Silicon incorporated amorphous carbon films for BioMEMS application

Ong, Soon Eng

2008

Ong, S. E. (2008). Silicon incorporated amorphous carbon films for BioMEMS application.
Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/5286>

<https://doi.org/10.32657/10356/5286>

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Silicon Incorporated Amorphous Carbon Films for BioMEMS Application

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

2008

Abstract

Amorphous carbon (a-C) or most commonly known as diamond-like carbon (DLC) is traditionally used as a protective or passivation coatings. The prospect of a-C, specifically low stress or stress free film for use in microelectromechanical systems (MEMS) has stirred up quite an interest in the scientific community. In the as-deposited state, the material exhibits extremely high compressive stress. In order for the micromachined structures to work, the films must have very low stress and very low stress gradients. Preliminary studies have shown Si doping not only reduces the stress, it can improve the haemocompatibility of a-C as well. Therefore, Si doped a-C is suitable for MEMS devices in medical applications. Amorphous carbon containing Si (a-C(Si)) exhibits some very desirable characteristics. However, many concerns (mechanical, biological and microfabrication) are still unaddressed, and the fundamentals of the current research findings are still unclear. In order to understand this material and for its successful incorporation into biomedical MEMS devices, the influences of Si incorporation into a-C network are studied in detail in this project.

Amorphous carbon films containing different concentration of Si are deposited via magnetron sputtering of graphite and Si targets. Atomic bonding configurations are analyzed, and their influences on the mechanical and biological properties are studied. The best a-C(Si) in terms of its bonding and mechanical characteristics is selected to undergo thermal treatment in order to further study the temperature effect on the various properties and behaviors.

The incorporation of Si into the a-C network alters the atomic bonding configurations. C-Si sp^3 bonds form through breaking up C=C sp^2 aromatic ring bonding structures. Therefore, with increasing Si, C-Si bond concentration increases while that of C=C bond decreases, and the concentration of C-C sp^3 is not affected. Amorphous carbon film containing ~37at.% Si is found to have the highest sp^3 bonding fraction. Post-deposition annealing of a-C(Si37.6at.%) shows

that it has a better thermal stability than the undoped a-C. The undoped a-C starts to graphitize as early as 200 °C, while the atomic structure of a-C(Si) is stable until at least 600 °C. However, a-C(Si37.6at.%) film produced under high deposition temperature cannot exhibit the same stability.

Hardness and elastic modulus are found to decrease first but start to recover from ~16at.% Si. The reduction in hardness and modulus is attributed to the decrease in film density. When more Si is incorporated, the increase in higher strength C-Si and C-C bonds and decrease in the weak π bonds eventually compensates the initial decrease in film density and recovers hardness and modulus. High temperature deposited a-C(Si) has poor and deteriorating mechanical hardness with increasing deposition temperature while room temperature deposited same coating is stable till ~600 °C in post-annealing. The findings are closely related to the atomic bonding behavior under the two different thermal processes. The residual stress of a-C is compressive, and is able to decrease with Si incorporation. The residual stress of a-C(Si37.6at.%) is found to be completely relaxed at around 600 °C with a release of 0.3 % strain.

The haemocompatibility of a-C(Si) is improved when the Si concentration is increased as quantified by human blood platelet adhesion assay. The total surface energy is found to be decreasing until ~16.6at.% Si. Below this concentration, the haemocompatibility improves due to the increase in sp^3 fraction. Beyond this concentration, increase in Si causes increase in polar to dispersive surface energy component ratio. The negatively charged polar component will discourage preferred affinity of platelets and proteins; as a result, haemocompatibility is also improved at high Si concentration. However, haemocompatibility deteriorates when a-C(Si37.6at.%) film is subjected to thermal annealing. Both COS7 fibroblasts and MG63 osteoblastic cells can adhere, spread and proliferate well on a-C and a-C(Si) films. The more hydrophilic film a-C(Si37.6at.%) is more conducive for cellular growth when the count is highest at

the end of the incubation period. The cell morphologies also indicate good initial attachment on the film surface, as well as a healthy growth leading to colonization.

Amorphous carbon and a-C(Si37.6at%) films have been incorporated into a Nitinol/a-C hybrid micro-cage to demonstrate the feasibility for such films to be micromachined. The actuation power or force, and response during thermal actuation for the a-C(Si)/TiNi/a-C trilayer film are higher than that of a monolayer TiNi. Although the cage is not fully closed as desired, it is able to be actuated (opening and closing) through thermal cycling between room temperature and $\sim 90^{\circ}\text{C}$.

It is known that the incorporation of a secondary element can reduce the residual stress of a-C. Such doping however can also decrease the hardness and elastic modulus of the material irreversibly. Si is identified as a candidate for this project due to its tetrahedral bonding nature (diamond-like bonding) and its carbide is the only one that is biocompatible. Results from this project shows that it is possible to lower the residual stress of a-C, and also possible to maintain and/or even better its hardness and elastic modulus; and it is as simple as increasing the Si concentration in the amorphous network. The resulted film is not only thermally stable; it is also haemocompatible and it exhibits no apparent cytotoxicity towards living biological cells. In addition, it can also be micromachined. The basis for the material properties and behaviors have been systematically analyzed and solved, while others have failed to do so. The most promising candidate for BioMEMS application is a-C with ~ 37 at.% of Si. However, the thermal treatment can sacrifice a certain degree of biocompatibility. Si concentration above ~ 40 at.% will not be studied in this project as at this concentration, amorphous silicon carbide phase will be present. Investigation on the incorporation of this secondary phase will take on a different approach, thus is out of the scope of this project.

Acknowledgement

The author wishes to express his sincere and deepest gratitude to supervisor Professor Sam Zhang and co-supervisor Associate Professor Du Hejun for their invaluable guidance and support.

Much appreciation also goes to Dr. Fu Yongqing and Dr. Jack Luo (University of Cambridge, UK) for their continuous support and collaborations.

The author gratefully acknowledges Dr. Tan Lip Kun, Sister Joanna and staff nurse Susie of National University Hospital, Blood Donation Centre for their help in the preparation of the platelet-rich-plasma. And most sincere thank to Dr. Ma Lwin Lwin from School of Material Science and Engineering for imparting the skill and knowledge of cell culturing.

Author also wishes to thank all the research scholars in the thin film research group, especially Mr. Wang Yongsheng, Mr. Li Yibin and Mr. Wang Huili who had been really helpful and supportive.

Most sincere appreciation also goes to all the technical staff of MAE Materials Lab A and B, and MicroMachines Centre for their technical and logistic assistance. Especially to Ms. Chow Shiau Kee, Mr. Leong Kwok Phui, Ms. Yeong Peng Neo, Mr. Wong Kim Chong, Mr. Pek Soo Siong and Mr. Nordin Kassim who had been exceptionally kind and helpful.

Last, but never the least, the author would like to express his heartfelt gratitude to his family for their continuous support all these years.

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1. Soon-Eng Ong, Sam Zhang, Hejun Du, Yongqing Fu: Fundamental principles and applications of microfluidic systems, *Frontiers in Bioscience*, 13 (7) 2757-2773 (2008)
2. Soon-Eng Ong, Sam Zhang, Hejun Du, Deen Sun: Relationship between bonding structure and mechanical properties of amorphous carbon containing silicon, *Diamond and Related Materials*, 16 (8) 1628-1635 (2007)
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List of Symbols & Abbreviations

Symbols

sp^2	Interaction between one 2s and two 2p orbitals to give three linear combinations lying in a plane, at 120 ° angles from one another (graphite-like bonding)
sp^3	Interaction between one 2s and three 2p orbitals to give four linear combinations pointing at the corners of a tetrahedron (diamond-like bonding)
ν_0	Phonon attempt frequency
E_a	Activation energy
α	Polarizability
r	Inter-atomic distance
F	Dispersive force
k_b	Boltzmann's constant
E	Elastic modulus
ν	Poisson's ratio
t_s	Substrate thickness
t_f	Film thickness
R_1	Wafer curvature before deposition
R_2	Wafer curvature with deposited film
M_s	Martensite transformation start temperature
M_f	Martensite transformation finish temperature
A_s	Austenite transformation start temperature
A_f	Austenite transformation finish temperature
T_l	Temperature hysteresis
$\gamma_{tot.}$	Total surface tension
γ_{lv}	Liquid-vapor interfacial tension
γ_{sv}	Solid-vapor interfacial tension

List of Symbols & Abbreviations

γ_{sl}	Solid-liquid interfacial tension
γ^{LW}	Apolar component of surface tension
γ^+	Acceptor polar component of surface tension
γ^-	Donor polar component of surface tension
I_D	Disorder peak intensity
I_G	Graphitic peak intensity
U_k	Kinetic energy
D_w	Target power density
V_s	Substrate bias
P_g	Gas pressure
M_t	Mass of target particle
M_i	Mass of incident particle
σ	Stress
σ_R	Recovery stress
ε	Strain

Abbreviations

a-C	Amorphous carbon
a-C(Si)	Amorphous carbon containing silicon
a-C:H	Hydrogenated amorphous carbon
DLC	Diamond-like carbon
ta-C	Tetrahedral amorphous carbon
MEMS	Microelectromechanical systems
BioMEMS	Biomedical microelectromechanical systems
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffractometry
SEM	Scanning electron microscopy

List of Symbols & Abbreviations

AFM	Atomic force microscopy
RTP	Rapid thermal processing
RIE	Reactive ion etching
DRIE	Deep reactive ion etching
LPCVD	Low-pressure chemical vapor deposition
SF ₆	Sulphur-hexafluoride
TMS	Tetramethylsilane
KOH	Potassium hydroxide
HNO ₃	Nitric acid
HF	Hydrofluoric acid
CTE	Coefficient of thermal expansion
SMA	Shape memory alloy
SME	Shape memory effect
PRP	Platelet rich plasma
PBS	Phosphate buffered saline
DMEM	Dulbecco's modified eagle's medium
EMEM	Eagle's minimum essential medium
FCS	Fetal calf serum
ANOVA	One-way analysis of variance
BWF	Breit-Wigner-Fano distribution

CHAPTER 1 ~ INTRODUCTION

1.1 Background

Studying or manipulating very small objects, such as living cells, calls for very small instruments. Therefore, scientists and engineers are looking to microelectromechanical systems (MEMS) to answer questions about the very basis of life, as well as the fabrication of micro-implants for therapeutic purposes. Until the mid-nineties, biological-microelectromechanical systems (BioMEMS) were basically confined to blood pressure sensors. Within these few years, a host of other less-publicized BioMEMS based devices were being used in medical equipment or were prototyped and are nearing entry into the market [1-7]. Traditionally, BioMEMS structures are silicon based (silicon, silicon dioxide, silicon nitride) due to the availability of the surface machining technology. Although the materials are biocompatible, they are found to be biofouling [8]. Their mediocre biological and mechanical properties inhibit their application in harsh corrosive environments, like in the human body, and limit the dynamic range of applications especially for devices that requires extensive relative contacts.

In the quest to improve the mechanical performance and reliability of MEMS, diamond and hard amorphous carbon have recently emerged as one promising class of materials. Diamond has the highest hardness (~100 GPa) and elastic modulus (~1100 GPa). Amorphous forms of carbon, specifically the tetrahedral amorphous carbon (ta-C), and diamond-like carbon (DLC), can also approach crystalline diamond in hardness (up to ~90 GPa) and elastic modulus

(~800 GPa). But the main appeal of these materials for the MEMS designer lies with their extreme wear resistance (compare to silicon), their hydrophobic surfaces that offer stiction resistance (parts don't stick together due to capillary forces from entrapped liquid), and their chemical inertness (allows use in aggressive chemical environments).

Recently, researchers have made considerable progress in the fabrication of MEMS structures fabricated from chemical vapor deposited (CVD) polycrystalline diamond [9]. The major disadvantage of CVD polycrystalline diamond is the high surface roughness, $>1\text{ }\mu\text{m}$ RMS, and this limits the minimum device dimensions (typical layer thickness are several μm with tens of μm in lateral dimension) and inhibits the use of multi-level processes to create complex MEMS structures [9].

Since the first fabrication of DLC, also called amorphous carbon (a-C) in 1971 [10], the material was largely studied and utilized as passivation or protective coatings. Only until the late nineties that the superior mechanical properties like high hardness, low stiction, low friction coefficient, low surface roughness, and chemical properties like biocompatibility, non-cytotoxicity and resistant to chemical corrosion, had attracted the attention of MEMS/BioMEMS field. Amorphous carbon is a metastable form carbon with carbon atoms bonded in sp^3 (diamond-like) and sp^2 (graphite-like) hybridizations. The dominance of the sp^3 bonding confers to it the diamond-like properties. Therefore, the relative ratio of the two hybridizations determines the properties of the material. In the as-

deposited state, the material exhibits extremely high levels of compressive film stress. In order for a-C to be successfully integrated into micromachined structures, the films must have very low stress and very low stress gradients. Through suitable post-deposition processing, significant amount of stress relief (near 100%) can be achieved [11]. The stress relief of DLC film-based MEMS offers several advantages to conventional silicon MEMS. The stress relief temperature of DLC is around 600 °C, which is much lower than the 1100 °C of typical MEMS structural material, polysilicon. This is important for reducing the thermal budget when MEMS is integrated with electronics [12]. The resulting stress free films are hard, optically transparent, moderately conductive, and near-atomically smooth (0.1 nm RMS roughness on Si, 0.9 nm roughness on SiO₂). These properties lend the material for use in surface-micromachined MEMS applications where small dimensions and complicated structures are desired. However, the one-time growth of a thick film ($> 10\ \mu\text{m}$) is not possible as the stress will be too large and ultimately cause the delamination of the coating. Repetitive cycles of deposition and stress relief annealing have to be performed to achieve a thick coating [13]. And this is not really commercially viable.

