteristic of multilayer samples 1 - 3 were similar. All their steady state (stage 2) coefficient of friction value corresponded to $\mu = 0.09$. Sample 4 with the highest amount of modulation have a steady state coefficient of friction at $\mu = 0.1$. However from the DFS of sample 4, the coefficient of friction seems to be able to decrease further if more cycles were permitted. Overall, the modulation was not observed to have an effect on the steady state coefficient of friction for the multilayer films. All the films started with a high initial coefficient of friction ($\mu = 0.17 - 0.2$) before dropping to a lower value around $\mu = 0.08$ then rose to their steady state value. To facilitate the discussion, the first drop from the initial high μ value to the lowest point will be termed "*initial drop*" and the rise of μ after this drop will be termed "*recovery*". The illustration of these two points with respect to the DFS is given in Figure 4-14.

Figure 4-14 Illustration of various characteristics observed on the dynamic frictional spectra of the films.

Although the stage 2 frictional characteristics did not vary with the modulation, there is an observable trend towards a longer stage 1 with an increase in modulation. The decrease in the gradient of the “*initial drop*” with the increase of modulation was evident in Figure 4-15. The coefficient of friction of sample 1 (least modulation), had an almost instantaneous “*initial drop*” from the initial start-up while sample 2 and 3, having higher modulation, only dropped to their lowest μ value after 2500 and 3000 cycles respectively. Sample 4 had the largest difference, the “*initial drop*” only dropped to the lowest level after 5000 cycles. The “*recovery*” period of sample 4 was also unusually longer. This indicated that the transfer layer formation during sliding could be dependent on the interfaces between the soft and hard sub-layers. Interface dependence behaviour of the coefficient of friction of a-C:H multilayer films were also observed by L. Knoblauch et al.[272, 273]

4-15 Dynamic friction spectra of the multilayer films sample 1 – 4, both before and after anneal. The choice of samples was such as to represent an increase (decrease) of modulation (sub-layer thickness) from sample 1- 4, with a consistent soft and hard sub-layer ratio.

Figure 4-16 categorized the DFS with respect to the soft to hard sub-layer ratio. The characteristics of the DFS of these films are similar to those

from Figure 4-16. No clear correlation between sub-layer content and friction coefficient is observed. Sample 6 (75 % hard sub-layer content) showed characteristics similar to sample 4 with the extended “*recovery*” period. For reference, a Si wafer was put through the same tribological experiment. Its DFS is presented in Figure 4-16. The noise of the spectra was at least an order higher than the multilayer films at 0.2. The mean value for the coefficient of friction for Si was $\mu=0.6$, which was much higher than the multilayer a-C films.

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Figure 4-16 Dynamic friction spectra of multilayer films sample 5, 1, and 6 accordingly, both before and after anneal. The choice of samples was such as to represent an increase hard sub-layer content from sample 5 – 1 – 6, with a consistent amount of modulation. Si reference sample also included. Dynamic friction spectra of a Si reference sample is also shown.

The DFS of the multilayer films after annealing are also reflected in Figure 4-15 and Figure 4-16. There was not much change in the DFS of the multilayer films after annealing. The characteristic slow “*initial drop*” and long “*recovery*” of sample 4 and 6 respectively were still observable after annealing indicating that the earlier observations were consistent with the material and not an experimental aberration. All their steady state (stage 2) coefficient of friction remained the same.

In general the coefficient of friction of the multilayer samples was excellent for tribological applications. No failure (delamination) of the films was observed throughout the experiments. Although some slight differences in the DFS were observed for some of the multilayer samples, their steady state frictional characteristics remains largely the same. This is expected since the transfer layer created during the sliding for all the multilayer samples are essentially the same. The results obtained from this experiment correlates well with others who had done pin-on-disk experiments with similar set-ups and test conditions.[220, 227, 260]In addition, from the results obtained, for tribological applications requiring frequent start-stop cycles, multilayer samples with low modulation would be more suitable.

The wear rates of the multilayer samples were examined next. From Table 4-3, all the films differ in their wear rates. Notably, the single layer ta-C films have a wear rate ($1.2 \times 10^{-8} \text{ mm}^3/\text{N.m}$) approximately 3 times smaller than its softer counterpart ($3.8 \times 10^{-8} \text{ mm}^3/\text{N.m}$). The Archard equation (Equation

(4-2)) states that the wear coefficient is inversely proportional to the hardness of the surface.

Equation (4-2): $Q = KW/H$

where Q is the total volume of wear debris produced per unit distance, W is the vertical (normal) load, H is the hardness and K is a constant. Comparing the wear rates of the films with their hardness obtained earlier, the results obtained do indeed correspond well with the Archard equation. The wear rates for the multilayer films showed a dependence on the total amount of hard layers in the film but no dependence on the thickness of individual layers. This was evident comparing samples 1 to 4 in Table 4-3. Their wear rates were the same at $\sim 2 \times 10^{-8} \text{ mm}^3/\text{N.m}$. However when comparing sample 6, 1 and 5, a decrease in the wear rate was observed as the total amount of hard layers increased (see Figure 4-17). The dependence of wear resistance to modulation is currently inconsistent in the literature with some reporting a decrease in wear resistance with increase modulation while others reported no clear correlations.[263, 273]

Figure 4-17 shows the variation of the wear rates for the multilayer films both before and after annealing. All the films showed a general slight increase in wear rates after annealing. This was not surprising considering that the soft sub-layers became more graphitic (increase in sp^2) upon annealing and thereby lowering the wear resistance of the film. This would also further explain why the highest increase in wear was observed for the sample with the highest soft sub-layer content (Figure 4-17A). From Figure 4-17B, the modulation of the film was not observed to have an effect on the thermal stability with respect to wear.

Figure 4-17 A. Wear-rates before and after annealing for multilayer films of different soft to hard sub-layer ratio. B. Wear-rates before and after annealing for multilayer films of different modulation.

4.7 Summary

Various mechanical and tribological properties of multilayer a-C films had been reported in this Chapter. The main focus of the studies was to investigate the effects of internal structuring and annealing, on material properties. Properties such as stress, indentation hardness, reduced modulus, surface roughness, coefficient of friction and wear were thoroughly examined and discussed in their respective sections.

The intrinsic compressive stresses of the as-deposited multilayer films were averaged at ~ 2.4 GPa despite film thickness of 1 μm . This is much lower than those of ta-C single layer films with stress at 7.8 GPa at only 100 nm. The stress characteristic indifference to compositional change was also discussed. A possible explanation related to substrate heating effects was given.

The H_{indent} of the multilayer films were observed to increase with hard sub-layer content and decrease with increasing (decreasing) layer interfaces (sub-layer period). The highest H_{indent} (41 GPa) observed for the multilayer films had only a 20 % difference from those of the ta-C prepared by the same system. This is despite close to a 50 % difference in stress. A strong correlation of H_{indent} with depth of indentation was also observed. A similar co-relation to indentation depth was observed for the E_r of the multilayer samples as well. However all the E_r of the multilayer samples plateau at ~280 GPa irrespective of film internal composition. The surface roughness, frictional characteristics and wear resistance of the multilayer films were all comparable to ta-C films tested under similar conditions.

For practical purposes, the annealing for all the multilayer films was done at 200 °C for 3 min. Stress reduction of ~30 % was observed for the multilayer samples. The mechanical and tribological properties of the multilayer films were all observed to be stable at this temperature showing little if any changes.

Overall, a-C multilayer film prepared continuously by the OPDB-FCVA in conjunction with substrate pulse bias showed good potential for multiple applications in coatings as well as structural components for MEMS. Properties of the film were demonstrated to be stable despite reasonable stress reductions after annealing. Furthermore, the annealing results also hinted at the possibility of stress reduction (with properties stability) of the multilayer films by annealing in air instead of a vacuum environment.

CHAPTER 5 MULTILAYER AMORPHOUS CARBON MEMS

5.1 Introduction

From the extensive mechanical and tribological characterization of the a-C multilayer films reported in the previous chapter, it can be seen that multilayer a-C have properties that are excellent for MEMS applications. However, besides material properties, the ability of the material to be processed using current MEMS techniques is also an important criterion. Specifically, it is important to access the materials structural integrity after a full MEMS fabrication process. Therefore, as a proof of concept for the use of multilayer a-C MEMS, this chapter will report on the various MEMS structures fabricated and tested using multilayer a-C films. Of specific interests were micro-cantilevers as these are simple MEMS structures that could be easily fabricated and tested.

Micro-cantilevers are simple 2D structures that could be fabricated using just 1 photolithographic mask and because of that, eliminates the need to do multiple aligning and thus reduce the complexity of the fabrication process. Moreover, they have been studied intensively over the past few decades as a MEMS device and structure, making it easier to do comparative studies (with Si cantilevers).

5.2 Experiment objective and Scope

The purpose of the study is not to give an in-depth discussion of a-C MEMS devices but rather an assessment on the viability of using a-C multilayer film as a structural material in MEMS. Although MEMS based on a-C films had been reported [45, 47, 274-278], there are currently limited information on MEMS based on a-C multilayers. To investigate the process capability of a-C multilayers films, a few structural elements were designed and fabricated. Of interest was also the compatibility of using current MEMS software to simulate device performance of micro-cantilever fabricated using a-C multilayer films. To achieve this, simulation of a first mode frequency response of a micro-cantilever would be compared to an actual frequency response of a fabricated a-C multilayer micro-cantilever tested by a laser vibrometer. Both the virtual and actual micro-cantilever would be based on the same dimensions.

5.3 Simulation and Modeling using IntelliSuite®

Before actual fabrication, a fully integrated MEMS software package, Intellisense Software Corporation's Intellisuite® Version 8 was used to facilitate the design and modeling of the device performance. Intellisuite® is a computer-aided-design (CAD) device-level simulation software with various interlinked modules for the design and optimization of MEMS devices. An overview of the

entire process flow is given in Figure 5-1. Since not all the modules were used in this study, only the modules used would be discussed.

Figure 5-1 Global view of process flow for Intellisuite® MEMS simulation

The first stage of the design involved drawing the mask layout. Using the layout editor, IntelliMask™, various 2D structures were designed and created. Examples of the more complicated design such as micro-gears and the Nanyang Technological University logo are shown in Figure 5-2. The software could also export the template for the mask design into .msk, .gds or .dxf formats for actual mask fabrication.