Owing to its amorphous nature, dopants can be incorporated into the matrix to moderate the properties of the material. That is, a-C can be tuned to cater to different MEMS/BioMEMS applications and devices. Although the mechanical properties can be tuned by various dopants, but as far as biological application is concerned, the selection of dopants has the top most priority. The most compatible

dopant to date will be silicon. Small amount of silicon incorporation reduces the intrinsic stress [14,15], as well as an increase in haemocompatibility [16,17]. And its resulted carbide is the only one that is biocompatible [18]. Therefore, a thicker and more biocompatible film can be deposited in a single deposition. However, the mechanical property like hardness might be sacrificed according to several studies [14,19,20]. Although silicon can reduce the stress, but the doped film can never be completely stress free. Annealing is still necessary to relieve the stress.

At the moment, most biological studies on silicon doped amorphous carbon (a-C(Si)) only revolve around low silicon concentration range (< 10 at.%). Although they are found to be haemocompatible, their cellular responses have not been studied. And none has attempted to fabricate micro-devices making use of this material.

Since the results of such a coating system is scarce and fragmented and many questions regarding the material's properties and behaviors are unanswered, a more systematic study should be carried out in order to realize the potential of a-C(Si) as biocompatible film suitable for BioMEMS applications.

1.2 Objectives

The objective is to understand the influence of silicon incorporation on the mechanical and biological properties of amorphous carbon. The atomic bonding and surface characteristics will be evaluated. The compatibility of a-C(Si) film with the current MEMS micromachining techniques will be demonstrated.

1.3 Scope

This project encompasses the following aspects:

(1) Synthesis of a-C(Si) films

The film will be deposited on silicon wafers using magnetron sputtering of graphite and silicon targets. The silicon concentration will be controlled by adjusting the silicon target power density. Selected a-C(Si) film will undergo two thermal processes. The thermal annealing is done *in situ* deposition (adjusting substrate temperature) and post-deposition annealing via rapid thermal processing. Atomic bonding configurations and surface characteristics will be investigated with X-ray photoelectron spectroscopy, Raman spectroscopy, atomic force microscopy, static contact angle measurement.

(2) Mechanical properties of a-C(Si) films

The hardness and elastic modulus of the films will be determined using nanoindentation, and the residual stress of the films will be evaluated using curvature method.

(3) *In vitro* behavior of a-C(Si) films

The haemocompatibility of the films will be evaluated via human blood platelet adhesion assay, where quantification is through the observation of platelet morphology and the number adhering to the film. Cellular response on the films will be evaluated through the culturing of soft tissue cell (COS7) and hard tissue cell (MG63), where cell proliferation and phenotype will be assessed.

(4) Microfabrication of a-C(Si) films

In order to demonstrate the possibility of micromachining a-C(Si), a nitinol/amorphous carbon hybrid film structure will be evaluated, and then micromachined into microcages via photolithography and reactive ion etching. The microcage will be actuated thermally.

1.4 Project Flow

The overview of this project is illustrated below in Figure 1.1:

Figure 1.1| Course of research for a-C(Si) films application in BioMEMS.

1.5 Thesis Organization

This thesis is organized as follows:

Chapter 2: Literature survey on a-C, a-C(Si) and TiNi films, as well as deposition and micromachining processes are presented.

Chapter 3: Describes the deposition and bonding characterization of a-C(Si) films and results on the effect of silicon concentration and thermal treatment are discussed.

Chapter 4: Mechanical properties of a-C(Si) – hardness, elastic modulus and residual stress will be discussed based on the effect from different silicon concentration and thermal treatment.

Chapter 5: The change of a-C(Si) surface energy with silicon concentration and when subjected to thermal treatment is discussed.

Chapter 6: Here the biological properties – haemocompatibility and cellular response, of a-C(Si) films will be discussed. The experimental procedure for human blood platelet adhesion assay and cell culturing of COS7 fibroblast and MG65 osteoblast-like cells will also be described.

Chapter 7: The design and characterization of a microcage fabricated based on a-C, a-C(Si) and TiNi trilayer film structure is described here.

CHAPTER 2 ~ LITERATURE REVIEW

Amorphous carbon (a-C) is used as the matrix for the a-C(Si) film, therefore it is necessary to understand its bonding and growth mechanism. For the application in BioMEMS, the micro-machining and biocompatibility of the material will also be reviewed. Since silicon is the selected dopant and the deposition employed is magnetron sputtering, their current statuses are also reviewed. A hybrid thin film actuator will be fabricated using both amorphous carbon and TiNi shape memory alloy. Therefore, the basic of the material's shape memory effect will be reviewed here.

2.1 Bonding in Amorphous Carbon

Amorphous carbon contains both sp^3 and sp^2 bonded carbon (refer to Figure 2.1). It is also called diamond-like carbon. In the sp^3 configuration, as in diamond, a carbon atom's four valence electrons are each assigned to a tetrahedrally directed sp^3 orbital with an angle of 109.5° apart each another, which makes a strong σ bond to an adjacent atom. In the sp^2 configuration as in graphite, three of the four valence electrons enter trigonally directed sp^2 orbitals equally separated by an angle of 120° , which form σ bonds in a plane. The forth electron of the sp^2 atom lies in a π orbital, normal to the σ bonding plane. This π orbital forms a weaker π bond with π orbital on one or more neighboring atoms.

Figure 2.1| The sp^3 and sp^2 hybridized bonding of carbon.

Figure 2.2 shows the amorphous carbon network generated by *ab initio* molecular dynamics. It shows the network for sp^2 -rich a-C and sp^3 -rich a-C (sp^3 fraction $> \sim 80\%$ is popularly known as the tetrahedral amorphous carbon or ta-C) respectively.

Figure 2.2| a) 2D low sp^3 carbon network generated by *ab initio* molecular dynamics by Galli *et al.* [21], minority sp^3 atoms are shown as white spheres; b) 3D high sp^3 carbon network generated by *ab initio* molecular dynamics by Marks *et al.* [22], minority sp^2 atoms are shown as black spheres.

2.2 Amorphous Carbon Growth Mechanism

Lifshitz *et al.* [23,24] used Auger analysis of the depth profiles of medium energy carbon ions incident on nickel substrates to show that the growth was sub-surface, and denoted the process as ‘**subplantation**’ (low energy subsurface implantation).

This process advances as follows;

(a) *Penetration*

Penetration of the impinging species into the subsurface layers of the substrate, with the penetration depth and distribution depend on the mass and energy of the impinging species and nature of the target material. Some of the impinging species may be backscattered and will not contribute to the net film growth.

(b) *Stopping*

Stopping of the energetic species via three energy-loss mechanisms: atomic displacements, phonon excitations and electron excitations (the latter two phenomena are sometimes collectively referred to as “thermal spikes”).

(c) *Site occupation*

The possible initial sites the impinging atoms occupy after being stopped are determined by the host matrix that serves as a “mold” for the structure of the growing film. Hyperthermal species trapped in a site may occupy another during further impingement of energetic species, either due to collisions or re-crystallization induced by compositional changes during deposition.

(d) Phase formation

The increase in concentration of the penetrating species in the host matrix results in the formation of an inclusion of a new phase, accompanied by the outward expansion of the substrate layer (internal subsurface growth).

(e) Surface composition

During the early stages of film growth, the surface is mainly composed of substrate atoms due to the subsurface penetration of the impinging particles. These substrate surface atoms are gradually sputtered and/or diluted by ion-mixing mechanisms until a surface consisting of only projectile species evolves.

(f) Film structure

Several factors determine the phase and structure of the film: (i) The “mold” effect of the host matrix that determines the possible site occupancies of the penetrating species and places constraints on initial evolution of the new phase; (ii) Preferential displacement of atoms with low displacement energies leaving atoms with high displacement energies in their more stable positions; (iii) Diffusion rates of vacancies and interstitials created in the deposition process. When the temperature is sufficiently low, the interstitials are immobile and their concentration increases with fluence until an athermal spontaneous transformation to a new phase occurs.

(g) Sputtering

The surface features of the evolving film and the efficiency of the deposition process depend on the sputtering yield of both substrate and trapped atoms by the impinging ions. Low sputtering yield is essential for efficient deposition and is necessarily less than unity for net film growth to occur at all.

(h) Film evolution

Evolution of a pure film from hyperthermal species impinging on a substrate consisting of atoms different from that of the bombarding species is feasible only when collisional ion-mixing and diffusion processes are small enough, so as to allow evolution of a pure layer. Therefore the “deposition” process has two stages: (i) initial “heterodeposition” followed by evolution of into a pure layer as described in (a) – (e) and (ii) “homodeposition” of energetic species adding to the pure film.

Lifshitz *et al.* [23,24] proposed that the sp^3 sites accumulate via preferential displacement of sp^2 sites. Moller [25] modeled preferential displacement in more detail and proposed that the sp^2 and sp^3 atoms would be displaced at a certain rates into interstitial sites, and then fall back at similar rates into sp^2 and sp^3 sites. The fraction of sp^3 sites increases if there is a preferential displacement of sp^2 atoms. However, this model arose from some early estimates of the displacement threshold in graphite and diamond of 25 and 80 eV respectively. The more recent direct measurement find a similar values for graphite (35 eV) and diamond (37-47 eV) [26,27], therefore preferential displacement is unlikely.

McKenzie *et al.* [28] noted that sp^2 bonded graphite occupies 50% more volume than sp^3 bonded diamond. This lead to the phase diagram of diamond and graphite shown in Figure 2.3, with diamond stable at higher pressure above the Berman-Simon curve, and therefore stabilize the high-pressure diamond-like phase.

Robertson [29,30] proposed that subplantation would create a metastable increase in density causing the local bonding to change into sp^3 . Preferential displacement is not required, as only the subsurface growth in a restricted volume is needed to get sp^3 bonding.

Figure 2.3| Berman-Simon P-T phase diagram for carbon. [28]

A number of numerical and analytical simulations substantiate the basic idea of the subplantation model [31-33]. The unsolved problem is in the details of

the relaxation process, which suppresses sp^3 bonding at higher ion energies and higher deposition temperatures.

In the following, the atomic scale processes will be discussed using Robertson's data [29,30,34]. In the energy range of 10 – 1000 eV, the carbon ions have a range of a few nm and their energies are lost mainly by elastic collisions with the substrate atoms (nuclear stopping). The cross-section of the collisions decreases as the energy is raised due to the repulsive part of the inter-atomic potential. Therefore, an ion of low energy incident on a surface sees an impenetrable wall of touching spheres. At a higher energy, the atomic radii decrease, so the interstices of the substrate are relatively wider. At some energy, the ion can pass through an interstice and so penetrate the surface layer. This ion energy is termed the penetration threshold, E_p .

The displacement threshold, E_d , is the minimum energy of an incident ion needed to displace an atom from a bonded site and create a permanent vacancy-interstitial pair. The ions when entering the surface must also overcome the substrate's surface binding energy, E_B . Thus the net penetration threshold for free ions is

$$E_p \approx E_d + E_B \quad 2.1$$

Considering carbon ions incident on an amorphous carbon surface [30], a low energy ion will not have enough energy to penetrate the surface, so it will just

stick on the surface, and remain in its lowest energy state which is sp^2 . If the ion energy is greater than E_p , then it will have a probability to penetrate the surface, and enter a subsurface interstitial site. This will cause an increase in local density, and so the local bonding will reform around that atom according to the new density. Robertson assumed that in the highly energetic conditions of ion bombardment existing during film growth, atomic hybridizations will adjust easily to changes in the local density, and become more sp^2 if the density is low and more sp^3 if the density is high.

When the ion energy increases, the ion range increases as well, hence the ion can penetrate deeper into the substrate. A rather small fraction of this energy is used to penetrate the surface, and another fraction of about 30% is dissipated in atom displacements [35]. The ion must dissipate the rest of this energy ultimately as phonons. This whole process consists of three stages: (a) a collisional stage of 10^{-13} s; (b) a thermalization stage of 10^{-12} s; and (c) a relaxation stage of 10^{-10} s. Process (b) and/or (c) allow the excess density to relax to zero, and cause a loss of sp^3 bonding at higher ion energies.

Referring to Figure 2.4, consider an incident beam of flux F with a fraction ϕ of energetic ions of energy E_i . The non-energetic fraction of the atoms or ions ($1 - f\phi$) will just stick on the outer surface, while some of the penetrating ions will relax back to the surface. This flux is proportional to a driving force, the fraction of interstitials below the surface, n .

Figure 2.4| Schematic diagram of densification by subplantation. A fraction of the incident ions penetrate the film and densify it, the remainder end up on the surface to give thickness growth.

In the steady state, the fraction of the ions remaining at the interstitial sites to give densification is $n = f\phi - \beta n$, where β is a constant. This gives

$$n = \frac{f\phi}{1 + \beta} \quad 2.2$$

A fraction n of the beam becomes subplanted inside the film and a fraction $(1 - n)$ is left on the surface as sp^2 sites. The subplanted fraction creates a density increment of

$$\frac{\Delta\rho}{\rho} = \frac{n}{1 - n} \quad 2.3$$

which gives

$$\frac{\Delta\rho}{\rho} = \frac{f\phi}{1 - f\phi + \beta} \quad 2.4$$

where ρ is the density of sp^2 carbon, and $\Delta\rho$ the density increase.

Figure 2.5 shows that penetration can occur in two ways, either directly or indirectly by knock-on. Knock-on penetrations only occur for the case of ion assisted deposition.

Figure 2.5| Schematic of the basic processes in subplantation: direct penetration, penetration by knock-on of a surface atom, and relaxation of a densified region.

The first numerical models assumed that relaxation occurs in the thermal spike stage of $\sim 10^{-12}\text{s}$ [29,30]. This will give a relaxation rate of $\beta \approx 0.016(E_i/E_0)^{5/3}$, where E_0 is the diffusion activation energy, and so

$$\frac{\Delta\rho}{\rho} = \frac{f\phi}{1 - f\phi + 0.016(E_i/E_0)^{5/3}} \quad 2.5$$

The thermal spike model proposes that all the excess energy of the ion is converted to thermal energy at a point or along the ion trajectory. Then the energy diffuses outwards by thermal diffusion creating an expanding front in which all

atoms inside the front have a similar thermal energy, by equipartition. The temperature profile of a spherical spike is

$$T(r, t) = \frac{Q}{c[4\pi Dt]^{3/2}} \exp\left(-\frac{r^2}{4Dt}\right) \quad 2.6$$

where r is the distance from the impact, t the time from the impact, D the thermal diffusivity and c the thermal capacity of the carbon. Q is the ion energy E_i minus that lost in displacements [36]. Taking $Q \approx E_i$ for now, Robertson assumed that the thermal spike allows atoms to diffuse back to the surface to relax the density to a lower, stable sp^2 density. He also assumed that relaxation occurs by thermally activated diffusion at a rate of

$$v = v_0 \exp\left(-\frac{E_0}{kT}\right) \quad 2.7$$

with E_0 being the activation energy for atomic diffusion. The total number of hops of all the atoms within one spike is the integral over the spike volume and time,

$$\beta = \int_{r_1}^{\infty} 4\pi n_0 r^2 \int_{t_1}^{\infty} v \exp\left(-\frac{E_0}{kT(r, t)}\right) dt dr \quad 2.8$$

where k is Boltzmann's constant, n_0 the atomic number density, v_0 the phonon frequency, r_1 the minimum radius of the spike and t_1 the minimum time of the spike. It is useful to put everything in dimensionless atomic units, with an atomic radius a . Robertson defines reduced distances $r' = r/a$, times $t' = v_0 t$, and a reduced

temperature $\tau = kT/E_0$. The heat capacity per atom is $3k$, so $c = 9k/4\pi a^3$, $D \approx v_0 a^2$, and $n_0 = 3/4\pi a^3$. Integration over t' is carried out and the integral over r' is converted to one over τ to give

$$\beta = \int_{\tau_1}^{\tau_2} \tau^{-8/3} \exp\left(-\frac{1}{\tau}\right) d\tau \quad 2.9$$

In the limits $\tau_1 \rightarrow 0$ and $\tau_2 \rightarrow \infty$ this gives

$$\beta = 0.016p \left(\frac{E_i}{E_0}\right)^{5/3} \quad 2.10$$

where p is a dimensionless constant of order 1. All the other quantities cancel out. This is the equation used in Equation 2.5.

Figure 2.6 shows that Equation 2.5 gives a good representation of the variation of density or sp^3 fraction with energy for tetrahedral-amorphous carbon (ta-C) deposited by filtered cathodic vacuum arc (FCVA) [30,37] with $E_0 = 3.1$ eV. The increasing sp^3 fraction at lower ion energy is controlled by the penetration probability f , and the decline in sp^3 fraction at high ion energy is controlled by the relaxation.

Figure 2.6| Comparison of calculated sp^3 fraction of ta-C according to subplantation model (Eqn. 2.5), with experimental data of Fallon *et al.* [37]

Despite this superficial agreement between theory and experiment, this model of deposition is still deficient. There are many faults with the thermal spike concept when applied to carbon deposition. A thermal spike is only truly valid for much heavier ions and higher ion energies, where the energy loss rate per distance (stopping power) is much higher, so the energy density is greater [38,39]. In carbon, energy equipartition does not really hold, so that the spike volume consists of a few excited atoms among much less excited atoms.

A satisfactory model of growth must account for

- The transition temperature to sp^2 bonding, being 400 – 500 K [40,41], despite the temperature in a thermal spike being 10^6 K.
- The variation of the transition temperature for sp^3 formation with ion energy [40].
- The variation of transition temperature with instantaneous growth rate [36,42]

2.3 Micro-Machining of Amorphous Carbon

Amorphous carbon can be micro-machined using conventional photolithography techniques [43-48]. The schematic representation of the major steps of the lithography patterning process is given in Figure 2.7.

Figure 2.7| Lithography patterning process: (a) application of photoresist; (b) UV exposure; (c) development; (d) etching; (e) photoresist stripping.

Depending on the micro-structure, either the a-C film or the silicon substrate can be etched to realize the structure. Yu *et al.* [43] and Mousinho *et al.* [46] realized their structures by etching a-C using reactive ion etching (RIE), Yu *et al.* [44,48] also used deep reactive ion etching (DRIE) to etch a-C, and Sheeja *et al.* [45,47] wet etched the silicon substrate to obtain the a-C structures.

2.3.1 Reactive Ion Etching

In RIE, the substrate is placed inside a reactor in which a single gas or several gases are introduced. Plasma is struck in the gas mixture using an RF power source, breaking the gas molecules into ions. The ions are accelerated towards, and react at, the surface of the material being etched, forming another gaseous material. This is known as the *chemical part* of reactive ion etching. There is also a *physical part*, which is similar in nature to the sputtering deposition process. If the ions have high enough energy, they can knock atoms out of the material to be etched without a chemical reaction. It is a very complex task to develop dry etching processes that balance chemical and physical etching, since there are many parameters to adjust. By changing the balance it is possible to influence the anisotropy of the etching, since the chemical part is isotropic and the physical part highly anisotropic the combination can form sidewalls that have shapes from rounded to vertical. A schematic diagram of a typical reactive ion etching system is shown in Figure 2.8 below.

Figure 2.8| Schematic of a typical parallel-plate reactive ion etching system.

A special subclass of RIE that continues to grow rapidly in popularity is deep RIE (DRIE). In this process, etch depths of hundreds of microns can be achieved on silicon with almost vertical sidewalls. The primary technology is based on the so-called "Bosch process", named after the German company Robert Bosch, which filed the original patent, where two different gas compositions are alternated in the reactor. The first gas composition creates a polymer on the surface of the substrate, and the second gas composition etches the substrate. The polymer is immediately sputtered away by the physical part of the etching, but only on the horizontal surfaces and not the sidewalls. Since the polymer only dissolves very slowly in the chemical part of the etching, it builds up on the sidewalls and protects them from etching. As a result, etching aspect ratios of 50 to 1 can be achieved. The process can be used easily to etch completely through a silicon substrate, and the etch rates are many times higher than anisotropic wet etching (depending on the formula of etchant, the temperature and agitation during etching, isotropic wet etching of silicon can be faster as compare to DRIE process).

Oxygen is used in the RIE process to etch a-C. The etching rate is known to increase with the RF power [43,46]. Mousinho *et al.* [46] also found that etching rate can increase if the process pressure is increased, but the scattering of the incoming ions for gas phase molecules causes lower anisotropy. Therefore, the ideal condition is low pressure and high RF power. The increase in RF power increases the DC self-bias and hence, increases the reactive ion flux [43]; more oxygen molecules are dissociated into oxygen atoms, thereby increasing the

chemical etching of the carbon atoms of the a-C films [46]. The results of Yu *et al.* [43] and Mousinho *et al.* [46] are presented in Figure 2.9 and Figure 2.10 respectively. It is unclear why the etching rate from Mousinho *et al.*'s study is three orders of magnitude higher than Yu *et al.*'s. From Raman spectroscopy results, Yu *et al.*'s film had a higher sp^3 C fraction, thus, the possible reason could be the film was harder to etch as compared to the a-C with higher sp^2 C fraction of Mousinho *et al.*'s. Figure 2.11 shows the micro-structures obtained by Mousinho *et al.* [46].

Figure 2.9| Oxygen plasma etch rate of a-C film as a function of discharge power. [43]

Figure 2.10| Oxygen plasma etch rate of a-C film as a function of discharge power and pressure. [46]

Figure 2.11| DLC micro-channel and micro-gear. [46]

Yu *et al.* [43] found that the etching rate in oxygen for metal containing a-C is relatively lower. They etched titanium-containing a-C using a mixture of tetrafluoromethane (CF_4) and oxygen, and found that the etching rate increases with increasing titanium content (refer to Figure 2.12). This is because the majority of the titanium in the film exhibit as titanium carbide [49], and titanium carbide can be easily etched away with CF_4 .

Figure 2.12| Etching rate of Ti containing a-C using RIE ($\text{CF}_4 + \text{O}_2$). [43]

Using X-ray photoelectron spectroscopy (XPS), Yu *et al.* [43] also revealed that in the case of a-C containing aluminum, the aluminum in the film exhibits in the form of oxides. And they suggested that aluminum oxides could be easily etched away with chlorine based gases.

Raman inspection shows no significant difference in the spectra between the as-deposited film, photo-resist protected area and etched area [43]. However, etching can roughen the surface significantly (refer to Figure 2.13).

Figure 2.13| AFM images of the a-C film: (a) as-deposited; $R_{\text{rms}} = 0.14 \text{ nm}$ and (b) etched area; $R_{\text{rms}} = 3.83 \text{ nm}$. [43]

2.4 Biocompatibility of Amorphous Carbon

The implantation of biomaterials into the human body allows it to re-establish biological and mechanical functions and therefore to increase the quality of life. Depending on the biomedical application, the implant has to withstand dynamical mechanical loads and must be able to perform a desired long-term biological interaction with the surrounding biological tissue. The load bearing properties of the implants are mainly controlled by the bulk properties of the implant whereas the interaction with the surrounding tissue is governed by the implant surface. The implant surface influences in particular the interaction and adsorption of different proteins, which in turn control cell adhesion and behavior. However, the overall reaction of the body to an implant is a system property that includes many different aspects, such as surface chemistry and texture, implant movement, biodegradation and surgical aspects. The highly corrosive environment and the low tolerance of the body to some dissolution products restrict the materials that can be used for implants.

2.4.1 Haemocompatibility

The major clinical issue in the use of blood contacting artificial materials is blood compatibility. When biomaterials come into contact with internal tissue of body, blood coagulation, i.e. thrombosis, may take place. The interaction of a biomaterial surface with blood stimulates *platelet* activation, coagulation and thrombus formation. The reactions of the body to a blood-contacting surface crucially depend on the surface, especially the chemical situation present at the

surface, the surface texture, the local flow conditions as well as other factors [50]. It is generally known that the increase in platelet adhesion, activation and aggregation on the surface exposed to blood precede the formation of a thrombus. A high ratio of the proteins *albumin/fibrinogen* adsorbed on the surface prior to cell or platelet attachment can be correlated with low number of adhering platelets and therefore a lower tendency of thrombus formation. Hence, a better inhibition of platelet and fibrinogen adhesion, and enhancement of albumin adhesion on the surface are basic prerequisites for blood compatibility.

Using platelet-rich-plasma (PRP) prepared from whole human blood and a parallel plate flow chamber, Krishnan *et al.* [51] showed that platelet adhesion is reduced on DLC comparing to titanium surface. Also, using Radioscintigraphy, they showed that the adherence of platelets to the material is determined by the shear rates at which the materials are exposed to the PRP. In-vitro experiment conducted by Jones *et al.* [52,53] showed that DLC surface expressed a lower area coverage of platelets than titanium, titanium nitride (TiN) and titanium carbide (TiC). Platelet activation, clotting of platelets and thrombus formation were observed on titanium containing surfaces, but no such reactions took place on DLC surfaces.

A higher ratio of albumin/fibrinogen adsorption was observed on the a-C surfaces than on titanium, titanium nitride (TiN) and titanium carbide (TiC), indicating the ability of a-C to prevent thrombus formation [53]. Cui and Li [54]

also showed the similar result when comparing a-C with carbon nitride (CN) and polymethymethacrylate (PMMA) with a-C having a higher albumin/fibrinogen ratio. The albumin/fibrinogen ratios from the two research groups are summarized in Figure 2.14.

Figure 2.14| Albumin/fibrinogen ratio for different surfaces. Data from Jones *et al.* [53] and Cui *et al.* [54]

Gutensohn *et al.* [55] analyzed the intensity of the platelet activation antigens CD62p and CD63. In their *in vitro* experiment they showed that a-C coating of AISI316L stainless steel coronary artery stents resulted in a decrease of the CD62p and CD63 antigens indicating low platelet activation on a-C and, therefore, a low tendency for thrombus formation. Additionally, they showed metal ion release from the stainless steel stents, which may negatively influence the haemocompatibility of a surface, could be suppressed by the a-C coating.

Platelet adhesion is found to be influenced by the sp^3/sp^2 ratio [56-59]. Chen *et al.* [56] studied the effects of different acetylene to argon flow ratios on the platelet counts, and found that the count was actually correlated to the sp^3/sp^2 ratio. From Figure 2.15, the platelet count is lower when the intensity ratio of D-band to G-band (Raman spectroscopy) is lower (equivalent to higher sp^3/sp^2 ratio). Yang *et al.* [57] also showed the similar phenomenon when they changed the D-band to G-band intensity ratio by changing the bias voltage (Figure 2.16).

Figure 2.15| Effects of $F_{C_2H_2}/F_{Ar}$ flow ratios on the intensity ratio of the D-band to G-band and platelet counts. [56]

Figure 2.16| Quantity of platelets adhered on the surface off the a-C:H films synthesized at different bias voltages (15 min incubation in PRP). [57]

Platelet activation on the surface of a material can be assessed by their degree of spreading and changing shape [53]. Thus, platelets are strongly activated by films deposited at higher bias voltage compared to those at lower bias voltage. The platelet attachment and morphology studies suggest that the adhesion behavior is related to the surface energy of the film. From Figure 2.17, the higher the bias voltage (lower the sp^3/sp^2 ratio), the lower the value of the polar component of the surface energy, and accordingly, the higher the activation of adherent platelets. Li and Gu [59] also found that the hydrophobicity increases when the sp^3 fraction increases, and hence a lower number of adhering platelets.

Figure 2.17| Effects of the bias voltage on: (a) Intensity ratio of the D-band to G-band and (b) Ratio of polar/dispersive component of the surface energy. [57]

2.4.2 Tissue Compatibility

Tissue compatibility studies of a-C films have been performed in-vitro by exposing DLC-coated materials to a variety of environments simulating the body ambience. These environments included *macrophages* (large white cell that engulf foreign bodies), *fibroblasts* (connective tissue forming cells) and *osteoblasts* (bone forming cells), three cell types typically found within periprosthetic tissues.