Figure 5-2 Complex geometries designed using IntelliMask™.

The next step involves the specification of the materials to be used during virtual fabrication. For standard material such as diamond, SiO_2 or poly-Si, their thin film (and bulk) characteristics could be found in the software's material database, Mematerial® module. Interesting, even cathodic arc deposited a-C (database file = C_Cathodic_arc_General) is available in the database. However the materials properties associated with the virtual a-C material is different from those of the experimentally derived properties of multilayer a-C. As such the properties were modified with values obtained in CHAPTER 4 and the new virtual multilayer a-C film was termed MLaC (database file = C_Cathodic_arc_MLaC).

The simulation for the process flow for the virtual fabrication using IntelliFab™ was next programmed into the software. Unfortunately, the virtual process flow does not allow for the “lift-off” procedure (discussed in later sections) used in the actual fabrication of the MEMS structure. As such, a modified process flow using virtual poly-Si (database file = PolySi_LPCVD_General) as the MEMS structural material was adopted instead.

The virtual poly-Si material will be substituted to MLaC at the last process step. The simplified simulated process flow is given in Figure 5-3.

Figure 5-3 Simulated process flow for the virtual fabrication

To get free standing structures, anisotropic etching of the underlying substrate would be necessary. To determine the necessary time needed for complete etching, the software's anisotropic simulator, ANISE® was used. This simulation module is a bulk micromachining etch simulator that accurately

determines 3D geometry of bulk Si after etching, taking into account the surface exposure, time, temperature, chemical used and etch stop used if any. The parameters would be different for different structures since the surface exposure to the chemical etchant would be different. A screen shot of a virtual etch by KOH is shown in Figure 5-4. Once the parameters were determined for a given structure, it is fed back to the virtual fabrication process and the final structure was ready for performance simulation.

Figure 5-4 Screen shot of virtual anisotropic etch of Si by KOH.

Difference aspect of MEMS devices could be simulated by the software, including piezoelectric, mechanical, electro-mechanical, fluidic and electrostatic response. The software uses 20-node brick parabolic elements for its 3D meshing algorithm (See Figure 5-5).[279] Once the structural element has been discretized, the geometries could be analysis by fully couple finite element analysis (FEA) and boundary element analysis (BEA) analysis methods.[279]

For the simulation conducted by this study, the investigation of the virtual 1st fundamental vibration response was done using the mechanical analysis module with automatic meshing.

Figure 5-5 3D Mesh of micro-cantilever prior to mechanical analysis. Discretized elements of the structure is visualized.

5.4 Fabrication of a-C multilayer MEMS structures

In order to fabricate the MEMS structures, glass photolithographic mask were fabricated (by an external company) using the template extracted from IntelliMaskTM discussed earlier. Patterns transfer from the mask to photoresist was done using standard UV lithographic methods. The outline and recipe of the pattern transfer process is given below:

1. Wafer was pre-cleaned by Piranha bath which consist of a 3:1 mixture of concentrated H_2SO_4 to H_2O_2 . This was done for 600 sec to remove organic contaminants from the surface of the wafer. This was preceded by a de-ionized water rinse followed by N_2 blow dry.
2. The wafer was primed by Hexa-Methyl-Di-Silazane (HMDS). HMDS was spin coated (5000 rpm, 60 sec) onto the surface to improve the adhesion of the photoresist which will be coated onto the surface of the wafer later.
3. The photoresist (AZ-7220 PR) was spin coated at 5000 rpm for 30 sec. This created a photoresist thickness of approximately 7 μm . The wafer was then baked for 30 sec at 100 °C to dehydrate the photoresist.
4. The pattern from the mask was transferred to the photoresist by UV exposure using the OAI 500 IR Mask Aligner.
5. The exposed photoresist was developed using AZ 300 MIF developer for 60 sec. This was followed by a de-ionized water rinse and spin drying at 1500 rpm for 30 sec.
6. A final inspection of the transferred features was done using a optical microscope before a final hard bake (100 °C, 240 sec) to seal in the pattern was done.

After the pattern was transferred onto the photoresist, the a-C multilayer films could then be deposited onto the substrate. A schematic of the structure fabrication process is outlined in Figure 5-6. The actual fabrication was done

using a simple “lift-off” technique first suggested by D. Sheeja for the fabrication of a-C micro-cantilevers.[118, 277] The a-C multilayer film was first deposited onto the patterned wafer by conditions specified in CHAPTER 4, specifically sample 1 from Table 4-1. The “unwanted” region (the “U” shape in Figure 5-6) was then removed by dissolving the underlying photoresist by acetone. This was accomplished by immersing the entire wafer in an acetone bath for ~600 sec. To create free standing 3D structures, KOH (40% concentration) was used to under-etch the bulk Si substrate. The scanning electron microscopy (SEM) micrographs of some of the structures fabricated are shown in Figure 5-7.

Figure 5-6 Fabrication steps for multilayer a-C micro-structures. A. A pre-cleaned Si <100> wafer. B. Patterned Photoresist on Si wafer. C. Deposition of a-C multilayer film. D. Removal of photoresist by acetone. E. Under-etch of Si substrate to reveal free standing structure.

Figure 5-7 SEM micrograph of various free standing structures fabricated.

5.5 Amorphous Carbon Multilayer micro-cantilever

With the fabrication of the structures completed, micro-cantilevers were examined. One of the most crucial aspects of using multilayer a-C in MEMS was the stress relief of the film by annealing as discussed earlier. It is therefore crucial to understand the effects, if any on fabricated structures after annealing at 200 °C for 3 min (as this was the condition identified as most efficient in CHAPTER 4).

Figure 5-8 A and B shows the SEM micrographs of micro-cantilevers (100 μm x 50 μm) prepared without annealing. From the images, the micro-cantilevers were clearly bent. This was caused by the relatively high

compressive stress of the a-C multilayer film. Using an optical profiler, the deflection of the micro-cantilevers was measured at $\sim 8.3 \mu\text{m}$. Figure 5-8 C and D shows the SEM micrograph of the cantilevers after annealing (the annealing was conducted before the KOH etching stage). No visible damage was observed on the micro-cantilevers. Moreover, the micro-cantilevers were clearly less deflected as compared to the earlier samples prepared without annealing. The measured deflection was reduced to less than $2 \mu\text{m}$. These results correlated well to the initial stress measurements of the multilayer a-C films (sample 6). From here, a positive qualitative assessment could be made on the viability of using a-C multilayer in conjunction with annealing for MEMS applications.

Figure 5-8 SEM micrograph of the micro-cantilevers fabricated with and without annealing. A. Micro-cantilever array fabricated without annealing. B. Close up on the micro-cantilever fabricated without annealing. C. Microcantilever array fabricated with annealing. D. Close up on the micro-cantilever fabricated with annealing.

After the qualitative assessment, a “T-frame” cantilever (see Figure 5-9 insert A) was tested for its resonance frequency using a laser vibrometer setup with an external piezoelectric driver and lock-in amplifier. The experiment was conducted in vacuum at 10^{-6} Pa. The experimental frequency response is given in Figure 5-9. Simulation of the frequency response of the cantilever was also conducted.

The simulated 1st fundamental response mode from IntelliSuite® gave the resonance of the cantilever at 212 kHz. This is in excellent agreement with experimentally measured response of 210 kHz. Not just had this proven the ability of using IntelliSuite® to simulate MEMS devices based on a-C multilayer films, the good agreement between experimental and simulation results also indirectly proved that the material properties characterized earlier were accurate (since the material data were input to the software during simulation and not pre-defined by the material database).

Figure 5-9 Frequency response from “T-Frame” micro-cantilever taken from a laser vibrometer. Insert A. SEM micrograph of micro-cantilever. B. Simulation visualization of micro-cantilever.

5.6 Summary

To summarize, this chapter reported on the simulation and fabrication of a-C multilayer MEMS structures. It was demonstrated that a-C multilayer films (after annealing) is a viable material for some MEMS applications. Simulation of the resonance response of the “T-frame” cantilever was in very good agreement with actual experimental results. The simulation results also indirectly confirmed the accuracy of the material properties characterized earlier in CHAPTER 4.

CHAPTER 6 GRADIENT AMORPHOUS CARBON FILMS

6.1 Introduction

6.1.1 Continuously graded films

As discussed in CHAPTER 4, there are two common types of depth variance in structural composite films. The first type uses discrete periodic layering and the second uses a gradually grading approach. This chapter will focus on the second approach. Continuously graded films differ from discrete periodic multilayer films in that the transition from one material into the next is gradual with no sharp boundaries between the materials. The films are usually graded compositionally between two materials such as fine-grain aluminium oxide infiltrated with aluminosilicate glass.[280] This contrasts with multilayered films where 2 or more materials are stacked into a single film.

The schematic of a compositionally graded film is shown in Figure 6-1. In the figure, the hypothetical graded film consisted of 2 materials referred to as material “A” and “B”. The film started (at the substrate) with a 100 % concentration of material A which gradually decrease (as concentration of material B increases) until it is fully replaced by material B. The transition from an A rich material to a B rich material is gradual and smooth. In essence, the bulk of the film could be classified as a big gradual interface between 100 %

material A at the substrate and 100% material B at the surface of the film. In practices, A and B need not be two different materials but could be the magnitudes of certain properties such as Young's modulus or hardness. For example, a graded metallic alloy composite could be formed by having a transition from a softer composition at the base to a harder composition at the surface.

Figure 6-1 Schematic of a compositionally graded film with two materials, “A” and “B”.

As with multilayer layer films, the main reason for the interest in graded films lies in its mechanical strengthening capability.[216] For example, during indentation, the local driving force for the crack propagation across an interface could be reduced by altering the gradients in elastic and plastic properties across the interface[207, 208] Moreover, a gradual transition in composition (as opposed to having a sharp interface) between two dissimilar materials at the interface could also improve interfacial bonding between them and thereby

improve adhesion.[6] However, besides mechanical properties, graded films could also provide for very interesting microstructures that is very different from uniform films.