The macrophage is a suitable cell for in-vitro biocompatibility testing, as it plays a major role in inflammation and the response to foreign bodies. Thomson *et al.* [60] have studied the inflammatory potential of a-C-coated tissue culture plates on a-C coating by measuring the levels of the lysosomal enzyme -N-acetyl-D-glucosaminidase in the culture medium following the exposure of macrophages to a-C coatings. Since lysosomal enzymes are released from macrophages during

inflammation; an increased enzyme level in the medium means that an inflammatory reaction has been elicited. They found no significant difference between the enzyme levels from a-C coatings and those from control tissue culture plate. This shows that a-C does not induce inflammatory reactions in the cells anymore than the tissue culture plate. Allen *et al.* [61] have also studied the effects of a-C-coated polystyrene plates on macrophages. The results showed that macrophages grew well on a-C-coated plates. Scanning electron microscopic examinations confirmed the normal behavior of cells and no evidence of extensive cell death, therefore showing no cytotoxicity was caused by the a-C coating. Li and Gu [59] observed a decrease in the number of adhering macrophages if the sp^3 fraction is higher.

The results of Allen *et al.* [61] in Figure 2.18 shows that there are no statistically significant differences between fibroblasts grown on control polystyrene plate and those grown on DLC coating. Morphological examination showed no evidence of cellular damage to the fibroblasts. In-vitro tests using murine fibroblasts showed that a-C deposited on a titanium alloy has a low level of cytotoxicity and acts as a diffusion barrier between the titanium alloy and the fibroblasts [62]. The tests also demonstrated good adhesion and spreading of the cells on the a-C surface.

Figure 2.18| Growth curves for human synovial fibroblasts growing on plain and a-C-coated polystyrene tissue culture plates. [61]

One of the most promising applications of a-C is in surface modification of artificial hip joint replacements. Therefore, a number of studies on the effects of these coatings on osteoblasts have been done. The results of Allen *et al.* [61] in Figure 2.19 indicated that no statistical differences between osteoblasts grown on control polystyrene plates and those grown on a-C coatings. Scanning electron microscopy showed that the cells adhered well to the a-C coatings and produced extensive filopodia. The results of Du *et al.* [63] showed that osteoblasts could migrate out of bone fragments, and could attach, spread and proliferate on the a-C coating, in an attempt to colonize the entire substrate surface. But the situation was different with uncoated silicon. The osteoblasts were able to attach on the wafers, but were unable to follow this attachment with spreading. Rodil *et al.* [64] and Olivares *et al.* [65] showed that the degree of osteoblasts adhesion measured at 24-hour attained higher value for a-C when compared to titanium and bare stainless steel (refer to Figure 2.20).

Figure 2.19| Growth curves for human osteoblasts growing on plain and a-C-coated polystyrene tissue culture plates. [61]

Figure 2.20| Adhesion of osteoblasts on the a-C, a-CN, Ti and bare stainless steel substrates after 24 hours. [65]

The number of reported in-vivo tests is significantly smaller than that of the *in vitro* ones. One paper reports an *in vivo* test performed by inserting 12 mm long, and 4 mm diameter stainless steel cylinders coated with hydrogenated a-C into cortical bone and muscular tissue of sheep [62]. Several implants were evaluated after 4 weeks and other after 12 weeks. It was found that the a-C coatings had no macroscopic adverse effects on the bone or muscle tissue. In another in-vivo study, a-C-coated cobalt-chromium (CoCr) cylinders were

implanted in intramuscular locations in rats and in transcortical sites in sheep (Figure 2.21). The specimens were retrieved 90 days after surgery and their histological analysis showed that the a-C-coated specimens were tolerated well in both body sites [66].

Figure 2.21| Transcortical implants in the lateral femoral cortex of sheep. [66]

2.4.3 Static Corrosion Test

Tiainen [67] investigated the corrosion characteristics of a-C-coated and uncoated AISI316L stainless steel, Ti6Al4V alloy and CoCrMo alloy in simulated body fluid (SBF). The tests were performed in 37°C with 10wt.% hydrochloric acid (HCl) distilled water solution for accelerated and with 1wt.% sodium chloride (NaCl) distilled water solution for body equivalent long term (~ two years) simulations of the natural conditions. The results as presented in Figure 2.22 showed that a-C drastically reduced the corrosion rate (about a factor of 10^5) of the substrate.

Figure 2.22| The results of the static corrosion tests in 10 wt.% HCl of DLC-coated and uncoated AISI316L, Ti6Al4V and CoCrMo [67]

2.5 Bonding Characterization of Amorphous Carbon

2.5.1 X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a technique used to investigate the composition of deposited films by ionizing surface atoms and measuring the energy of ejected photoelectrons. The method requires the sample of interest to be bombarded with low energy X-rays, produced from an aluminum or magnesium source, with an energy of $h\nu$, where h is the Planck's constant (6.62×10^{-34} Js) and ν is the frequency (Hz) of the radiation. These X-rays cause electrons to be ejected from either a valence or inner core electron shell. The kinetic energy of the electron, KE , is given by $KE = h\nu - BE$, where BE is the binding energy of the atom. If the energy of the ejected photoelectrons was measured, its binding energy

which is the energy required to remove the electron from its atom can be calculated. Some important facts about the sample under investigation can be learned from the binding energy: 1) the elements from which it is made; 2) the relative quantity of each element; 3) the chemical state of the elements present; and 4) lateral and depth distributions (profiles).

The change in chemical state (inter-atomic bonding) will cause a shift in the binding energy. In a-C, there are two main hybridizations, namely sp^3 diamond and sp^2 graphite (as discussed in §2.1). Since both are formed by bondings of carbon atoms, the chemical shift between that of sp^3 and sp^2 is small. That is, the binding energy of the two as determined from XPS will be relatively closed to each other. Therefore, there will be a superpositioning of the C 1s core level peak due to the contribution of the two hybridized carbons. The peak of amorphous carbon is thus broadened. In order to determine the contribution of each hybridized carbon in the film, the C 1s peak can be deconvoluted. It was found that the full-width-at-half-maximum of both the sp^3 peak and the sp^2 peak tend to be wider than those from pure diamond and graphite [68]. This is attributed to the environment within the a-C film with mixed sp^2 and sp^3 bondings. A deconvoluted C 1s peak is shown in Figure 2.23. This regime for the approximation of the sp^2 and sp^3 concentration in the a-C is widely used [68-71].

Figure 2.23| Example of the fits of the C 1s peak from a XPS spectrum. [68]

2.5.2 Raman Spectroscopy

Raman spectroscopy is widely used, being a routine, non-destructive way to characterize the structural quality amorphous carbons. Raman effect is possible because of the strain dependence of the electronic polarizability. And it is light scattering by the change in polarizability due to lattice vibration. The difference in energy between the incident photon and the Raman scattered photon is equal to the energy of a vibration of the scattering molecule. A plot of intensity of scattered light versus energy difference (or shift) is a Raman spectrum.

The Raman spectra of diamond, graphite and some disordered carbons are compared in Figure 2.24. Diamond has a single Raman active mode at 1332 cm^{-1} , which is a zone-centre mode of T_{2g} symmetry. Single crystal graphite has a single Raman active mode, which is the zone-centre mode at 1581 cm^{-1} of E_{2g} symmetry

labeled 'G' for 'graphite'. The zone-centre optical modes in graphite can be decomposed into irreducible representation [72,73],

$$\Gamma = 2B_{2g} + 2E_{2g} + A_{2u} + E_{1u} \quad 2.11$$

The A_{2u} and E_{1u} modes are infrared active, the B_{2g} modes are optically inactive and the E_{2g} modes are Raman active. The symmetry of the E modes restricts the motion of the carbon atoms. The two different E_g modes occur because adjacent planes can vibrate in phase or with opposite phase [72,73]. The two in-plane Raman active E_{2g} modes are found to occur at frequencies of 1581 cm^{-1} (E_{2g2}) and 42 cm^{-1} (E_{2g1}). The peak at 1581 cm^{-1} from the Raman active zone-centre mode of graphite, assigned to the C–C stretching mode [72,73], is also referred to as the G-peak. When the long-range order of the graphite is disrupted (disordered graphite), a second peak appears at about 1355 cm^{-1} referred to as the D-peak; 'D' for 'disorder'. The D-peak is associated with in-plane vibrations and results from structural imperfections. The Raman spectra of most disordered carbons remain dominated by these two G and D modes of graphite, even when the carbons do not have particular graphitic ordering [74].

Figure 2.24| Comparison of typical Raman spectra of carbons. [34]

The G mode of graphite at 1581 cm^{-1} has E_{2g} symmetry and it involves the in-plane bond-stretching motion of pairs of carbon sp^2 atoms. This mode does not require the presence of sixfold rings, and so it can occur at all sp^2 sites, not only in rings. It is always in the range between $1500 - 1630\text{ cm}^{-1}$. The D-peak around 1355 cm^{-1} is a breathing mode of A_{1g} symmetry. This mode is forbidden in perfect graphite and only becomes active in the presence of disorder. And its peak intensity is connected to the presence of sixfold aromatic rings [74]

Figure 2.25 shows the various factors that can shift the G and D peaks in either direction and alter their relative intensity.

Figure 2.25| Schematic of the factors affecting the position and heights of the Raman G and D peaks of non-crystalline carbons

Ferrari and Robertson [74] found that the Raman spectra of all disordered carbons can be classified within a three-stage model of increasing disorder. The Raman spectrum is considered to depend on

1. clustering of the sp^2 phase,
2. bond disorder,
3. presence of sp^2 rings or chains, and
4. the sp^3/sp^2 ratio.

The above factors act as competing forces on the shape of the Raman spectra, as shown in Figure 2.25. Ferrari and Robertson [74] defined an amorphitization trajectory ranging from graphite to ta-C consisting of three stages, as shown in Figure 2.26:

1. graphite $\rightarrow$ nanocrystalline graphite,
2. nanocrystalline graphite $\rightarrow$ a-C, and
3. a-C $\rightarrow$ ta-C.

Figure 2.26| Schematic variation of the Raman G peak wavenumber, and I_D/I_G ratio with degree of disorder [74]

Stage 1 corresponds to the progressive reduction in grain size of ordered graphite layers, while keeping aromatic rings. As the grain size decreases, phonon confinement causes the phonons to disperse upwards from 1581 cm^{-1} , so this causes an up-shift of the G-peak to $\sim 1600\text{ cm}^{-1}$. The D mode is forbidden in an ideal graphitic layer, but the disorder causes it to appear.

In Stage 2, defects are progressively introduced into the graphite layer causing disordering and the loss of aromatic bonding, but with a purely sp^2

network. The disordering and loss of aromatic bonding weaken the bonds, thus causing the G-peak to shift downward to $\sim 1510 \text{ cm}^{-1}$. The number of ordered rings now decreases and I_D starts to decrease. While the intensity of the G-peak remain unchanged as it is only related to bond stretching of sp^2 pairs. The I_D/I_G decreases with increasing amorphization. The end of Stage 2 corresponds to a completely disordered, almost fully sp^2 -bonded a-C consisting of distorted sixfold rings or rings of other orders (maximum 20% sp^3). A typical example is sputtered a-C [75,76].

In Stage 3, when passing from a-C to ta-c, the sp^3 content rises from $\sim 10\text{-}20\%$ to $\sim 85\%$. This changes the sp^2 configuration from mainly rings to short chains [74]. The bond length of the chains (olefins) is shorter than that of the rings, so they have higher vibrational frequencies. Therefore, the G-peak increases from $\sim 1510 \text{ cm}^{-1}$ to $\sim 1570 \text{ cm}^{-1}$. The D-peak is absent in curve fit, and the G-peak skewness falls to almost zero (more symmetric) at high sp^3 content [77].

2.6 Silicon Doping of Amorphous Carbon

Silicon is in the same group as carbon in the periodic table, and it has a cubic diamond structure. It has four valence electrons and each electron pair constitutes a covalent bond. Unlike carbon atoms that will hybridize, silicon atom can and only forms σ bonds with adjacent atoms. Considering this bonding configuration for silicon, it is considered as a promising element to promote sp^3 -hybridized bond formation by modification of the chemical bonding configuration in a-C film. The

theoretical argument for this has been treated by Friedel using the method of moments to estimate the changes in the density of states in a carbon-silicon system, the amount of tetrahedral sp^3 bonding should increase with increasing interaction between C and Si [78]. A detail mapping of the bonding structure requires at least four factors: (1) the overall sp^3/sp^2 hybridization ratio; (2) the chemical arrangement between carbon and silicon (fraction of Si-Si, Si-C and C-C bonds); (3) the degree of clustering of sp^2 bonds; and (4) the silicon content (C/Si ratio).

Since the material is to be applied in the biological field, the selection of dopants is of top priority. For example, pure Ti, Ta and W are biocompatible, however they alloys with C, i.e. TiC, TaC and WC, cause undesirable consequences like heavy metal disease [18]. Silicon is also carbide forming; the alloyed material (SiC) however is biocompatible and has been used widely as a coating for stents.

The following sections will discuss the effects of Si doping.

2.6.1 Effects of Silicon on Bonding in Amorphous Carbon

Data from a few authors in Figure 2.27 show that the Raman G-peak position downshifts as the Si concentration increases. The shift of the G-peak position to lower frequency can be partially attributed to a reduction in compressive stress when silicon is introduced into the films, since the longer de-strained bonds vibrate at lower frequencies [20]. The presence of Si-C bridging bonds can also weaken

the adjacent C-C bonds, resulting in a downward frequency shift of both the D and G peaks, and a decrease in the I_D/I_G ratio (refer to Figure 2.28). On the other hand, the simultaneous downshift and decrease in I_D/I_G can also be accounted for by the creation of higher disorder in the film [79]. The latter suggests that Si doping reduces the average size of the sp^2 -bonded clusters [80] and promotes the formation of sp^3 bonding in the a-C(Si) film. The enhancement of sp^3 bonding is related to the Si valence structure, as mentioned earlier, only forms four-fold coordinated network (Si-C).

Figure 2.27| Variation of G-peak position as a function of Si concentration. Data from Jung *et al.* [81], He *et al.* [14], Kulikovskiy *et al.* [15] and Papakonstantinou *et al.* [19]

Figure 2.28| Variation of I_D/I_G ratio as a function of Si concentration. Data from He *et al.* [14] and Papakonstantinou *et al.* [19]

2.6.2 Mechanical Properties

The intrinsic compressive stresses of the a-C films were significantly reduced by the incorporation of Si (as shown in Figure 2.29). The substitution of Si for C atoms leads to a strain relaxation process since the bonding length is increased from 1.54 Å (C-C) to 1.89 Å (Si-C) [82] in the adjacent sites of the incorporated Si atoms. As calculated by Ferrari *et al.* [11], only a 1 % strain variation is needed for a significant decrease in film stress. Jung *et al.* [81] also suggested that the formation of Si-C plays a role in releasing the bond angle distortion.

Figure 2.29| Variation of compressive stress as a function of Si concentration. Data from He *et al.* [14] and Kulikovskiy *et al.* [15]

However, results of the hardness measurement are different among research groups. Figure 2.30 shows that both an increase and decrease in hardness with increasing Si content are observed. Since Si promotes the formation of sp^3 -hybridized bonds and suppresses the formation of sp^2 -bonded aromatic clusters, therefore the hardness is expected to increase. But at the same time the bonding of Si-C (320 kJ mol^{-1}) is weaker than the native C-C bond (411 kJ mol^{-1}) [81], which will ultimately cause a decrease in hardness. What makes one effect stronger than the other? At present, there is no comprehensive theory which can predict and explain this behavior.

Figure 2.30| Variation of hardness as a function of Si concentration. Data from He *et al.* [14], Kulikovskiy *et al.* [15] and Papakonstantinou *et al.* [19]

2.6.3 Biological Properties

As discussed in an earlier section, the haemocompatibility depends on the sp^3/sp^2 ratio of the film. And the hydrophobicity increases with the increase in the sp^3 fraction, thus enhancing the accumulation of albumin compare to fibrinogen, which in turns lowers the platelet adhesion [56-59] and the risk of thrombus formation. Since the incorporation of Si can promote the sp^3 -hybridized bond formation, a-C(Si) should be a good candidate as biomaterial, especially in blood-contacting environments. Pyrolytic carbon has been used as a coating on different types of implanted prostheses, and when it is alloyed with Si, it shows excellent thrombus resistance [16]. a-C(Si) is cheaper and more readily available than pyrolytic carbon.

Okpalugo *et al.* [17] studied the effect of different Si concentrations in *hydrogenated* amorphous carbon and found the surface energy decreases with increasing Si content. They also compared the platelet aggregation count in undoped and doped samples as a function of annealing temperatures. Referring to Figure 2.31, their results showed a much lower count for the Si-doped samples throughout a temperature range of 200-600 °C.

Figure 2.31| Platelet aggregation count on the sampled 240,000 μm^2 area of film, for platelet seeded for 30 min. [17]

Okpalugo *et al.*'s [17] study is restricted only to hydrogenated a-C(Si) with a Si doping concentration of less than 10 at.%. An unhydrogenated counterpart might have different behavior and properties. Will an increase in the Si concentration affect the surface energy of the material? There is very little research at the moment on the blood compatibility of a-C(Si), and the results are scarce and not very assuring. Many researchers in the biopolymer field preferred hydrophilic surfaces, because it minimizes the adsorption of proteins (including

albumin), hence eliminating or preventing the first step of thrombus formation [83]. If a hydrophobic surface is more haemocompatible than hydrophilic one, then one can suggest using Teflon (which is very hydrophobic; contact angle of water at $\sim 120^\circ$) as a blood contacting coating. However, Teflon, though very hydrophobic, has protein-binding capacity. Despite Teflon's reputation as a non-stick material, serum proteins bind almost instantly to its surface, principally via hydrophobic interactions. It also shows high protein retention [84]. Thus is wettability alone a sufficient prerequisite for haemocompatibility?

2.7 Magnetron Sputtering of Amorphous Carbon

Sputtering is preferred for industrial applications because of its versatility, its widespread use to sputter many materials, and its ease to scale up. The deposition conditions can be controlled by the plasma power and gas pressure, but are reasonably independent of the substrate geometry and condition.

It is the most common process for the deposition of a-C. And the most common form uses the direct current (DC) or radio frequency (RF) sputtering of a graphite target by argon plasma. Due to the low sputtering yield of graphite, magnetron sputtering is often used to increase the deposition rate. Magnets are placed behind the target causing the electrons to spiral, thus increasing their path length. This enhances the degree of ionization of the plasma. The schematic diagram of a typical magnetron sputtering system is shown in Figure 2.32.

Figure 2.32| Schematic diagram of a magnetron sputtering system.

A magnetron uses a static magnetic field configured at the cathode location. The magnetic field is located parallel to the cathode surface. Secondary electrons that are emitted from the cathode due to ion bombardment are constrained by this magnetic field to move in a direction perpendicular to both the electric field, E (normal to the surface) and the magnetic field, B . This is known as $E \times B$ (E cross B) drift. This drift causes electrons to move parallel to the cathode surface in a direction 90 degrees away from the magnetic field. If the magnetic field is set up correctly, this $E \times B$ drift can be arranged to close on itself, forming a current loop of drifting secondary electrons (refer to Figure 2.33).

Figure 2.33| The magnetic field configuration for a circular planar magnetron cathode.

These secondary electrons are essentially trapped in a region close to the cathode. Eventually they lose their kinetic energy due to collisions with gas atoms (ionization) or with other electrons (electron heating), and the net result is an extremely dense plasma in this drift ring. Visually this is quite easy to see in a magnetron sputtering system. The drift path lights up dramatically and the density is very much higher in this region. The location of this ring is also known as the *etch track* because the erosion of the cathode is highest here and deep grooves can be eroded onto the cathode (refer to Figure 2.34). Ions that are made in the drift region have a high probability of hitting the cathode that is close by. This results in even more production of secondary electrons and eventually producing a denser plasma.

Figure 2.34| Etch track on a sputtering target.

Since ion bombardment helps the formation of sp^3 bonding, the magnetic field can be configured to pass across to the substrate, so this causes the argon ions to also bombard the substrate, producing an “unbalanced magnetron”. A bias voltage (DC/RF) can be applied to the substrate to vary the ion energy. Hydrogenated amorphous carbon (a-C:H) can be produced by reactive sputtering using a plasma mixture of argon and hydrogen or methane. And the doping of other elements like titanium or silicon can be done by co-sputtering of the respective target together with the graphite target.

Sputtering can also be assisted by ion beams. Two argon ion beams are normally used, creating both the sputtering flux for the graphite target and the ion plating flux for the substrate. A beam of argon ions can be used to sputter from the graphite target to create the carbon flux, and a second argon ion beam can be used to bombard the growing film to densify the film or encourage sp^3 bonding [85,86]. This is called ion beam assisted deposition (IBAD).

Techniques that have been successfully used to produce tetrahedral amorphous carbon (ta-C) films include filtered cathodic vacuum arc (FCVA) [11,28,87-89], pulsed laser deposition (PLD) [90-92], low energy cluster beam deposition (LECBD) [93, 94], mass selected ion beam (MSIB) [95]. A disadvantage of sputtering is that it can have a relatively low ratio of energetic ions to neutral species, so that it does not produce the hardest DLC films with a high sp^3 fraction. Attempts to deposit unhydrogenated amorphous carbon films rich in sp^3

C–C bonds with sputtering techniques (non ion assisted) have been unsuccessful until Logothetidis [96] and Logothetidis *et al.* [97,98] successfully deposited the tetrahedral amorphous carbon (ta-C) films with 85-90% sp^3 fraction using radio frequency (RF) magnetron sputtering at room temperature.

In a sputtering process, there is a wide range of deposition parameters that can be properly tuned [96] to produce carbon films with the characteristic properties of tetrahedral amorphous carbon (ta-C) or other new properties and structures. However, there only exist a narrow region of deposition conditions to provide these values where film rich in sp^3 bonds can be formed.

2.8 Nitinol Shape Memory Alloy

In 1961, researchers at the US Naval Ordnance Laboratory discovered shape memory effect (SME) in TiNi; and they were the first who discovered the unique properties of the alloy [99]. The martensitic transformation of TiNi was fully described in 1965, when the term “memory” was first used to describe the shape recovery behavior [100]. Sputter deposited TiNi thin films exhibiting shape memory characteristics were first demonstrated by Miyazaki *et al.* [101]. They found the phase transformation temperatures for shape memory behavior are strongly affected by film composition, sputtering condition and post-deposition annealing [101- 107]. For example, temperature hysteresis and type of transformation are found to be dependent upon the film composition. Three types

of transformation have thus been reported in various TiNi-base films [105,106]: austenite parent phase (B2 phase, cubic structure) → martensite phase (B19' phase, monoclinic structure) and B2 phase → R phase (rhombohedral structure) in binary alloys; and B2 → O (orthorhombic structure) → M phases in Cu-modified alloys.

Currently, the two most commonly used shape memory alloys (SMA) in engineering applications are TiNi-based and copper-based alloys. TiNi is better suited for use as a microactuator because it has greater shape memory strain (up to 8% versus 4 to 5% for the copper-base alloys), tends to be much more thermally stable, has excellent corrosion resistance and has much higher ductility as compared to the copper-base alloys, which have medium corrosion resistance and are susceptible to stress-corrosion cracking [108]. This large strain makes it possible to use for larger travel of moving parts such as applications in liquid-flow microvalves.

The mentioned advantages of the TiNi-based alloy can be harnessed to provide a unique and powerful actuator. As an actuator, it is capable of up to 8% strain and 500 MPa recovery stress, the work density is reported to be as high as $5 \times 10^7 \text{ J/m}^3$ [109] and, if strains are kept below 2%, TiNi actuators can survive millions of cycles [110]. More recently applications of SMA in MEMS have led to the development of TiNi in the form of sputter deposited thin film [111,112].

2.8.1 Shape Memory Effect

The shape memory effect (SME) occurs due to a temperature and stress dependent shift in the material's crystalline structure between two different phases, martensite and austenite. Martensite, the low temperature phase, is relatively soft whereas austenite, the high temperature phase, is relatively hard. Consider the highly simplified two-dimensional representation of the material's crystalline arrangement shown in Figure 2.35. Each box represents a grain of material with its corresponding grain boundaries. The grains form a heavily twinned structure, meaning they are oriented symmetrically across grain boundaries. The twinned structure allows the internal lattice of individual grains to change while still maintaining the same interface with adjacent grains. As a result, shape memory alloys can experience large macroscopic deformations while maintaining remarkable order within its microscopic structure [113].

Figure 2.35| Schematic illustration of the mechanism of the shape memory effect.

When a shape memory alloy is mechanically deformed in the martensitic state, it can return to its original shape of the parent phase when temperature is raised to above the reverse transformation temperature A_f . The process is known as one-way SME because the shape change occurs only upon heating. Subsequent cooling the material will not reverse the shape change to the deformed configuration.

It is possible for the alloy to remember both its parent shape and martensite shape simultaneously if 1) the sample is strongly deformed in the martensitic state; 2) precipitates are introduced in the sample by heat treatment; 3) the sample is heated in the restrained condition; or 4) the sample is subjected to a “training treatment,”. This is called the two-way SME (TWSME), although the strength to recover the martensite shape is weaker. The origin of the TWSME essentially derives from the character of the martensitic transformation - martensite nucleation is very sensitive to the stress field [114]. Recently, the effect was explained as being caused by an anisotropic dislocation structure developed in the austenitic matrix [115-117]. The dislocation structure creates an anisotropic stress in the matrix, which guides the formation of martensite into variants of preferential orientations in relation to the deformation adopted in the training procedure, thus resulting in a macroscopic shape change during subsequent thermal transformation cycles. However, the recoverable strains in TWSME are always significantly less than those involved for the one-way SME in the same alloy [118].

It has been known that near-equiatomic and slightly Ni-rich TiNi alloys show a two-way shape memory effect after a suitable heat treatment under elastic constraint [119]. Since this effect enables TiNi thin film to deform spontaneously both upon cooling and heating without any bias force, the TWSME is useful for miniaturizing and simplifying actuators [120]. A microactuator using such TWSME of a TiNi thin film was first demonstrated by Kuribayashi *et al.* [121]. It is found that the effect is related to the precipitation process and distribution of fine Ti_3Ni_4 plate precipitates in the matrix, and is sensitive to aging treatment conditions such as temperature and time. The constraints during the aging treatment produced preferentially oriented precipitates that have an intrinsic stress field around them, causing the TWSME to occur.

The macroscopic behavior of SME can be illustrated by Figure 2.36. The characteristic temperatures, M_s (martensite transformation start temperature), M_f (martensite transformation finish temperature), A_s and A_f as indicated in the graph refer to the temperature at which the transformation to martensite starts and finishes, and the temperatures at which the reversion to austenite starts and finishes, respectively. There is hysteresis associated with martensitic transformations. In other words, the transformation temperatures differ upon heating and cooling. The magnitude of the hysteresis, T_1 , depends upon the alloy, but values of 5K ~ 40K are typical for shape memory alloy systems.

Figure 2.36| Typical transformation versus temperature curve for a specimen under constant load (stress) as it is cooled.

2.9 Summary

Amorphous carbon is traditionally used as a protective coating on cutting tools to impart hardness and wear resistance and as a passivation coating on magnetic hard-disks to prevent damage to the magnetic layers. Recently, the prospect of a-C, specifically low stress film for use in MEMS has caught the attention of the researchers. In the as-deposited state, the material exhibits extremely high compressive stress. In order for the micromachined structures to work, the films must have very low stress and very low stress gradients. The stress relief of a-C film-based MEMS offers several advantages to conventional Si MEMS. The stress relief temperature of a-C is around 600 °C, which is much lower than the 1100 °C of typical MEMS structural material, poly-Si. This is important for reducing the thermal budget when MEMS is integrated with electronics.

Owing to the material's amorphous nature, dopant can be incorporated into the matrix to moderate the properties of the material. Preliminary studies have shown Si doping can increase the tetrahedral bonding. Also, haemocompatibility is improved with Si incorporation as the number of adhered platelets is reduced, lowering the tendency to form thrombus (blood clog). Therefore, Si doped a-C is promising for MEMS devices in medical applications either *in vitro* or *in vivo*.