6.1.2 Continuously graded Amorphous Carbon films

As explained in section 2.3, the microstructure of a-C films could consist of an almost infinite variety of sp^2/sp^3 composition with different densities. Therefore, in theory a-C films could be graded gradually by varying its density throughout the thickness of the film. Furthermore, this could be accomplished easily by varying the ion energy of the incident ions during deposition. The a-C graded films made this way should have interesting characteristics in terms of its microstructure and other properties. In addition, their annealing characteristics would be interesting as well.

One of the most interesting structural features expected in a graded a-C structure would be the possible formation of self-aligned graphitic material within the film's macrostructure. Aligned graphitic material were observed in multilayer a-C films after a 600 °C anneal as well as in a-C films deposited under high temperatures.[105] The formation of the oriented graphitic material is usually associated with an internal stress field within the film but the exact mechanism for their formation is still not very well understood. [107] The graded a-C film structure thus provides an excellent opportunity to investigate the formation of graphitic alignment. This is because the continually varying microstructure within the graded film would provide the means to introduce

strain both in-situ (by the film's structure itself) and ex-situ (by annealing) into the material.

Currently there is almost no information available in the literature on graded a-C films. This study is therefore the first systematic study of the microstructure of graded a-C films fabricated through the continual variation of ion energy during deposition. The microstructure information provided in this study would thus provide a foundation for future research on the other properties of graded a-C structures.

6.2 Experiment Objective and Scope

The main investigation conducted in this chapter will be on the microstructure of graded a-C films and their annealing effects. The films fabricated in this study are termed gradient a-C films to differentiate from multilayer a-C films investigated in CHAPTER 4. Besides studying the as-deposited microstructure of the films, their microstructure changes after annealing would also be investigated. 3 sets of gradient film representing the various possible ways to create graded a-C films will be discussed. The 3 sets represent gradient films with an:

- 1) Increment density function,
- 2) Decrement density function, and

3) Mixed density function.

The microstructure studies were conducted by cross-sectional TEM, STEM EELS and Raman spectroscopy.

Due to the nature of the deposition system and the way the gradient a-C films were deposited, calibration of the deposition system for film uniformity was not possible. Therefore, although samples of the same set were deposited simultaneously, their thickness could vary. As such for direct cross-sectional comparisons between the samples of the same set, the thickness of the samples was proportionally varied to accommodate for the difference. This was done by amplifying the thickness through a direct multiplication (stretching) of the smaller length scale by a constant factor throughout the length. This is not expected to affect the study on the microstructure of the films since multiple TEM micrographs taken from different samples of the same set showed different thickness but had the same micro and macrostructure features. However comparison of the intrinsic stress measured (tabulated in Table 6-1) before and after annealing would not be accurate because their stresses would be affected by the difference in thickness. Therefore no comparative study would be done on the stresses of the films.

A point to note is the definition of “depth” in the later discussions. “Depth” in this study is defined as the measurement of thickness from the surface of the film to the point of interest. That is, a depth of 0 μm represented the surface of the film.

6.3 Films fabrication

The term gradient a-C film was used to describe the graded a-C films because their internal density varies as a function of depth in the films. In essence, their internal microstructure (specifically their density) had a gradient profile. To create these density gradients in the films, the C⁺ ion energy were continually varied during the deposition by changing the substrate voltage bias.

The gradient a-C films prepared in this study were deposited by an OPDB-FCVA system coupled with a dc substrate biasing system. The dc bias is operated via a separate computer terminal using a self-coded software to run various voltage functions during deposition. Typically voltage changes could be programmed to within ± 0.1 V. To create the desired density profile in the gradient films, the dc bias system was first preloaded with the voltage function (with respect to time) and set to run simultaneously during deposition.

Due to the dc bias involved in the operation, the substrate heats up substantially faster than with using pulse voltage bias. To prevent excessive heating of the substrate, continuous depositions were limited to a maximum of 1 min. After each minute of continuous deposition, the substrate was allowed to self-cool in the vacuum chamber for another 1 min before the next deposition cycle. These self-cooling periods are termed “breaks” and reflected in Figure 6-2.

Figure 6-2 Voltage (negative) variation during the deposition of different gradient films. **A.** Voltage variation for set 1. (Density increment function) **B.** Voltage variation for set 2. (Density decrement function) **C.** Voltage variation for set 3. (Mixed density function)

Three sets of films were fabricated in this study. Each set of films contain various samples with each sample approximately 15 mm by 15 mm in size. All samples of the same set were deposited simultaneously to ensure that deposition conditions were the same for all samples in the set. The substrate voltage profile during deposition for each set is shown in Figure 6-2. The initial high constant voltage during deposition for set 2 and 3 was done to create an initial low stress layer. This was done to create an initial “cushion” for better

adhesion and to absorb the exceeding large stresses during the deposition of films in set 2 and 3. Earlier experiments to create gradient films (with profile from set 2 and 3) without the initial layer were not successful as the films would either be partially or totally delaminated before any substantial thickness could be achieved.

To determine the annealing characteristic of the films, selected samples from each set would be annealed for 10 min at a set temperature in the RTA. The classification of the various gradient a-C films and their annealing conditions (if any) is given in Table 6-1. It should be noted that all the samples represented different films. For example, X1, X1-400 and X1-600 are three different samples of the same set and thus their differences in film thickness.

Table 6-1 Deposition conditions for the various different gradient films

Set	Density function	sample code	Annealing temperature (°C)	Film thickness (nm)	Film stress (GPa) (± 0.5)
1	increasing density	X1	-	238	9.8
		X1-400	400	200	7.8
		X1-600	600	109	5.3
2	decreasing density	X2	-	232	7.4
		X2-600	600	287	4.9
3	mix density	X3	-	215	7.5
		X3-600	600	291	3.2

6.4 Micro and Macrostructure of Gradient a-C films

6.4.1 Density increment film

Sample X1 was prepared according to conditions specified in Table 6-1 and Figure 6-2. No indication of delamination was observed. The intrinsic stress measured was ~ 9.8 GPa and the film thickness was approximately 238 nm. Since the film was deposited with a gradual change of ion energies, the internal film structure was expected to vary smoothly across the depth of the material. Figure 6-3 A, shows the cross-sectional TEM micrograph of the as-deposited X1 film. Clearly the smooth transition (of material internal structure) expected from the a-C/Si interface to the surface of the film was not present; instead there were “irregularities” throughout the film’s internal structure. A layered structure similar to those of multilayer films was observed throughout the entire depth of the film. The discrete ordering of these layers was unusual since unlike multilayer a-C films (see

Figure 4-2) where layering were intentionally engineered into the structure of the film by varying the ion energy in discrete steps, X1 was deposited with continually (linearly) decreasing ion energy.

Figure 6-3 A. Cross-sectional TEM micrograph of sample X1. The Si/a-C interface is on the left and the film surface is on the right B. Selected area diffraction pattern of sample X1. Diffused rings and strong arcs are present indicating crystalline structure present in the amorphous matrix.

Figure 6-3 B showed the selected area diffraction pattern (SADP) of the cross-sectional film. The diffraction pattern is correctly aligned with respect to the image in Figure 6-3 A. From the SADP, two features were clear. The first was the diffused rings expected with amorphous materials and the second were two strong arcs present in the vicinity of the graphite-like $\{002\}$ reflections. These arcs indicated the presences of orientated graphitic material with their basal planes normal to the substrate.[36, 107, 226] From the SADP, it could be deduced that there was some measure of medium range order within the amorphous carbon matrix.

To locate the oriented graphitic material within the film's structure, a dark field (DF) image was taken with an objective aperture positioned over one of the arcs. The DF image is shown in Figure 6-4, where the orientation of the image

is the same as those of the bright field (BF) image taken in Figure 6-3 A. The brighter regions (higher intensity) in the DF image corresponded well with the observed layering in the BF image in Figure 6-3 A. From this, it could be deduced that the film consisted of at least 2 types of microstructure. The brighter regions in the film's TEM macrograph corresponded to the oriented graphitic material while the darker regions corresponded to isotropic a-C.

Figure 6-4 Dark field cross-sectional TEM micrograph of sample X1 with the objective aperture over one of the arcs observed in Figure 6-3 B.

To investigate the “layering” closer, a higher resolution close-up image was taken and depicted in Figure 6-5 A. The orientation of the image was consistent with the earlier images. The two bands of layers were clearly visible in the micrograph. Aligning this image with the earlier DF (see Figure 6-4) image, it can be confirmed that for the close-up image, the brighter regions

consisted of the oriented graphitic material while the darker regions were of isotropic a-C. The insert Figure 6-5 B showed a high resolution image of one of the lighter bands further proving the presence of the aligned graphitic material.

Figure 6-5 A. Close-up cross-sectional TEM micrograph of sample X1. B. High resolution TEM image of aligned graphitic region. Measurements in red indicated the thickness of the aligned region. Measurements in blue outlined the mean distance between each aligned region.

On visual inspection, the aligned layers did not seem to be randomly distributed across the thickness of the film but rather follow a predictable trend. It was clear from the image that the region nearer to the substrate has a higher concentration of the aligned material compared with the top of the film. The size of the aligned regions also showed a decrease in width as it progresses towards the top of the film. Using ImageJ (imaging software) to calculate the exact

dimensions of the various layers, two observations could be made on the periodic distribution of the aligned layers. First the volume (as measured by cross-sectional thickness in red) of the aligned layers increases with respect to the depth of the film. In fact, the measured increase was almost linear. Second, by studying the position of the align layers with respect to depth, it could be quantitatively verified that the layers were periodically (equally) distributed. From Figure 6-5 A, the distance between each aligned layers were shown to be ~30 nm with the distance (full blue lines) taken from the center (dotted blue lines) of each layer.

This observation of non-random distribution represented a possible methodology in the deliberate introduction of aligned graphitic material in an otherwise amorphous matrix. More importantly, this could bring about the fabrication of devices based on oriented graphite that are embedded in a-C. As such their growth mechanism deserves a more in-depth study.

To examine the microstructure further, a plasmon energy spectrum across the middle of the cross-section of the sample was shown in Figure 6-6. A gradual density increment from the a-C/Si interface to the top of the film was evident in the figure (the methodology used to calculate the mass density from the Plasmon energy us given in CHAPTER 3 section 3.4.2). This confirmed that the film was of a gradient nature and the density was indeed varied by changing the ion energy during deposition. However, the gradual increase of density was also interrupted periodically by abrupt drops in density. These abrupt changes

in density were not unexpected since earlier TEM images had already identified regions of aligned material interspaced periodically across the depth of the film.

Figure 6-6 Cross-sectional plasmon energy line scan across the middle of X1. The density variation calculated from the plasmon energy is also shown.

To assess the relationship of the quantitative measured abrupt changes in density with the qualitative observed layering or bands in the TEM image (see Figure 6-5 A) shown earlier, the two figures were correctly aligned and superimposed in Figure 6-7. From this figure, the brighter bands correlated with the abrupt density changes perfectly. From the figure it can be confirmed that the abrupt changes were indicative of the aligned graphitic layers.

Figure 6-7 Plasmon energy/density versus depth of the film X1, superimposed onto its cross-sectional TEM micrograph.

To explain the various observations made on X1, the mechanism for the formation of self oriented graphitic material within the film must first be discussed. The mechanism for the formation of oriented materials in uniform films was reported by D. R. McKenzie et al [281-283] on the basis of energy minimization of the Gibbs free energy. They hypothesized that for materials with elastically anisotropic molecules, certain orientation of the molecules with respect to the macroscopic structure would be preferred as the total energy (bulk strain energy, surface energy and interface energy contributions) of the system could be minimized.

In their theory, the formation of preferred orientation was determined by two distinct factors. The first is the atomic mobility of the material network. This

factor would determine the available atomic configurations for the material system. During deposition and in the absence of deliberate substrate heating, the mobility of the surface atoms is largely only affected by the kinetics of the incident ions. This is because in the absence of other excitation sources, the surface atoms could only inherit the increase in mobility from the energy transferred due to the thermal spikes (See page 17) generated during ion bombardment. Therefore, the higher the ion energy, the greater is the mobility of the surface atoms. This factor is usually discussed in terms of deposition temperature, T_{dep} , since it is closely related to atomic mobility during deposition. As such further analysis would be discussed in terms of T_{dep} .

Elevated T_{dep} (either through higher ion energy bombardment or direct substrate heating) during deposition had always been an important factor in the alignment of graphitic material in a-C films.[47, 284] Critically, the transition temperature, T_s , need not be high (<150 °C) for the formation of alignment where the basal planes are perpendicular to the substrate.[105] Simulations by N. A. Marks[284] indicated that during deposition with ion energy at -70 eV and high substrate temperatures, the initial high density ta-C growth could switch abruptly to an almost 100% highly oriented sp^2 film with low density. The abrupt change occurs once the T_{dep} reaches T_s .

The second determining factor is the substrate thermodynamic effect such as the intrinsic stress field generated during deposition. This would determine the preferred orientation of the anisotropic molecules. In the case of highly stressed thin films, where the overall energy of the material have a large

contribution from elastic strain (Equation (2-4)); Significant overall energy minimization could be achieved by the pre-disposition of atomic configurations that offers strain relief. Therefore, in highly stressed materials (with elastically anisotropic molecules), the stress field would be a significant factor in the preferred orientation of its molecules.

The adequacy of McKenzie's model to explain the preferred orientation of graphitic domains in a-C was later verified by MD simulations conducted by N. A. Marks et al[284]. Their simulations demonstrated the combined importance of relaxation on the picosecond scale (thermal spike self-annealing) and the millisecond scale (thermally-activated rare events), and showed that oriented sp^2 structures arise only when sufficient thermodynamic progress is made towards lower energy configurations. The structural phase that appears is the one that has the minimum energy under the stress (strain) conditions during the thermal spike and subsequent relaxations.

Although there are other theories on the formation of the preferred orientation of anisotropic materials (such as sputtering[285] and channelling[286]) the theory based on the elastic strain energy seem to best describe the current observations on the gradient samples.

Adopting McKenzie's theory, the observed formation of aligned graphitic regions in X1 can thus be explained as follows: As with uniform a-C films deposited with ion energy ranging between 100 – 1000 eV, X1 was deposited with high intrinsic compressive stress (see section 2.2.1 and 2.2.2). Therefore if the material network has a substantially high T_{dep} (or when the T_{dep} approach

T_s), the anisotropic sp^2 hybridised carbon molecules would have enough mobility to be oriented in such a way as to reduce the overall energy of the film (substrate thermodynamic effects).

Since X1 was deposited with continually changing ion energy, this meant that the T_{dep} of the film was also continually varying, and the T_s could be crossed multiple times during deposition. The entire process was also further complicated by the deliberate interruptions (breaks) during the deposition. Due to the breaks, the deposition had to be view as separate periods (8 periods in all for X1) in-between breaks. To facilitate the discussion, the periods would be labelled from 1 – 8. With period 1 defined as the period closest to the Si substrate (beginning of deposition).

Each period would start cold (room temperature, low mobility) and get heated up (increase in mobility) by ion bombardment during deposition. This meant the T_{dep} of the a-C film started low at the beginning of each period and increased during the duration of the period. Additionally, the rate of increase of T_{dep} within each period would be proportional to the ion energy during deposition for that period (assuming constant deposition rate). Since the ion energy was decreased gradually throughout the deposition of X1, the rate of increase of T_{dep} would be slower with subsequence periods (i.e. period 1 heats up faster than period 8 in X1).

Growth of isotropic a-C would be predicted to switch abruptly to oriented graphitic layers once the T_{dep} crosses the T_s during the deposition. Therefore each period (layer in the film) would start as isotropic a-C and when the T_s was

crossed during deposition, the growth would revert to an oriented sp^2 configuration. This model would predict that for X1, the isotropic a-C layer within each period would get thicker with subsequence periods. This is because, as mentioned earlier, the T_s would be crossed faster in the earlier periods compared with the later ones. From the TEM images of X1 (Figure 6-5 A), it can be observed that the initial a-C portion of the periods indeed got progressively thicker with subsequence periods. This confirmed the prediction of the model. Furthermore, the model would also explain the seemingly periodic distribution of the aligned layers in X1. Clearly the reason for the periodic arrangements lies with the controlled deliberate breaks during deposition. Moreover, the density drops associated with the graphitic alignments observed in Figure 6-7 also verified the change of the a-C to lower density oriented sp^2 sheets according to N. A. Marks' simulation.

A similar observation was also reported by C. A. Davis et al[287] when they did EELS analysis on the cross-section of an a-C film deposited with elevated substrate temperatures. They observed that although the a-C film was deposited at a constant energy level of 90 eV, the sp^3 fraction of the film was not constant throughout the entire film. In fact, the sp^3 fraction of the film was observed to be significantly higher at the bottom of the film (near the substrate) than near the surface. They attributed this to the temperature increase (due to ion bombardment) during the deposition process, hypothesising that as the temperature of the substrate increases beyond certain a transition temperature the sp^2 bonds would no longer be converted to sp^3 bonds. (In their paper, they adopted the ion subplantation model for the formation of sp^3 bonds in the a-C

film) Moreover, they also observed an increase in the long range ordering of the sp^2 rich regions which they attributed to the increase in the atom mobility in the region of the ion bombardment. As such, their hypothesis although slightly different from the one presented here shares very similar deductions and predictions based on the substrate temperature effects during film growth.

After the initial investigation of as-deposited X1, ex-situ thermal effects were studied next. X1-400 and X1-600 were representative of X1 after annealing at 400 °C and 600 °C respectively. Figure 6-8 shows the Raman spectra of X1, X1-400 and X1-600. The spectra have been displaced vertically for clarity, but otherwise are displayed using the same vertical axis. Before the discussion on the Raman spectrum of the films, it is worth noting that unlike cross-sectional EELS which could give the exact micro-structural properties at different thickness of the gradient films, the Raman data obtained could only be used as an overall general description of the entire film.

The spectra of X1 and X1-400 were comparable and could be fitted with a single BWF lineshape. The G peak positions for X1 and X1-400 were 1559 cm^{-1} and 1563 cm^{-1} respectively, indicating no significant G shift in their spectra. Also their coupling factors, Q were approximately the same at ~ -4 . From these results, annealing at 400 °C did not produce much change in the microstructure of X1. However changes in the spectrum of X1-600 were clearly evident. The spectrum could not be fitted with a single BWF lineshape and it was necessary to include a second lorentzian centred at about 1380 cm^{-1} (the D peak). The G peak had also shifted to 1585 cm^{-1} and the Q decrease to ~ -6 .

In all, from the Raman spectra, the films all had relatively intermediate value of Q which is indicative of relatively higher sp^2 content in the films when compared with ta-C (typically a Q of less than -20 is indicative of sp^2 content of less than 20%[202]). In addition, the evolutions of the D peak and G shift for X1-600 hinted at the formation of graphitic clusters after a 600 °C anneal. For more exact microstructure studies, X1-600 was subjected to further study by STEM EELS.

Figure 6-8 Raman spectra of X1, X1-400 and X1-600. The spectra are fitted by a BWF and lorentzian for the G and D peak respectively.

The TEM micrographs and SADP of X1-600 is shown in Figure 6-9. The distinct layers observed in the as deposited X1 due to the deliberate breaks were no longer observable. A visual assessment of the micrographs indicated that the aligned graphitic region seems to have extended beyond the initial

separate layers into the bulk of the entire film. The strong arcs due to the {002} graphitic reflections were still present in the SADP and the DF micrograph with the objective aperture over the arcs confirmed that close to the entire film (80%) have been transformed into aligned graphitic material.

Figure 6-9 TEM micrographs of X1-600. **A.** Bright Field micrograph of X1-600 with selected area diffraction insert. **B.** Dark field micrograph taken with objective aperture over one of the arcs. (left Si substrate, right surface of film)

The cross-sectional plasmon energy spectra of X1-600 shown in Figure 6-10 was superimposed on the TEM micrograph shown in Figure 6-9 A. The density variation across the depth of the material corresponded well with the contrast features of the TEM micrograph. Similar to X1, the higher density regions of X1-600 still corresponded with the isotropic a-C while the lower density region corresponded with the aligned graphitic region. Overall the density across the thickness of the film seems to have stabilized into 3 separate regions.

Figure 6-10 Plasmon energy/density with respect to depth of the film X1-600, superimposed on its cross-sectional TEM micrograph.

To visualize the exact changes in microstructure after annealing, the density variation of both X1 and X1-600 was aligned (accommodating for thickness variation) and shown in Figure 6-11. It is clear that the density throughout the entire thickness of the film had decrease after annealing although the density gradient is still present in X1-600. From the figure, the amount of density change (decrease) is not observed to be uniform throughout the interior of material. The reason for this non-uniformity is unclear at present.