Amorphous carbon containing Si exhibits some very desirable characteristics. However, many concerns are still unaddressed, and the fundamentals of the properties are still unclear. In order to understand this material and for its successful incorporation into biomedical MEMS devices, the following issues need to be investigated:

- Amorphous carbon doped with Si is found to have a higher diamond-like component. But what is the mechanism for this increment?
- There are different results on the mechanical properties like hardness and modulus. Some groups showed a drop in the properties, while other shows improvement. Why is there such difference?
- It is well known that high hardness is always accompanied with high residual stress in a-C films. If Si doping can reduce the stress, will the mechanical properties be sacrificed?

- Si doping of a-C has shown improved blood compatibility. However, the cellular response is still very much unknown. Assuming both blood and tissue compatibilities are good, so what causes these desirable responses? Are the increases in diamond-like fraction and change in wettability the reasons, as put forward by several research groups?
- A number of groups have shown the possibility to micromachine a-C films. Can the Si doped variant be microfabricated as well, as the conventional micromachining procedures are designed to etch Si?

In this project, a systematic investigation on the influences of incorporating Si into a-C will be conducted. The fundamentals of the evolution of mechanical and biological properties are the focal areas of study. The feasibility of incorporating the doped film into a microsystem will also be demonstrated.

CHAPTER 3 ~ BONDING IN AMORPHOUS CARBON CONTAINING SILICON

The properties of the a-C(Si) films are affected by the nature of their interatomic bondings. Therefore, it is necessary to characterize and understand the bondings of these films. This chapter will describe the synthesis of the films and the bondings of the deposited films with different silicon concentrations and thermal treatments. The effects by the different silicon concentrations and thermal treatments on the interactions between silicon and carbon atoms will be discussed in detail based on the results from X-ray photoelectron spectroscopy and Raman spectroscopy.

3.1 Synthesis of a-C(Si) Films

3.1.1 Deposition of a-C(Si) Films

Magnetron sputtering was used to deposit the a-C(Si) films with different silicon concentrations. The system used was an *E303A Magnetron Sputtering System (Penta Vacuum)*. In each batch, one piece of 4-inch (diameter) and several pieces of diced (100) monocrystalline single side polished silicon wafers were deposited. Prior to deposition, the 4-inch wafers were chemically cleaned in a *piranha bath* (a mixture of 3:1 concentrated sulphuric acid to hydrogen peroxide solution) at 120 °C for 1 hour, and then rinsed several times with deionized water, followed by spin drying and finally dehydration baking in an oven at 120 °C for 1 hour. The diced pieces of wafer were ultrasonically cleaned in acetone for 20 min (the acetone was renewed at 5 min intervals) and was then followed by ultrasonic cleaning in

ethanol for 10 min. The substrates were then blow-dried with nitrogen and finally baked in an oven at 120 °C for 1 hour.

Figure 3.1| Schematic diagram of E303A Magnetron Sputtering System. The distance between the target and substrate was approximately 100 mm. The magnetrons with shutters holding the C and Si targets were tilted approximately 30° inward with reference from the vertical axis. Shutters were closed during target pre-sputtering and were opened for actual deposition. A pair of ceramic heaters was located 10 mm below the substrate holder. The silicon samples were placed near the circumference of the substrate holder so that they can be under the magnetrons.

The silicon substrates were placed in the sputtering chamber. Before the actual deposition, the substrates were plasma cleaned with Ar for 20 min at a radio frequency (RF) induced substrate bias of 300 V to remove the surface oxide. The sputtering targets were then pre-sputtered for 10 min. The actual deposition began thereafter.

Fixed sputtering parameters:

- Base pressure : 4.5×10^{-3} Pa
- Process pressure : 800×10^{-3} Pa
- Ar flow rate : 50 sccm
- Substrate bias : -10 V (RF-induced)
- Substrate rotation : ~16 rpm
- C target power density : 7.4 W/cm^2 (DC)

Adjusted sputtering parameter:

- Si target power density: 0, 0.5, 1.0, 1.5, 2.0, 2.5 W/cm^2 (RF)

The deposition times were varied accordingly to achieve a similar coating thickness of ~300 nm for all the batches. The thickness was determined by a *Dektak 3SJ Profilometer* that has a probe that scans across a step created by the deposited film. A strip on the silicon substrate was covered with photoresist. The photoresist was then stripped after the deposition to create the step. The uniformity of the coating thickness was between 15 – 25 nm across the whole piece wafer. The portion directly under the magnetrons was slightly thicker than the portion further away.

3.1.2 Thermal Treatment

The samples were thermally treated in-situ and post deposition to study the effects on the bonding, and the mechanical and biological properties of a-C(Si) films.

3.1.2.1 High Temperature Deposition

The depositions of a-C(Si) with a selected concentration of silicon were done at high temperature to achieve *in situ* deposition annealing. The substrate holder was heated by two ceramic coils. The substrate temperatures at which the depositions were done were 100 °C, 300 °C and 500 °C.

3.1.2.2 Rapid Thermal Processing

After deposition, the samples were annealed in a *Jipelec Jetfirst100 Rapid Thermal Processor*. The temperature was recorded by a thermocouple when the annealing temperature was below 500 °C and by a pyrometer when the annealing temperature was above. The chamber was evacuated by a rotary pump for 3 min and then purged with 2000 sccm flow of Ar gas for 2 min. The process was repeated for five cycles to remove adsorbed oxygen and other adsorbed molecules from the chamber. The temperature ramping rate was fixed at 20 °C/sec, and the annealing time was 3 min for all the samples. The cooling rate was around 6 °C/sec. The annealing was done in an Ar-protected atmosphere. The flow was 2000 sccm and the pressure was about 1 atm.

3.2 Experimental Details

3.2.1 X-Ray Photoelectron Spectroscopy

The atomic concentration and bonding configurations of Si and C were characterized by X-ray photoelectron spectroscopy (XPS). The spectra of binding

energy can be used to determine the elements present, relative quantity of each element and chemical state of the elements present. A *Kratos AXIS X-ray photoelectron Spectrometer* using monochromatic Al-K α (1486.71 eV) x-ray radiation, operating at 15 kV in vacuum of 10^{-6} Pa was employed to characterize the a-C(Si) films. First a survey scan between 0 and 1250 eV with a step size of 1.0 eV was done to determine the elements present in the film, and then it was followed by a narrow scan of step size 0.1 eV at the binding energy range covering the peak position of the detected elements. The atomic concentrations of the elements were calculated based on the integrated peak area ratio. The deconvolution of the C 1s peak was done using the *XPSpeak* program using the Gaussian distribution function. The fitted curves had a reduced Chi-square of 1.2 or less to ensure convergence. The respective contribution of the various bonding configurations was calculated based on the deconvoluted peak area ratio.

3.2.2 Raman Spectroscopy

Besides XPS, the bonding of a-C(Si) was also characterized by Raman spectroscopy, a nondestructive method where information about the bonding can be determined through peak shift and width. A *Renishaw Raman Spectroscope RM1000* using a HeNe laser source with an excitation wavelength of 633 nm, and a scan area of about $3.14 \mu\text{m}^2$ was used. The data acquisition region was from 800-2000 cm^{-1} , and the laser power used was ~ 1 mW. The peaks were deconvoluted with the *Origin 6.1* program. The formulation and script for the Breit-Wigner-

Fano function and Lorentzian function pair fit was self-written into the program. The fitted curves had a reduced Chi-square of 1.2 or less to ensure convergence.

3.3 Effect of Silicon Concentration

XPS analysis was conducted to determine the atomic concentration of the various elements present in the films. The Si concentrations of the films are presented in Table 3.1. The deconvoluted C 1s XPS peaks for pure a-C and a-C(7.4at%Si) are shown in Figure 3.2. Comparing the XPS full-width-at-half-maximum (FWHM) with that of graphite (0.6 eV) and diamond (1.0 eV) [122], the C 1s peaks obtained in this study were much broader: 1.6 eV for the undoped film and 2.0 eV for the Si-incorporated films. Therefore, there are contributions from different C bonding configurations to the C 1s peak. With increasing Si concentration, broadening of the C 1s peak is observed. The deconvolution of the spectra show that the broad C 1s peaks are composed of four peaks corresponding to C-O, C-C, C=C and C-Si bondings. The four peaks are well separated, by ~0.7 to 1.5 eV, and are positioned respectively at ~286.6 eV, ~285.2 eV, ~284.3 eV and ~283.5 eV. The FWHM of these peaks were determined to be ~1.3 to 1.7 eV (C-O), ~1.2 to 1.4 eV (C-C), ~1.2 to 1.4 eV (C=C) and ~1.1 to 1.4 eV (C-Si).

The C=C peak appearing at 284.3 eV is assigned to sp^2 bonding. The sp^3 component is at a higher binding energy, 285.2 eV, for the C-C, or at a lower binding energy, 283.5 eV, for the C-Si bonds. The effect of Si concentration on the evolution of the chemical bonding state was analyzed from C 1s core level

spectra. From Figure 3.3, the C-Si contribution is proportional to the Si concentration. There is a gradual decrease in the C=C (sp^2) bonds with increasing C-Si contribution, while the amount of the C-C bonding (sp^3) remains relatively unaltered. The results show that the Si atoms preferentially substitute for the sp^2 -hybridized C atoms during sputter implantation. Although the C-C (sp^3) contribution does not increase in the global C 1s core level, the contribution of C-Si increases when more Si is incorporated into the network (more Si atoms are bonded to C atoms), whereas the contribution of the carbon-carbon bonding (C=C sp^2 and C-C sp^3) decreases. The calculated ratio of the C-C (sp^3) to carbon-carbon bonding network (c.f. Figure 3.4) shows that there is actually an increase in the sp^3 fraction.

Table 3.1| Si atomic concentration as a function of the sputtering power density of the Si target.

Samples	Si Target Sputtering Power Density (W/cm^2) (RF)	Si (at.%)
a-C(Si0at.%)	-	0
a-C(Si7.4at.%)	0.5	7.4
a-C(Si16.6at.%)	1.0	16.6
a-C(Si24.9at.%)	1.5	24.9
a-C(Si32.3at.%)	2.0	32.3
a-C(Si37.6at.%)	2.5	37.6

Figure 3.2| C 1s peak deconvolution for a) a-C and b) a-C(Si7.4at.%) films. With increasing Si concentration, the C 1s peak broadens. The C 1s peak was composed of four peaks, where the corresponding bonding configurations are C-Si (283.5 eV), C=C (284.3 eV), C-C (285.2 eV) and C-O (286.6 eV).

Figure 3.3| Contribution of different bonding configurations as determined from C 1s peak with increasing Si concentration. There's a decrease in the contribution of C=C (sp^2) and an increase in C-Si as Si atomic concentration is increased. The C-C (sp^3) concentration is relatively unaffected. This shows a Si preferential substitution of sp^2 -hybridized C.

Figure 3.4| sp^3 fractions in carbon-carbon bonding network with increasing Si atomic concentration. Si atoms break the sp^2 -hybridized aromatic ring bonding structures, removing two π bonds per substituted C atom and promote the formation of sp^3 -hybridized C-C bonding configuration.

Figure 3.5 shows the Raman spectra of the a-C(Si) films and disordered graphite. The G and D peaks ($\sim 1580\text{ cm}^{-1}$ and $\sim 1330\text{ cm}^{-1}$ respectively) of the disordered graphite are used as a guide for the Raman band positions for the laser excitation wavelength used (633 nm). The Raman spectra were deconvoluted into G and D peaks [123] (c.f. Figure 3.6), and the results (i.e., G and D peak shift, variation in the FWHM, and the intensity ratio of D to G peaks with increasing Si concentration) are presented in Figure 3.7, Figure 3.8 and Figure 3.9. From Figure 3.3, Si atoms preferentially substitute the sp^2 -hybridized C atoms during sputter implantation; the incorporation of Si breaks the sp^2 -hybridized aromatic ring bonding structures. This removes two π bonds for each C atom substitution and thus promotes the formation of the sp^3 -hybridized C-C bonding configuration. This argument is supported by the results from Raman spectroscopy. Figure 3.9 clearly shows the decrease in the relative intensity of the D-peak. The breaking of

the sp^2 sixfold aromatic rings bonding structure causes a decrease in the intensity of the D-peak, since the presence of the D-peak is due to the presence of the sp^2 aromatic rings (Figure 3.10). This shows an increase in the overall disordering of the C-network, and the chance of sp^3 formation enhances.

Figure 3.5| Raman spectra of a-C(Si) films and disordered graphite. G-peak of disordered graphite is at $\sim 1580 \text{ cm}^{-1}$, and the D-peak is $\sim 1330 \text{ cm}^{-1}$. It is clear that the G peaks downshift to lower wavenumbers as the Si concentration increases. The peak at $\sim 960 \text{ cm}^{-1}$ is the 2nd order Raman band of Si substrate and it increases when Si concentration is higher.

Figure 3.6| Raman spectra of a) a-C(Si0at.%) and b) a-C(Si37.6at.%) films. Both G and D peak positions are downshifted with the increase of Si concentration. The relative intensities of the D-peak to G-peak lower significantly at higher concentration of Si. The 2nd order peak intensities of Si increase with increasing Si concentration.

Figure 3.7| Raman G and D peak positions with increasing Si concentration. Both peaks downshifted toward lower wavenumbers when the Si concentration is increased. The downshifting is caused by the heavier Si atoms and increased disordering.

Figure 3.8| Raman G peak FWHM with increasing Si concentration. FWHM of the peak increases slightly with the increase of Si concentration. This is due to the increase in disordering and decreases in sp^2 cluster crystallites size.

Figure 3.9| Raman D to G peak intensity ratios with increasing Si concentration. The ratio decreases with the increase in Si concentration. It is caused by the breakdown of the sp^2 -bonded aromatic ring structures, and the increase in sp^3 fraction.