Figure 6-11 Density variation across the cross-section of X1 as-deposited and after annealing at 600 °C (X1-600).

The results from X1-600 are important as it shows a possible route to externally induce graphitic alignment in an otherwise amorphous film. This could possibly give rise to applications such as embedded interconnects. (Further elaborations on the application arising from the gradient carbon films would be given in later sections) Hence it is important to investigate further the nature of how ex-situ annealing could induce the formation of graphitic alignment in gradient a-C films.

To understand the nature of annealing on the gradient film, two separate processes would be discussed. The first is the lowering of the density of the film upon annealing. This is closely related to the formation of sp^2 bonds. The second is the increase of alignment observed in the bulk of the material after annealing.

It may seem unexpected at first that large changes in density were observed after annealing at only 600 °C since ta-C had been reported to be stable up to even 1100 °C.[77] However it should be noted that sample X1 and all the other gradient films fabricated by this study are not ta-C. In fact, much of their constitution consist of low density graphitic (sp^2 rich) regions as evident in Figure 6-3 and Figure 6-7. Hence the annealing behaviour of gradient a-C films should not be directly compared to that of ta-C films.

A good platform to discuss the behaviour of the gradient film during annealing would be through the ab initio CPMD liquid quench simulation plot discussed in section 2.4. For ease of discussion, Figure 2-3 is modified and reproduced here in Figure 6-12. The figure shows the total energy per atom relative to diamond for a range of a-C density produced using CPMD liquid quench calculation.

Figure 6-12 The energy per atom for a range of 125 atom amorphous carbon networks produced using ab initio Car-Parrinello MD liquid quench calculations. The zero energy is chosen to be the energy per atom of crystalline diamond calculated under the same simulation conditions. (reproduced from Figure 2-3) [65, 107]

During annealing the atomic mobility of the film will be increased and if the temperature is high enough, the entire system of atoms could re-arrange themselves structurally to reduce its total internal energy. From Figure 6-12 an a-C network could lower its total internal energy either through an increase or decrease of density. For a-C network with low densities such as point A on the figure, it will reduce its total energy through a further reduction in density as presented by the red arrow. However for a-C with an intermediate density range such as that of point B, two possible routes are open to the material network for

energy reduction. It could increase its density further, expressed by the green arrow, or overcome the initial energy barrier (the initial increase of total energy or “up-slope” on the curve) and lower its density further, represented by the blue arrow. The choice of the route by the material network would thus be determined by the annealing temperature as well as the original density of the network. For high sp^3 content ta-C with density at $\sim 3.0 \text{ g cm}^{-3}$, a high temperature would be needed before the initial energy barrier could be overcome and further density reduction is possible. This is the reason for the stability of ta-C in relatively high temperatures.

For the case of the gradient a-C films, there is no single point on the simulation plot that is representative of the whole film; instead a partial range of density in the x-axis is representative of the range of density within the gradient films. However, considering that almost the entire volume of X1 film had a density lower than 2.6 g cm^{-3} and even the highest density measured was only $\sim 2.7 \text{ g cm}^{-3}$, it is thus expected that the density across the entire film would decrease after annealing at 600°C . Therefore the observed lowering of density in X1-600 was a consequence of the entire atomic network in the film reducing its total internal energy.

The formative mechanism of the perpendicular alignment of the basal plane of a-C to the substrate was explained earlier. In particular, 2 factors (atomic mobility and substrate thermodynamic effects) were highlighted. In the present case of induced alignment through annealing, the atomic mobility is no longer provided by the thermal spikes effects as there were no energetic ion

bombardments but is instead provided by the high annealing temperature. However, the main driving factor is the substrate thermodynamic effects, particularly the bi-axial stress of the material.

Studies on a-C multilayer films had shown that graphitic material oriented with their basal planes perpendicular to the substrate had spontaneously appeared after annealing at 600 °C when none were present earlier.[107] This was due to the strain in the film caused by the lowering of density in the low density layers. The alignment was a response to the build-up bi-axial stress field caused by the strain. The alignment was particularly dense near the interface between the high and low density layers. This was because the bi-axial stress was the largest at the interfaces.

By comparison, the gradient a-C film could be thought of as an enlarged interface between two a-C networks of different densities. Hence during annealing, a large bi-axial stress field would be built up (due to the lowering of density) within the bulk of the gradient film. The molecules having gained enough mobility due to the high temperature would thus re-configure themselves to best lower this strain. The observed expanded alignment regions in X1-600 was thus a consequence of the graphitic material orientating themselves to best minimize the strain due to the bi-axial stress.

After the detail discussions of the as-deposited and anneal characteristic of X1 it would be interesting to examine if the hypothesis regarding the gradient films could also be applied to sample X2 and X3. These films will be discussed next.

6.4.2 Density decrement film

Details of sample X2 preparation are tabulated in Table 6-1 and Figure 6-2. No indication of delamination was observed. The intrinsic stress measured was ~ 7.4 GPa and the film thickness was approximately 232 nm. X2 was designed to be a “mirror-reflected” image of X1 in terms of the fabrication process. Instead of the ion energy increment function of X1, it is designed with an ion energy decrement function. However, X2 is not a perfect reflection of X1 as it had an initial low density layer. Nevertheless, it would be interesting to examine the microstructure of X2 and X2-600 in reference with X1 and X1-600 respectively.

Figure 6-13 shows the TEM micrographs of as-deposited X2. The orientation of the films was the same as those of X1. The low density “cushion” layer was clearly seen as a distinct bright layer in Figure 6-13 A. From the contrast difference of the micrograph (across the depth of the film), it can be qualitatively observed that the film got more dense as it builds up. This is inferred from the figure as the regions closer to the substrate was darker compared to the regions near the surface. A quantitative assessment of this would be presented later from the cross-sectional plasmon energy spectrum.

Figure 6-13 Cross-sectional TEM micrograph of as-deposited X2. **A.** TEM micrograph of the whole cross-section with SADP insert. **B.** Partial close-up on the film showing distinct layers. **C.** High resolution image of one of the layers showing aligned graphitic material.

From the SAPD, the arcs due to the $\{002\}$ graphitic reflections were present confirming the presence of aligned graphitic planes within the film. Moreover, the micrographs also show the distinct layering first observed in X1. The layering observed in X2 was less prominent compared to X1 and they were only present in the top half of the film. From the close-up image in Figure 6-13 B and C, these layers were confirmed to be due to the aligned graphitic material. More importantly, the measured thicknesses of these layers were larger for layers closer to the surface of the film than layers near the substrate. This is in contrast to X1 (which had the opposite effect) and therefore in perfect

agreement with the hypothesis that the periodicity was controlled by the cooling intervals and ion energy during deposition.

From the cross-sectional plasmon energy spectrum of X2 superimposed on its TEM micrograph shown in Figure 6-14, the density distribution of the film was observed. As expected, the “cushion” layer at the a-C/Si interface was of low density. This layer was followed by a high density (2.9 g cm^{-3}) region that gradually decreased to a lower density of 2.0 g cm^{-3} at the surface of the film. This density variation profile confirmed the earlier visual assessment that the density was increasing with depth. Moreover, this also indicated that the film was indeed following a density profile that was purposefully design and engineered by the manipulation of the ion energy during deposition.

Figure 6-14 Plasmon energy/density versus depth of the film X2, superimposed onto its cross-sectional TEM micrograph.

Although the aligned layers were not clear on the background micrograph in Figure 6-14, the plasmon linescan clearly shows the same “irregularities” observed earlier in X1. These irregularities or sudden drops in density were associated with the regions of aligned graphitic layers. In addition, they were observed to increase in magnitude as the density of the film decreases which is in agreement with the earlier measured thickness variation of the aligned layers in the film. The same explanation given for the periodic layering in X1 could thus be used for X2. The annealing behaviour of X2 was examined next.

As X2-600 was representative of X2 after annealing at 600 °C they were both presented together. Figure 6-15 shows the vertically displaced Raman spectra of X2 and X2-600. None of the spectra could be fitted with a single BWF lineshape and it was necessary to include a second “D” Lorentzian peak centred at about $\sim 1380\text{ cm}^{-1}$. The G peak positions for X2 and X2-600 were 1577 cm^{-1} and 1588 cm^{-1} respectively, indicating a slight G shift after the anneal. The Q had also increased from an initial value of -20 for X2 to -6 for X2-600. The I_D/I_G ratio for X2 and X2-600 were 1.0 and 1.1 respectively. These results indicate that the as-deposited X2 film was at first relatively low in sp^2 bonds but increased its sp^2 content significantly after the 600 °C. The increase in the I_D/I_G ratio after the anneal also suggested a slight increase in graphitic cluster sizes after the anneal.[202]

Figure 6-15 Raman spectra of X2 and X2-600. The spectra are fitted by a BWF and lorentzian for the G and D peak respectively.

The Raman spectra were clearly different between X1 and X2 as evident comparing Figure 6-8 and Figure 6-15. For example, X1 have no indication of any graphitic crystallites before annealing but X2 clearly shows a strong presence of these crystallites as deposited. Since Raman spectroscopy could only probe the overall structure of the films; these differences in the spectra could not have been due solely to the differences in density profile. In fact, if both films were perfectly opposite but symmetrical in their macro-structure and density distribution, their Raman spectra would be expected to be very similar (Slight differences could be present due to the biasness of the Raman spectrum towards the top surface of the film).

Although it is possible that the initial low density layer was partially responsible for the difference, it is more likely that the difference was a consequence of a fundamental difference in how both films were formed. In the discussion thus far, the microstructure of the gradient films were thought to be controlled only by the ion energy during deposition, but it is also possible that the evolving substrate (the underlying a-C layer that was being deposited on) had some significant influence on the final structure. Factors such as the way the stress was build up during deposition are important parameters during deposition as well. This was evident during the fabrication process discussed in section 6.3 where it was explained that X2 films could not be fabricated without the initial “cushion” layer as the initial rapid stress build up would cause the film to be delaminated from the Si substrate before a substantial thickness could be achieved.