Figure 3.10| Carbon motion in a) G mode and b) D mode. G mode is due to the relative motion of sp^2 carbon atoms and can be found in chains as well; and D mode is prohibited in crystalline graphite. [123]

The decrease in I_D/I_G intensity ratio with increasing Si corresponds to the decrease in the average crystallite size of sp^2 -bonded clusters [123], as well as the increase in sp^3 fraction [124]. The disordering and loss of aromatic bonding cause the amorphous-carbon signature peak to downshift [79,123], as illustrated in Figure 3.5 and Figure 3.7, which show the downshifting of both the D and G peaks to lower wavenumbers with increasing Si concentration. However, the amount shifted on a-C(Si) (downshift to $\sim 1431\text{ cm}^{-1}$ for a-C(Si37.6at.%)) is much higher than undoped DLC. Results from Ferrari and Robertson [123], Prawer *et al.* [125] and Anders *et al.* [126] show that the minimum position for the G-peak is never less than $\sim 1500\text{ cm}^{-1}$. Then the peak position upshifted to higher wavenumbers as the sp^3 increases, corresponding to Stage 3 in the model proposed by Ferrari and Robertson [123]. In a-C(Si), the G-peak will not upshift when the sp^3 is increased; the trend is similar to hydrogenated DLC [123] and hydrogenated a-C(Si) [127]. In our results, the more severe downshift of unhydrogenated a-C(Si) is due to the presence of Si-C bridging bonds [128] and the lowering of C=C vibration modes by the heavier Si atoms in the C network [20]. It is also partially attributed to a

reduction in compressive stress when silicon is introduced into the films, since the longer de-strained bonds vibrate at lower frequencies [20]. The width of G peak scales with disorder, and corresponds to the crystallite size of the sp^2 -bonded clusters. As shown in Figure 3.8, the FWHM of G peak increases; therefore it further substantiates the other results on the increase of network disordering and the decrease of sp^2 crystallites.

The Raman peak at $\sim 960\text{ cm}^{-1}$ is the 2nd order peak of crystalline Si (c.f. Figure 3.5). It is a peak from the Si substrate, and not from the doped film. The peak intensity increases as the Si concentration is increased, because optical transparency of the a-C(Si) increases when more Si is incorporated. This has been visually verified from the samples deposited on glass slides. This is expected since more opaque C=C (sp^2) structures have decreased and the remaining are olefinic (having wider optical gap [123]) rather than rings. Jungnickel *et al.* [129], Chen and Robertson [130] and McCulloch *et al.* [131] all calculated that the band gap increased with decreasing sp^2 content in amorphous carbon networks.

3.4 Effect of Temperature

3.4.1 Comparing a-C and a-C(Si)

Firstly, the curve deconvolution regime will be explained. The deconvolution was done using a mixed Gaussian and Lorentzian distribution function for Raman spectra when the G-peak was at lower wave numbers ($< \sim 1550\text{ cm}^{-1}$). The Breit-

Wigner-Fano (BWF) and Lorentzian distribution functions were used for fitting the G-peak and D-peak respectively when the G-peak upshifted to higher wave number ($> 1550 \text{ cm}^{-1}$). The BWF function has an asymmetrical lineshape depending on the skewness coefficient Q . The Lorentzian lineshape is recovered when $Q^{-1} \rightarrow 0$. This function is widely used for fitting the G-peak of tetrahedral amorphous carbon (ta-C) where it is always at a higher wavenumber ($\sim 1580 \text{ cm}^{-1}$) [125,132,133]. The BWF function is calculated and fitted from the following equation [34];

$$I(\omega) = \frac{I_0 [1 + 2(\omega - \omega_0)/Q\Gamma]^2}{1 + [2(\omega - \omega_0)/\Gamma]^2} + [a + b\omega] \quad 3.1$$

where I_0 is the peak intensity, ω_0 is the peak position, Γ is the full width at half maximum (FWHM), Q^{-1} is the BWF coupling or skewness coefficient, and $[a + b\omega]$ is the linear baseline correction for the lineshape. Because of the skewness of the line shape, the maximum of the BWF occurs at

$$\omega_{\max} = \omega_0 + \frac{\Gamma}{2Q} \quad 3.2$$

As shown in Figure 3.11, fitting using two symmetrical lineshapes is not suitable when the G-peak was upshifted towards higher wavenumber (becoming more graphitic). This is because of the asymmetry of the vibrational density of state (VDOS) of graphite or amorphous carbon, dominated by sp^2 crystallites [134]. There is an abrupt drop in the VDOS at the high-frequency end of the G-peak, therefore an asymmetrical lineshape like a BWF with a rapid decline on the

high frequency end will produce a much better fit. The use of the BWF function lineshape is merely because of the suitability, and there is no Fano resonance present in a-C or a-C(Si) films.

Figure 3.11| Deconvolution of a-C(Si0at.%) annealed at 800 °C using a) two symmetrical functions; b) BWF for G-peak and Lorentzian for D-peak. A much better fit can be achieved using the asymmetrical BWF function for the G-peak fitting. This is due to an abrupt drop in the VDOS at the high-frequency end of the G-peak of graphite or amorphous carbon that is dominated by sp^2 crystallites.

Figure 3.12 and Figure 3.13 show the evolution of the Raman spectrum with annealing temperature of a-C(Si0at.%) and a-C(Si37.6at.%) films respectively.

Figure 3.12| Evolution of the Raman spectrum of the a-C(Si0at.%) films with increasing annealing temperature. Intensity of the D-peak increases significantly from 400 °C and above. G-peak position upshifts to $\sim 1590 \text{ cm}^{-1}$ gradually with increasing annealing temperature. This is due to the nucleation of sp^2 sites and the formation and clustering of aromatic ring structures.

Figure 3.13| Evolution of the Raman spectrum of the a-C(Si37.6at.%) films with increasing annealing temperature. The spectrum maintains up to 600 °C, and then a sudden upshift of G-peak and increase in D-peak intensity when temperature is further increased.

The respective spectra of both the films were deconvoluted with the regime of curve-fitting function selection discussed earlier. The deconvolution results - Raman G-peak shift, variation in the FWHM, and the ratio of D to G peak intensity with increasing annealing temperature of the two films are presented in Figure 3.14, Figure 3.15 and Figure 3.16 respectively.

Figure 3.14| The Raman G-peak positions of a-C(Si0at.%) and a-C(Si37.6at.%) films with increasing annealing temperature. The G-peak of a-C upshifted gradually and reached $\sim 1590 \text{ cm}^{-1}$ at about $600 \text{ }^{\circ}\text{C}$. The G-peak of a-C(Si37.6at.%) maintained its position until about $600 \text{ }^{\circ}\text{C}$, and then an abrupt upshifting to $\sim 1590 \text{ cm}^{-1}$. It is because the Si prevents its bonded C atoms from clustering into aromatic rings and thus suppresses the growth of the crystallites below $600 \text{ }^{\circ}\text{C}$. The abrupt upshifting is caused by the breakdown of the metastable sp^3 bonded C.

Figure 3.15| The Raman G-peak FWHM of a-C(Si0at.%) and a-C(Si37.6at.%) films with increasing annealing temperature. FWHM of a-C decreases gradually and reached the lowest point ($\sim 104 \text{ cm}^{-1}$) at about $600 \text{ }^{\circ}\text{C}$. FWHM of a-C(Si37.6at.%) increases until $600 \text{ }^{\circ}\text{C}$, and then an abrupt decrease to $\sim 100 \text{ cm}^{-1}$. Si suppresses the clustering of sp^2 sites and prevents the growth of crystallites sizes to at least $600 \text{ }^{\circ}\text{C}$ before the breakdown of the sp^3 bonded C.

Figure 3.16| The Raman intensity ratios of the D over G peaks of a-C(Si0at.%) and a-C(Si37.6at.%) films with increasing annealing temperature. I_D/I_G of a-C(Si0at.%) increases gradually and reached a maximum of ~ 1.18 at 1000 °C. I_D/I_G of a-C(Si37.6at.%) maintained at relatively low value ($\sim 0 < I_D/I_G < \sim 0.13$) until 600 °C, then a sharp increase and reached a value of ~ 1.59 at 800 °C. I_D/I_G increases with increasing in-plane correlation length or grain size of the sp^2 clusters. Si suppresses the clustering of sp^2 sites and prevents the growth of crystallites sizes to at least 600 °C before the breakdown of the sp^3 bonded C.

In Figure 3.12 and Figure 3.14, the G-peak of the undoped a-C upshifts to a higher wavenumber as the annealing temperature is increased. The G-peak position reaches $\sim 1589 \text{ cm}^{-1}$ (graphite peak position) at $\sim 600 \text{ °C}$. This shows the removal of disorder and the increasing dominance of crystallites. These phenomena are substantiated by the decrease in G-peak linewidth (Figure 3.15) and the increase in I_D/I_G ratio (Figure 3.16). When disordering is removed, the sp^2 -hybridized aromatic rings will start to form and nucleate into crystallites. D-peak intensity increases as the number of aromatic ring structures increases, and the I_D/I_G ratio is found to be related to the in-plane correlation length or grain size of the sp^2 clusters [123]. The FWHM decreases when the disorder is removed, and

because the amorphous carbon has begun the crystallization process into graphite that is 100 % sp^2 bonded.

From Figure 3.13 and Figure 3.14, the G-peak and D-peak of the a-C(Si37.6at.%) only start to upshift above ~ 600 °C. But the degree of upshifting is more pronounced than in the undoped counterpart. The result is in good relation with the G-peak linewidth and I_D/I_G ratio results. The decrease in G-peak linewidth (c.f. Figure 3.15) and increase in I_D/I_G ratio (c.f. Figure 3.16) only started above ~ 600 °C. The FWHM of the a-C(Si37.6at.%) actually increases when the annealing temperature is between ~ 200 °C to ~ 600 °C. This shows an enhanced disordering, and is probably due to the promotion of bonding between C and Si atoms within the network. It is clear that the Si atoms bonded to C atoms prevent the nucleation of the sp^2 aromatic clusters and probably also sp^3 to sp^2 conversion when the annealing temperature is increased. In other words, the activation energies for the nucleation of sp^2 C and sp^3 to sp^2 conversion are increased for Si doped a-C. The same cannot be applied to a-C with little amount of Si doping.

After ~ 600 °C, there is a rapid upshifting of the a-C(Si37.6at.%) G-peak position, an abrupt decrease in the G-peak linewidth and an increase in I_D/I_G ratio. This temperature range is probably the yield point for the C-C (sp^3) bonding configuration. Above ~ 600 °C, the bonding starts to breakdown (sp^3 is the metastable state of C) and release more C with dangling bonds into the amorphous matrix. This causes an instant increase in the nucleation of sp^2 sites and aromatic

clusters, therefore causing an abrupt change in Raman results. The disappearance of the Si substrate 2nd order peak at $\sim 960 \text{ cm}^{-1}$ shows the decrease in the optical transparency of the film due to an increase formation of more opaque sp^2 structures. These results are in good agreement to those of Ferrari *et al.* [11] with ta-C with sp^3 fraction of $\sim 87\%$. Referring to Figure 3.17, the G-peak upshifting, FWHM decreasing and I_D/I_G increasing only started above the annealing temperature of $\sim 600^\circ\text{C}$ - $\sim 800^\circ\text{C}$, below that, the results do not change significantly.

Figure 3.17| The evolution of Raman I_D/I_G ratio, G-peak position shift and G-peak FWHM with increasing annealing temperature. Data from Ferrari *et al.* [11]

3.4.2 Comparing Thermally Treated a-C(Si)

Figure 3.18a shows the Raman spectra of a-C(Si) thin films deposited at different substrate temperatures. The signature peak can be deconvoluted into the graphitic (G) and disorder (D) peaks. The peak situated at 960 cm^{-1} is a signal from the bottom Si substrate, and not from the Si inside the a-C films. The G-peak is the signal from the sp^2 C bonding pair inside the a-C(Si) film, and the D-peak arises due to breathing modes of the aromatic clusters. Figure 3.18a clearly shows the increase in the relative intensity of the D-peak with increasing deposition temperature. The formation and clustering of the sp^2 aromatic ring bonding structures when there is an increase in the C=C sp^2 bondings causes an increase in the intensity of the D-peak. The deconvolution result of intensity ratio of D to G peaks, I_D/I_G , is presented in Figure 3.19. The increase in I_D/I_G intensity ratio with increasing deposition temperature corresponds to the decrease in disordering as mentioned earlier, and the increase in the average crystallite size of sp^2 -bonded clusters [123], as well as a decrease in sp^3 fraction [124]. The ordering and formation of aromatic bonding structure cause the amorphous-carbon signature peak to upshift [79,123], and this phenomenon is clearly illustrated in Figure 3.18a, which show the upshifting with increasing deposition temperature.

When the a-C(Si) films deposited at room temperature are subjected to post-deposition annealing, as shown in Figure 3.18b, the Raman spectra show an unchanged G-peak position, and then an increase in D-peak intensity at $\sim 700\text{ }^\circ\text{C}$. This illustrates no drastic change in the internal bonding configuration when the

film is annealed to $\sim 600^\circ\text{C}$; graphitization has not taken place. Graphitization or substantial increase in the sp^2 -bonded clusters will upshift the G-peak to around 1580 cm^{-1} , in response to the ordering and the increasing dominance of crystallites. From Raman spectroscopy results, the Si atoms bonded to C atoms prevent the nucleation of sp^2 aromatic clusters and retard the conversion of C sp^3 bonds to sp^2 when the annealing temperature is increased. After $\sim 600^\circ\text{C}$, there is a rapid upshifting of the a-C(Si) G-peak position, an abrupt decrease in the G-peak linewidth and increase in I_D/I_G ratio (Figure 3.19). Above $\sim 600^\circ\text{C}$, the C sp^3 bondings start to breakdown. This causes an instant increase in the number, as well as the nucleation of sp^2 sites, and aromatic clusters.

Figure 3.18| Raman spectra of a-C(Si): a) deposited at different temperature; b) annealed at different temperature after deposition. The doped Si cannot prevent the

nucleation and clustering of sp^2 C during deposition at high temperature; as indicated by the increase in D-peak intensity and upshifting of the G-peak. But the dopant is able to prevent the graphitization process during post-deposition annealing. The clustering of sp^2 C aromatic rings is prevented, and the conversion of sp^3 C to sp^2 C is also retarded.