Figure 6-16 shows a collection of TEM micrographs of X2-600. From the BF image, the film seems to have consolidated itself into two distinct regions. The DF image taken with the objective aperture over one of the arcs is also shown in Figure 6-16 B. The DF image shows clearly the spread of the aligned layers in the top half of the film.

Figure 6-16 Cross-sectional TEM micrographs of X2-600. A. BF image of X2-600 with SADP insert. B. DF image of X2-600 with objective aperture on the {002} arc. High resolution mapping of the width and depth of the film was also shown. The scale bar for all the high resolution images are the same.

A high resolution mapping procedure was also used to examine the cross-section of the film. This was done to determine if the regions of graphitic alignment were sporadically distributed or “connected” as one continuous mass. The mapping was done by examining overlapping high resolution images. Some of these high resolution images were shown as inserts in Figure 6-16 with the same scale bar. Interestingly, the entire aligned region was largely continuous with only some patches of amorphous regions interspaced randomly within the aligned region.

The cross-sectional plasmon energy linescan of X2-600 is shown in Figure 6-17 superimposed onto its TEM micrograph. As with X1 after annealing at 600 °C, the density across the entire film had decreased. Moreover, the density distribution corresponded very well with the two distinct regions in the micrograph. The aligned region had an expected low density of $\sim 2.0 \text{ g cm}^{-3}$ while the isotropic amorphous region had a density of $\sim 2.4 \text{ g cm}^{-3}$. This is comparable with X1 where the aligned region generally has densities lower than 2.1 g cm^{-3} . Although much of the density gradient is no longer apparent in the aligned region of the film, a slight density gradient is still observable in the isotropic amorphous region.

Figure 6-17 Plasmon energy/density versus depth of the film X2-600, superimposed onto its cross-sectional TEM micrograph.

Thus far, although there are some unexpected differences between X1 and X2, many of the hypothesis originally made on X1 are holding true for X2 as well. After the investigation of both the density increment and decrement films, the next section will be on the analysis of a mixed film.

6.4.3 Mixed density film

Details of sample X3 preparation are tabulated in Table 6-1 and Figure 6-2. No indication of delamination was observed. The intrinsic stress measured was ~7.5 GPa and the film thickness was approximately 215 nm. X3 was a combination of both X1 and X2. As with X2, it had an initial low density

“cushion” layer. The film started (near the Si substrate) with a density decrement function followed by a switch at mid way to a density increment function. Characteristics of both X1 and X2 were thus expected within the microstructure of X3.

Figure 6-18 shows the cross-sectional TEM micrograph of X3 together with the SADP and cross-sectional plasmon linescan superimposed on the TEM micrograph. For consistency between Figure 6-18 A and B, both micrographs were oriented with the surface of the film on the left and a-C/Si interface on the right. This would be the orientation of all the micrographs shown in this section.

From the figure it could be observed that the film had layers of graphitic alignment clustered in the middle of the film. Since X3 was fabricated with lower ion energy at both extremes (surface and interface) of the film and higher ion energy in the middle (as evident in Figure 6-18 B), it is thus expected that majority of the graphitic alignment would be concentrated at the middle of the film.

Macro-structurally, X3 could be viewed as a combination of X1 and X2. The bottom half of X3 (near the substrate) could be viewed as X2 with the aligned graphitic layers concentrated at the top. While the top half (near the surface of the film) could be viewed as X1 with the aligned graphitic layers concentrated at the bottom. The macrostructure of X3 is thus exactly what was expected. Internal structural changes after annealing were discussed next.

Figure 6-18 Cross-sectional TEM micrographs of X3. Both images were aligned with the surface of the film on the left and a-C/Si on the right. **A.** BF image of X3 with SADP insert. **B.** Cross-sectional STEM plasmon energy profile superimposed on TEM micrograph.

The Raman spectra of both X3 and X3-600 were presented together in Figure 6-19. Both of the spectra were fitted with a BWF lineshape for the G peak and Lorentzian lineshape for the D peak. Although the intensity of the D peak for the as-deposited X3 appears to be negligibly small, attempts to fit X3 without the second Lorentzian was not successful. The G peak positions for X3 and X3-600 were 1573 cm^{-1} and 1586 cm^{-1} respectively, indicating a slight G shift after the annealing. The Q for both films was approximately the same at ~ 7 . These results indicated that there were some graphitic crystallites clusters in the as-deposited film and that after annealing, the crystal size increased slightly. The sp^2 content was also high for both X3 and X3-600. These results were expected since X3 is basically a combination of both X1 and X2.

Figure 6-19 Raman spectra of X3 and X3-600. The spectra are fitted by a BWF and lorentzian for the G and D peak respectively.

Figure 6-20 shows the cross-sectional TEM micrograph of X3 together with the SADP and cross-sectional plasmon linescan superimposed on the TEM micrograph. The DF micrograph was used in the background of the linescan as the contrast on the BF image was difficult to decipher directly. As expected, the SADP clearly shows the $\{002\}$ arcs. The DF image also indicated that the film was almost completely changed to oriented graphitic material. The only region that is still isotropic a-C was at the higher density regions (near the interface and surface of the film). Once again the observed micrograph of X3 was a direct combined image of X1 and X2 after annealing. In essence, the annealing characteristic of X3 was exactly as expected in a film that has elements of both X1 and X2.

Figure 6-20 Cross-sectional TEM micrographs of X3-600. Both images were aligned with the surface of the film on the left and a-C/Si on the right. **A.** BF image of X3-600 with SADP insert. **B.** Cross-sectional STEM plasmon energy profile superimposed on DF image.

These results do not just re-affirm the hypothesis made earlier regarding gradient a-C films; it has also indicated that the unique microstructure and macrostructure of gradient films were repeatable. This means that direct control of self-aligned graphitic layers within an isotropic a-C film could be established by fabricating gradients films with different density orientation. Ex-situ inducement of these aligned graphitic materials was also possible by annealing. This study thus path the way for devices and applications that could be directly built with a-C films.

6.5 Application of Gradient a-C films

After the analysis of the internal structure of the various forms of gradient a-C films, two important implications could be drawn from the results. First, the internal structure (specifically the aligned regions) in the gradient a-C film could be manipulated by controlling the deposition temperature and density gradient. In fact, the gradient films could potentially be made fully aligned and without isotropic regions by careful control of the ion energy profile during deposition. Second, by applying thermal treatment, the aligned regions in the film could be expanded in a predictable way. This meant that by having localized annealing, specific regions on the films could be made aligned while leaving untreated areas still isotropic. This control of graphitic ordering in an amorphous matrix is very interesting from an engineering viewpoint because it opens up possibilities in many applications. The reason for this interest lies specifically with the unique properties of the self oriented graphitic layers.

These oriented graphitic planes are inter-wrapped densely packed graphite sheets (graphene), which is the strongest two dimensional structure known and has high in-plane thermal and electrical conductivity.[288, 289] For this reason, arrays of aligned CNTs with their axes normal to the plane of the array are being considered as heat sinks and electrical interconnects.[290] The oriented graphitic material shown in this study have all of the advantages of CNTs arrays without the limitations of low packing density, high deposition temperatures and the need for catalysts. As such, the gradient a-C films could be used as a platform to introduce aligned graphitic materials for use in vertical

interconnects. Figure 6-21 shows how the oriented graphitic material could be use in a vertical interconnect array via a CMOS-compatible process by growing oriented carbon films at room temperature.

Figure 6-21 Schematic process flow for the implementation of aligned graphitic material in VIA.

The first step of the process would be the patterning of the initial horizontal metal contacts and VIA holes. This would be followed by the deposition of gradient a-C designed so that only the top of the gradient a-C is still isotropic. The top isotropic layer is then polished off by chemical mechanical

polishing (CMP) and the second metal contact layer deposited to finish the electrical pathway.

Another possible application for the gradient a-C films is in embedded 3-dimensional conductive tracks. This uses the principle of thermally induced alignment of graphitic material in the gradient a-C films to build conductive tracks within the film. The process is explained in Figure 6-22.

Figure 6-22 Schematic process flow for the implementation of embedded conductive tracks.

The initial layer of metal contacts is first patterned followed by the deposition of the gradient a-C film. This gradient film would be designed with a

global conductive layer consisting of a layer of aligned material interspaced in relatively insulative isotropic a-C. Next, selected region of the film would be annealed with a high energy narrow beam laser. This would expand the aligned graphitic layer to link up with selected metal contacts closing the electrical pathways. Using this method, embedded multilayered 3-dimensional conductive tracks could be fabricated without multiple lithographic steps.

The methods and applications describe above are just two examples at the possible use of the gradient film in electronics. Besides interconnects, applications such as solid-state thermal drains and thermal pumps could also be investigated. Other applications in areas of mechanical coating and even N/MEMS are also possible.

6.6 Summary

The internal structure of density graded a-C films and their annealing characteristic were studied in detail in this chapter. The main focus of the investigation was to examine how the orientation of density profile in a gradient a-C film would affect the formation of aligned graphitic materials. The micro and macrostructure of the films were thoroughly examined by STEM EELS linescans, TEM micrography and visible Raman spectroscopy.

The 3 types of films investigated all had periodic layers of aligned graphitic materials in their film structure. A theory of how the aligned graphitic

layers were formed based on the deliberate self cooling breaks was given and confirmed to be compatible with all 3 sets of gradient a-C films studied.

The annealing characteristic the gradient films revealed that the aligned graphitic region could be “expanded” beyond its original boundaries. Furthermore, the periodic layers of aligned graphitic material observed in the as-deposited films had all become a single bulk layer of aligned material after the 600°C anneal. An explanation for the observed inducement of aligned material based on density lowering and energy minimization was given.

Overall, gradient a-C film prepared by the OPDB-FCVA in conjunction with substrate dc bias showed good potential for controlling aligned graphitic material in an otherwise isotropic a-C film. These gives rise to the possibility of various applications and devices that could be directly embedded in a-C films such as electrical interconnects, thermal pumps and heat sinks. Other possible use of the a-C gradient films such as structural materials in N/MEMS and advanced coatings should also be explored in the future.

CHAPTER 7 CARBON NANOMATTRESS

7.1 Introduction

The previous chapters (CHAPTER 4 - CHAPTER 6) had been centered on the discussions on hybrid carbon films formed through the manipulation of sp^2/sp^3 composition in a-C films. They represented carbon hybrids films fabricated by varying the concentration of the various hybridization modes available to a-C. This chapter would address a totally different kind of carbon hybrid material synthesized by fusing two completely different allotropies of carbon. In some sense, this new material epitomizes the meaning of carbon hybrid.

Tribological issues such as friction, wear and vibration in mechanical systems have plagued developers of mechanical devices since their earliest developments.[291] These problems are especially acute now in the rapidly advancing areas of N/MEMS due to the extreme surface to volume ratios these devices have. The traditional method to address these issues would be to integrate dampers and low friction materials together in the devices. However, unlike in macro environments, implementation of such protection on the sub-micrometer scale is either unfeasible or extremely costly in terms of fabrication complexity. A more feasible solution would be to use an intrinsic damping material that has a hard and low friction surface to lower wear for rubbing and

sliding contacts and yet has high compressibility and elastic properties for energy dissipation and load recovery. Finding materials with some of these individual characteristics is not difficult but fabricating one with all of them is almost impossible due to the conflicting nature of these attributes.

7.1.1 CNT films and CNT reinforced polymeric films

Composite polymeric films reinforced by CNTs as well as aligned CNTs films are possible candidates for the above problem. Cao et al,[292] demonstrated that freestanding films of vertically aligned MWCNTs exhibited super-compressible foamlike behaviour during uniaxial compression. Compression stress-strain curves also showed large hysteresis indicating substantial energy loss (damping) possibly due to the friction between the MWCNTs' surfaces during movement. Suhr et al [25] also demonstrated that epoxy films with MWCNTs fillers exhibited a 1400 % increase in damping ratio over the baseline epoxy due to interfacial shear. Both studies indicated that CNT films and its composite could potentially be used as intrinsic damping material within small scale devices.

However, the key weakness of these systems is their surfaces. Aligned CNTs film is not a "solid" continuous film but rather densely packed one dimensional CNTs held together through their common substrate and weak Van der Waals forces between the individual tubes (see Figure 7-1 A). Therefore once the CNT film is exposed to forces transferred through a sharp object (small area relative to surface of CNTs film) only a fraction of the CNTs on the

surface will effectively absorb the force, causing stress concentrations on the film (see Figure 7-1 B). Polymeric films reinforced with CNTs improve the stress distribution of the composite film through load transfer from the polymer to the CNTs network. However the composite films are highly dependent on the interface between the CNTs and the polymer for efficient load transfer and the composite themselves have no wear protection whatsoever as these films are generally soft due to their polymer base. [22]

Figure 7-1 A. Schematic of aligned CNT film. B. Stress concentration formed from a sharp force. The aligned CNTs directly below the force were deformed to accommodate to the force. Dimensions of the structures were exaggerated for clarity of presentation.

7.1.2 Carbon nanotube-Amorphous carbon hybrid

To overcome the weaknesses of CNT based films but yet still retain viscoelastic properties, a 2D on 1D approach was used to fabricate a unique 2 tier hybrid material consisting of a hard upper a-C layer fused together with an underlying aligned MWCNT film. This carbon hybrid structure is termed carbon nanomattress (CNM). The schematic of the CNM is shown in Figure 7-2.

Figure 7-2 A. Schematic of CNM. B. The Sharp force was redistributed to the entire CNT network below the a-C layer effective reducing stress concentrations on the CNM. Dimensions of the structures were exaggerated for clarity of presentation.

The CNM uses the top a-C layer as a hard and wear resistant surface for protection against sliding contacts while simultaneously using the bottom elastic

aligned MWCNTs layer for vibration damping and shock absorption. Despite the unique properties of the CNM, it is fabricated without resorting to complicated system processes. Moreover, the fabrication method of the CNM uses the same platforms as that for synthesizing MWCNTs and depositing a-C films which are both scalable for industrial adoption. In short, the CNM fulfils many of the requirements needed for a solution to resolve problems associated with tribology at the sub-micrometer scale. It is also worth noting that before the author published his findings, this hybrid material has never been reported in the literature.

7.2 Experimental Objective and Scope

The CNM is a new material with many of its properties still currently unknown and could only be inferred from the characteristic of its component materials. The characterization of the CNM is also made more difficult due to its unique material structure. The reason for the difficulties lies with the limitations and assumptions of current standard mechanical characterization techniques for thin films. For example, hardness for thin films is usually derived from micro or nano-indentations, however for the case of the CNM, indentation experiments could not be performed as the underlying CNTs would absorb most of the forces. Even cross-sectional micro-structural studies by TEM EELS are extremely difficult since the CNM could not be prepared conventionally for TEM.

The purpose of this chapter is thus to serve as an introduction to the CNM, emphasizing primary on the fabrication method and micro-structure of the top a-C film. The last section of this chapter would also report on the potential application of this material.

7.3 Film Fabrication and Characterization

The CNM was fabricated in two stages. The first stage involves the growth of the underlying aligned MWCNT film on the Si substrate while the second stage creates the upper a-C layer. For the first stage, the aligned MWCNT film was grown on 100 mm Si substrate using Ni as the catalyst as described in section 3.2.2 of CHAPTER 3. The physical attributes of the MWCNTs such as length and diameter are controlled by the deposition time, forming gas flow and Ni catalyst thickness, sintering time and temperature.[187] A typical aligned MWCNT film grown on Si substrate is shown in Figure 7-3.

Figure 7-3 FE SEM micrograph of aligned CNT film grown on Si substrate. The average height of the CNT film is $\sim 7\ \mu\text{m}$ with average diameters of $\sim 200\ \text{nm}$.

The second stage of the fabrication process involves the growth of the a-C on top of the MWCNT film. This was achieved by directly coating the aligned MWCNT film with a-C using the OPDB-FCVA described earlier. In order to confine the coating to just the top of the aligned MWCNTs and not throughout the length of the nanotubes, a negative substrate pulse bias (Pulse parameter 3000 V, 600 Hz, 25 μs) is employed during deposition. Due to the substrate bias, the carbon ions are attracted primarily to the tips of the MWCNTs forming elongated a-C nano-spheres as shown in Figure 7-4. These nano-spheres were formed by the continuous coating of the tips of the MWCNT by the carbon plasma. From Figure 7-4, it can be observed from the top and side view of the nano-spheres that they are conical shaped with a semi-circular top.

Figure 7-4 SEM and TEM micrograph of elongated a-C nano-spheres. A. Cross-sectional SEM micrograph of the partially coated CNT film. B. Close-up on the CNTs. The tips of the CNTs are observed to be coated with a-C forming the elongated conical shaped tip. C and D. SEM top view of the spheres. E. TEM micrograph of the side view of one of the spheres. The Ni catalyst is still attached to the base of the sphere. F. TEM micrograph of the top view of the sphere.

With prolong deposition, the spheres will increase its size and eventually overlaps with each other and coagulates into a solid film. Figure 7-5

chronographs the growth of the spheres with deposition time showing the growth and eventual coagulation of the a-C film. It should be noted that the time needed for the formation of the top a-C layer is dependent on the size and density of the underlying MWCNTs as well as the intensity of the carbon plasma. As such, the time needed for complete formation of the top a-C layer is different for different aligned MWCNTs samples.

Figure 7-5 SEM micrographs showing the growth of the a-C top layer of the CNM. All the micrographs were taken with the same scale bar of 500 nm and could be compared directly. The average diameter of the a-C nano-spheres were indicated below each micrograph.

After the a-C nano-spheres have completely coagulated together, the top surface of the aligned MWCNTs would then become a relatively flat surface for further a-C depositions. Moreover, with subsequence deposition, this top layer could thicken considerably without delamination. Typically, the top a-C layer could be deposited to 5 – 8 μm thick. The cross-sectional micrograph of a fully formed CNM is shown in Figure 7-6. From the figure, a dense upper layer of a-

C ($\sim 5\ \mu\text{m}$) is observed attached to the top of the MWCNT film. The MWCNT below the a-C top layer were visibly uncoated by the carbon plasma.

Figure 7-6 Cross-sectional FE SEM micrographs of completed CNM. A thick layer of a-C film can be observed attached to the tips of the aligned MWCNT film.

To verify that the top layer of the CNM was indeed a solid continuous film, a CNM sample was intentionally damaged by scraping the top of the film using a pair of tweezers. Figure 7-7 shows part of the damage areas. As can be observed, the top layer of the film was cracked in insert A and peeled off in insert B. Importantly, from these figures, it can be observed that the a-C film on top of the aligned MWCNTs was indeed a solid layer and not just compacted a-C nano-spheres.

Figure 7-7 SEM micrograph of CNM with deliberate damage. A. The top layer of the CNM was cracked. The underlying MWCNTs on the right portion of the CNM could be observed to be bent slightly. B. Solid chunks of the a-C film were peeled off.

After the top layer of the CNM was verified to be a continuous film, its microstructure was determined next using Raman spectroscopy. The Raman spectrum of the CNM top surface is shown in Figure 7-8. The spectrum could be fitted with a single BWF lineshape with the G peak position at 1559 cm^{-1} with Q at ~ 6 . The G position and Q could not give a definitive value for the exact concentration of sp^2 content in the film, however by comparing the Q value and G peak position with the values consolidated by S.Prawer,[202] it is likely the sp^2 content is between 30 %-40 %, which is typical of a-C films produced by the OPDB-FCVA with the substrate bias conditions used. This confirmed that the top layer was indeed a hard a-C (DLC) film.

Figure 7-8 Raman spectrum of the top surface of the CNM.

The CNM was designed such that the upper a-C layer would provide a hard and wear resistant surface while the underlying MWCNT would provide for shock absorbing and damping properties. Therefore when the CNM is subjected to a large concentrated force; the upper a-C layer would transfer the load to the underlying MWCNTs which could temporarily deform to absorb the force (See Figure 7-2 B). However one of the concerns of this method is the high structural toughness of the MWCNTs. Estimates of the Young's modulus of CNTs using theoretical calculations as well as experimental measurements put the figures at an average of 1 TPa,[293-295] which is much higher than even ta-C. As such, with large concentrated forces, the top a-C could be damaged before the MWCNTs start to deform.

One method to address the above concern would be to fabricate the CNM with aligned MWCNTs films that have high porosity (low density) and

individual tubes having high aspect ratios. With fewer tubes supporting the top film, the ratio of the a-C film surface area to that of the total MWCNTs' axial area would increase. As such, any vertical compression stress on the top a-C layer would be increased when transferred to the underlying MWCNT film. Furthermore, with more slender tubes, the MWCNTs would be more likely to bend with a smaller axial stress. Therefore a CNM fabricated using a low density MWCNT film with thin tubes, would likely cause bending of the MWCNTs first before inducing any deformation to the a-C layer during vertical loading.

During vertical compression, two changes are expected within the CNM.

- i) Change in the structural properties, geometry and lateral free space between the MWCNTs.
- ii) Change in the nature of interaction between the individual MWCNTs, including interface adhesion and energy dissipation due to entanglement and impedance of the CNTs during movement.[292]

Therefore, most of the elastic properties of the CNM would be dependent on the physical dimensions of the MWCNTs since the dimensions determine the stiffness of the MWCNTs. While the damping properties would be dependent on the interaction between the MWCNTs as energy dissipation are a result of the frictional losses due to the rubbing of the MWCNTs with each other.[25, 292]

From the above discussions, the viscoelastic properties of the CNM would be largely dependent on the density of the CNTs within the film as well as the physical dimensions and type (single versus multi-walled) of the CNTs. Hence it should be possible to fabricate CNM with various damping as well as shock absorbing properties that can be controlled by the dimensions of the CNTs and their area density. Since controlling these parameters of the CNTs is already well established, the fabrication of specific films, each with its own unique damping characteristic should be feasible. The CNM is thus a hybrid material with tunable intrinsic viscoelastic properties protected with a hard a-C outer layer.

7.4 Application of Carbon Nanomattress

As a material system with tunable viscoelastic characteristics and an ultra hard and wear resistant outer surface, the CNM is a suitable material for protective coatings in mechanical devices and in N/MEMS. The CNM is especially useful in devices requiring not just wear resistance but also shock protection and mechanical damping. Besides applications in protective coatings, the CNM could also be use as structural elements in devices as well. This is accomplished by using stiffer underlying MWCNTs (by forgoing the viscoelastic properties) to create more rigid CNM structures. Furthermore, the CNM could also be stacked up to form multilayered structures as well.

Moreover, the formation of the a-C film on top of a semi-rigid substrate also provides for an interesting alternative for coating thick a-C films. One of the main problems with as-deposited a-C (especially ta-C) was its intrinsic compressive stress which limits the thickness of the coating. By using the CNM approach, ultra thick as-deposited ta-C could be achieved. This is done easily by first using a high substrate bias during the initial deposition period to form a thin coagulated a-C surface on the MWCNTs. After which, high sp^3 content ta-C could be deposited on top of this elastic surface by changing the substrate bias to -100V while the carbon deposition is still ongoing. In this way, a thick layer of ta-C could be coated without delamination as the underlying MWCNTs substrate would act to “cushion” the high stress of the top ta-C film by deforming while still adhering to it.

7.5 Summary

This chapter primarily reports on the fabrication of a unique 2 tier carbon hybrid material termed CNM. The CNM was fabricated by a 2D on 1D approach through fusing a hard upper a-C layer together with an underlying aligned MWCNT film. This was done by directly coating the tips of the MWCNTs with a-C using the OPDB-FCVA with high substrate bias. The carbon hybrid material fabricated this way has both the advantage of a hard and wear resistant surface due to the a-C top layer, as well as intrinsic viscoelastic properties due to the MWCNTs film. Applications for this new material range from sub-micrometer mechanical protection to N/MEMS.

CHAPTER 8 CONCLUSION & RECOMMENDATIONS

8.1 Conclusion

Three different types of carbon hybrid material systems were discussed in this thesis, including multilayer a-C films, gradient a-C films and the CNM. The investigation of these materials represented the extension of the work on composites whose constituent components are based solely on carbon materials. Different aspects of these carbon hybrids had been investigated including, synthesis techniques, micro/macro-compositions, mechanical, tribological and thermal characteristics.

Under the investigation of multilayer a-C films, the mechanical, tribological and thermal properties of thick 1 μm continuously deposited films were investigated thoroughly. This investigation revealed that relatively low stress multilayer a-C films, with mechanical and tribological properties comparable to ta-C could be achieved by controlling the layering composition (within the multilayer a-C films) in conjunction with short (3 min) and low temperature (200 °C) annealing. Critically, due to the low annealing temperature needed to lower the stress of the films, MEMS devices based on multilayer a-C films could be fabricated using standard lithography. As a proof of concept that this was possible, various MEMS structures using multilayer a-C films were simulated and fabricated as well.

This thesis also demonstrated the growth of gradient a-C films through a continually changing substrate bias during a-C deposition by the OPDB-FCVA. The internal density of this type of carbon hybrid film was shown to be continuously varied throughout the thickness of the film, in accordance to the bias voltage profile set during deposition. Importantly, vertically (with respect to the substrate) self-aligned graphitic materials were observed within the a-C material both as-deposited and after annealing. The investigation also revealed that the density profile (and deposition conditions) in the films would affect the location of the aligned graphitic material within the amorphous matrix. Annealing at 600 °C was also shown to promote further alignment of the graphitic planes. Lastly this thesis also reported on the fabrication techniques needed to synthesize the CNM.

All in all, this thesis has contributed to the field of material science by extending the work multilayer a-C films and introducing two new carbon hybrid materials. Truly, from the work reported here, the prospects of developing composite based on only carbon materials are enormous and as such, work on this area should be extended.

8.2 Recommendation for future research

It is evident in this thesis that the investigation on all three carbon hybrid materials exhibit good prospects in various applications. Further work in the

fundamental research and applications of these materials and other carbon-carbon hybrids is therefore highly recommended.

The study of the multilayer a-C films have shown that the evolving a-C film is highly dependent on the substrate temperature during deposition and further studies into the substrate heating effects on the films would be very useful. In addition, the mechanical, tribological and thermal properties of multilayer a-C films have also been shown to be excellent for MEMS applications. Moreover the fabrication of simple MEMS structures based on multilayer a-C films were also shown to be feasible. Therefore the next recommended work on this material is towards fabricating actual working MEMS devices which could leverage on the excellent mechanical properties of the composite film. MEMS such as micro-actuators, gear assemblies and comb-drives are suitable candidates. However, before this could be realized, some issues regarding the fabrication techniques must be addressed. Thus far, this thesis had only reported on the use of a “lift-off” method to create MEMS structures, but this surface technique would not be sufficient to build more complex structures requiring multiple masks. To truly be able to use the multilayer film for complex MEMS, direct etching of the film would be needed. Studies into the etchant and process parameters needed would thus be useful. One point to note is that since the multilayer film is non-uniform in nature, precise control of etch-rates using chemical means would be difficult. Therefore etching by reactive O₂ plasma such as those employed by deep reactive ion etching would be recommended.

Besides multilayer a-C films, the two new composite materials introduced in this thesis also shows great promise in engineering applications. From the micro-structural investigations of the gradient a-C film presented in this thesis, control of the self-aligned graphitic sheets within the isotropic a-C matrix was demonstrated to be possible by varying the ion energy of the carbon plasma during deposition. This result thus opens the possibility of using the remarkable properties of highly anisotropic graphitic sheets to build very novel applications. Embedded 3D interconnects based on highly oriented graphite and high thermal conductivity carbon coatings are just such examples. However, before this material could be used for these applications, their fundamental properties must first be determined. Properties such as thermal conductivity and electrical conductivity should be further evaluated. It would also be interesting to compare the properties of these aligned graphitic sheets prepared by the gradient a-C method, with aligned CNTs prepared by CVD techniques, which is also currently being developed for IC interconnect applications.

The gradient films should also be investigated for use in coatings for mechanical applications as well. This is because the gradient a-C films with vertically aligned graphitic planes should demonstrate higher hardness and elastic modulus when compared with typical a-C films. The reason for this lies in the ultra high in-plane elastic modulus of graphite, which in theory is higher than those of the C-C sp^3 bonds of diamond. As such, characterization of the mechanical properties of the gradient a-C film is highly recommended. Another aspect of the gradient film worth investigating is the effects of non-linear substrate biasing during the deposition of the film. The experiments conducted

so far only revealed the internal structure of gradient films produced via linear changes in the substrate bias. The effects of a non-linear change in carbon ion energy during deposition is still unknown and thus worth investigating.

The last hybrid material presented in this thesis has many areas to be studied as well. Although the viscoelastic properties of aligned CNTs films had been reported, no information is currently available for the properties when their top surface is rigidly confined, such as in the case of the underlying MWCNTs in CNM. A dynamic mechanical analysis of the viscoelastic properties of CNMs with different types of underlying CNTs would thus be an interesting study. Moreover, the viscoelastic response of multilayered CNM would be interesting as well. On a separate note, the CNM also presents an opportunity to study the growth of a-C on a non-rigid surface. Most theoretical and experimental studies conducted on a-C so far had been on a-C deposited on fixed substrates and as such had to deal with the bi-axial strain impose on the carbon network causing compressive stress. Using the CNM approach, a-C could be deposited on a “floating” substrate of aligned CNTs eliminating the effects of a rigid substrate thus enabling researchers to further understanding the growth mechanism of a-C without the influence of a bi-axial strain. This aspect in fundamental a-C research is very important and would help others in understanding better the mechanism of a-C growth and therefore is highly recommended.

AUTHOR'S PUBLICATIONS & AWARDS

Awards

1. **Institute of Engineers, Singapore Prestigious Engineering Achievement Award** (2007) for "Nano-engineered Carbon Hybrid Material Systems"

In recognition of an outstanding engineering project which has made significant contributions to Singapore's development

2. **Tan Kah Kee Young Inventors Award (Silver, Open Category)** (2008) for "Carbon Nanomattress"

Journals

Published/in press/accepted

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Preparation/revision/submission

11. E. H. T. Teo, M. Shakerzadeh, B. K. Tay, D. W. M. Lau, D. G. McCulloch, M. B. Taylor, J. G. Partridge, D. R. McKenzie, "Self-alignment of graphitic planes in composite gradient amorphous carbon films" (preparation)
12. E. H. T. Teo, M. Shakerzadeh, B. K. Tay, "Self-ordering of graphitic planes in an amorphous carbon matrix: Applications in embedded 3D interconnects" (preparation)

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