Figure 3.19 I_D/I_G ratio of a-C(Si) thermally treated at different temperature. The increase in the intensity of the D-peak indicates the increase in ordering, decrease in sp^3 C fraction and increase in the size of sp^2 clusters. These phenomenon starts at a much lower temperature during high temperature deposition.

The effect of temperature on the evolution of the chemical bonding state was analyzed from C 1s core level XPS spectra. The C=C peak appearing at 284.3 eV is assigned to the sp^2 bonding configuration. The sp^3 component can be found at higher binding energy of 285.2 eV for the C-C, or at the lower binding energy 283.5 eV for the C-Si bonds. The percentage of each bonding configuration is taken as the ratio of the area under the respective peaks over the whole C 1s peak. The typical deconvoluted C 1s peak (a-C(Si37.6at.%) deposited at 100 °C) is shown in Figure 3.20.

The results of high temperature deposition are summarized in Figure 3.21a. C=C sp^2 -hybridized and C-Si sp^3 -hybridized bonding configurations increase, whereas the C-C sp^3 -hybridized bonding configuration decreases drastically when the deposition temperature is increased. The decrease in the C-C sp^3 bonds shows that the bulk of them are being converted into C=C sp^2 and C-Si sp^3 bonds. The heat provided during the deposition process has given C-C sp^3 metastable bonds enough energy to reach a more stable state, that is, the C=C sp^2 bonding configuration. The heat energy also promotes the bonding between C and Si atoms, therefore also increasing the C-Si bonding configuration.

The evolution in the bonding configurations of a-C(Si) films subjected to annealing is different, Figure 3.21b. C-Si sp^3 bond fraction increases slightly from 400 °C to 600 °C, and both C-C sp^3 and C=C sp^2 fractions decrease after 400 °C. There is a drastic increase in the amount of C=C sp^2 bonds and decrease in C-C sp^3 bonds above 600 °C; illustrating the onset of $sp^3 \rightarrow sp^2$ conversion in the bulk. The conversion though, seems to take place at a lower temperature of ~400 °C, but the free or under-coordinated Si bond with the newly converted and existing sp^2 C forming more C-Si bonds. But once all Si atoms are bonded, there is no deterrence of sp^2 C formation and clustering.

Figure 3.20| The deconvoluted C 1s peak of a-C(Si37.6at.%) deposited at 100 °C.

Figure 3.21| The contribution of different bonding configurations from C 1s peak of a-C(Si): a) deposited at different temperature; b) annealed at different temperature after deposition. The sp^3 C decreases rapidly during high temperature deposition, indicating fast $sp^3 \rightarrow sp^2$ conversion. However, at post-deposition annealing, this conversion is being retarded to a higher temperature. C-Si sp^3 bonds increase because Si preferentially bond with sp^2 C (as discuss in earlier sections).

The bond strength of a C-Si bond is 320 kJ/mol, and for C-C sp^2 -hybridized bond is 411 kJ/mol [81]. The strength is high enough to ensure mechanical integrity if the fractions are high (especially for C-C). But when more C=C sp^2 -

hybridized bonds are created via the thermal treatments, the hardness falls (to be discussed in a later section). The reason is the π bonds associated with the C sp^2 bondings. The strength of these van der Waals bonds is only 7 kJ/mol [135]. Therefore, both $sp^3 \rightarrow sp^2$ conversion and sp^2 site clustering are main reasons for the thermal degradation of the mechanical properties of these films. These two phenomena exhibit Arrhenius type behavior. Since $sp^3 \rightarrow sp^2$ conversion is a distinct transition not allowing a proper Arrhenius plot, the activation energies of this conversion in high temperature deposition and annealing are estimated from $kT \ln(\nu_0 \tau)$, using a phonon attempt frequency of $\nu_0 \sim 1 \times 10^{14}$ and an experimental time $\tau \sim 1$ s. Taking the transition temperature as 100 °C for high temperature deposition and 700 °C for annealing, the activation energies for the bulk $sp^3 \rightarrow sp^2$ conversion are ~ 1.1 eV for high temperature deposition and ~ 2.7 eV for post deposition annealing. The I_D/I_G ratio is a measure of sp^2 clustering [123], so the activation energies of sp^2 clustering in high temperature deposition and annealing are extracted from the Arrhenius plots of the I_D/I_G ratio. It is found that the activation energy for sp^2 clustering during high temperature depositions is ~ 0.07 eV (Figure 3.22a), and ~ 0.34 eV for post deposition annealing (Figure 3.22b).

Figure 3.22| Arrhenius plots of: a) I_p/I_g for post deposition annealing of a-C(Si); b) I_p/I_g for high temperature deposition of a-C(Si). The fitted straight lines have the relation: $\ln(y) = \ln(y_0) - (E_a/k_b)(1/T)$. The activation energies, E_a can be determined by multiplying the slopes of the plots with Boltzmann's constant, $k_b = 8.617 \times 10^{-5}$ eV/K. It is found that the activation energy of sp^2 clustering under high temperature deposition is 0.07 eV, and it is five times lower than the activation energy under post-deposition annealing, which is 0.34 eV.

When the thermal processing is done *in situ* during deposition, the Si atoms are not able to prevent the nucleation of sp^2 aromatic clusters and the conversion of sp^3 bonds to sp^2 . During high temperature deposition, in contrast to post-deposition annealing, additional energy is provided by the bombardment of the sputtered specie. The energy possessed by an impinging particle is converted into thermal energy at a point [136] or along a line (trajectory) [35], and then the energy disperses outwards by thermal diffusion. Instead of quick dissipation of the energy from the impinged particles and then get quench-in at room temperature

deposition, the heat at high temperature deposition will allow the impinged atoms to diffuse and rearrange themselves into a more stable position and bonding configuration. For C bondings, the stable configuration will be C=C sp^2 -hybridized bonds. In other word, the a-C(Si) films start to graphitize *in situ* during deposition when the deposition temperature increases.

3.5 Summary

Si incorporation into the a-C network changes the internal bonding configuration. Results from XPS show that there is an increase in C-Si sp^3 bonds, a decrease in the C=C sp^2 bonds, and C-C sp^3 bonds remain relatively unaltered. This shows that Si preferentially bonds with sp^2 configured C, and this is confirmed by the Raman spectroscopy results. The most convincing evidence is the decrease in the intensity ratio of the disorder peak against the graphitic peak (I_D/I_G). The D-peak is only due to sp^2 aromatic rings. Since the peak intensity decreases as Si is incorporated, it means that the ring structures are destroyed or broken up. This will disorder the amorphous network, i.e. there will be more C to C chains instead of rings. Once disorder is increased, there will be more chance for the formation of C-C sp^3 -hybridized bonds. The increase in network disordering and the decrease in sp^2 cluster size are also reflected by the increase in the FWHM of the G-peak and downshifting of the spectrum.

During post-deposition annealing, a-C(Si37.6at.%) exhibit better thermal stability than the undoped a-C. The undoped a-C starts to graphitize as early as 200 °C, while the atomic structure of a-C(Si) is stable until at least 600 °C. The Raman spectrum of a-C shows a decrease in the G-peak FWHM, an increase in the I_D/I_G ratio and upshifting of the spectrum when the annealing temperature is increased beyond 200 °C. All these behaviors indicated the breaking down of C-C sp^3 bonding, and their conversion into C=C sp^2 bonds, i.e. the decrease in network disordering. In addition, the sp^2 C chains and rings are also clustering. The a-C(Si), on the other hand, only exhibits this characteristic when the temperature is above 600 °C, where there is a rapid increase in the I_D/I_G ratio, upshifting of the spectrum and a decrease of the FWHM of the G-peak.

However, the a-C(Si) is not thermally stable during high temperature deposition. The graphitization characteristics of a-C(Si) deposited at higher temperature is rather similar to a-C under post-deposition annealing. The activation energies for C $sp^3 \rightarrow sp^2$ conversion and sp^2 clustering are both very much lower than the annealed a-C(Si). The thermal stability of a-C(Si) arises from the deterrence of these conversion and clustering. The under-coordinated Si atoms bond with the newly converted and existing sp^2 C forms more C-Si bonds during post-annealing. When the film is deposited at high temperature, the Si atoms are not able to prevent the nucleation of sp^2 aromatic clusters and the conversion of bonds, as additional energy is provided by the bombardment of the sputtered specie. Instead of a quick dissipation of energy from the impinged particles, the

additional energy cause the atoms to diffuse and rearrange themselves into a more stable position and bonding configuration, i.e. C=C sp^2 -hybridized bonds. Therefore, graphitization starts early under high temperature deposition.

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As discussed in the preceding chapter, the bonding of the a-C(Si) films will change when the films are having different silicon concentration and/or when they are subjected to thermal treatment. The interatomic bondings within the films dictate their mechanical properties and the properties are expected to change accordingly. The mechanical properties such as hardness, elastic modulus and stress of the a-C(Si) films were characterized and will be discussed in this chapter.

4.1 Experimental Details

4.1.1 Hardness and Elastic Modulus

The hardness and elastic modulus of the films were determined using the nanoindentation method. Due to the thinness of the films, microindentation's large indenter tip and high load is not suitable as the influence of the silicon substrate will be overwhelming. *MTS Nanoindenter (XP)* uses a Berkovich diamond tip and loading in mN range to make indentations in nanometer range, and is therefore the preferred equipment for hardness and modulus characterization for thin films. The indentation depth was set to 30 nm (10 % of the coating thickness) to prevent influence of the relatively softer Si substrate. Six indentations were made to determine the average hardness and modulus of the films. The hardness value was calculated by the system software employing the Oliver and Pharr method [137].

4.1.2 Residual Stress

The stresses of the films were determined by measuring the 4-inch wafer curvature. This method is suitable for coating-on-substrate bimorph configuration. A *Tencor FLX-2908 Laser System* was used for the measurement. The 4-inch wafer curvature was determined by a laser profilometer before and after film deposition. The stress was calculated from the Stoney's equation [138] based on the curvature change.

$$\sigma = \frac{E}{1-\nu} \cdot \frac{1}{6} \cdot \frac{t_s^2}{t_f} \cdot \frac{1}{R} \quad 4.1$$

where

$$R = \frac{R_1 R_2}{R_1 - R_2}$$

and E is the elastic modulus of a (100) silicon wafer ($E \approx 1.3 \times 10^{11}$ Pa), ν is Poisson's ratio of a (100) silicon wafer ($\nu \approx 0.28$), t_s is the substrate thickness, t_f is the film thickness, R_1 is the wafer curvature before deposition, R_2 is the wafer curvature with the deposited film. This formula was derived based on several explicit assumptions:

- (i) Both the film thickness t_f and the substrate thickness t_s are uniform and $t_f \ll t_s \ll R$, where R is the system radius;
- (ii) The strains and rotations of the plate system are infinitesimal;
- (iii) Both the film and substrate are homogeneous, isotropic, and linearly elastic or thermoelastic;
- (iv) The misfit strain state is in-plane isotropic or equi-biaxial; and

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- (v) The misfit strain state is spatially constant over the plate system's surface.

Assumptions (iv) and (v), of equi-biaxial, spatially constant misfit strain, cannot be checked directly. However, the system curvature can be measured. An equi-biaxial, spatially constant curvature, as results from these assumptions, corresponds to a substrate deformation that is exactly spherical. That is practically never the case for a real thin film-substrate system. If the deformation is not spherical, the assumptions of equi-biaxiality (iv) and of spatial uniformity (v) may not necessarily be met. Therefore, the accuracy of the measurement based on Stoney's formula may be in question. However, it was decided that it should be used in this work as it provides a mean of comparison with results of other research groups that are also using the method.

The curvature of a bare 4-inch silicon wafer was first measured with the system. The curvature was measured again after film deposition. In both cases, fifty data points were obtained across the diameter of the wafer to determine the curvatures. The stress value was then calculated by on Equation 4.1. The films were ~300nm, which were much thinner than the silicon substrate ($> 470 \mu\text{m}$), thus to fulfill one of the critical assumption mentioned above. Three stress measurements were performed to determine the average stress value.

4.1.3 Surface Roughness

The surface morphology and roughness were determined using a *Digital Instrument Dimension 3000* atomic force microscope in the tapping mode, and

Shimadzu 9500J2 atomic force microscope under constant force in the contact mode. Three to five scans were done for each sample, and the average roughness values and their respective standard deviation were processed for each sample.

4.1.4 Fabrication of Micro-Cantilever (Design 1)

Micro-cantilever design 1 will be used to demonstrate the effect of the films residual stress. The micromachining steps are illustrated in the following:

Prior to the photolithography, $\sim 1.8 \mu\text{m}$ of SiO_2 were thermally grown by *Tystar Oxidation Furnace* to be used as an etch-stop layer. The wafers were then chemically cleaned in a piranha bath at 120°C for 1 hour. Then they were rinsed several times with deionized water, followed by spin-drying and finally dehydration baking in an oven at 120°C for 1 hour.

Step 1:

AZ9260 photo-resist was first spin coated using a *CEE Spin Coater* at a rotational speed of 2000 rpm for 25 sec. The resulting thickness was approximately $7 \mu\text{m}$. Afterwhich, the wafer was baked on a hotplate at 110°C for 4 min to cure the photo-resist. The wafer was loaded into a *Karl Suss MA6 Mask Aligner* ready for UV exposure. The patterns were on a chrome-plated glass mask, and were

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transferred onto the wafer by the UV exposure of the photo-resist. The exposure time was 25 sec. The wafer was then developed in AZ 421K developer until the exposed areas were dissolved. The wafer was then rinsed with deionized water and blown dry.

Step 2:

The silicon dioxide layer was etched using reactive-ion etching (RIE), using a *Technics Micro-RIE Series 800-II*. Its plasma consisted of 90% tetrafluoromethane (CF_4) and 10% O_2 . The RF-induced power was 250 W and the process pressure was ~160 mTorr. The silicon dioxide layer was checked periodically during the etching to observe the full removal. The total etching time was approximately 30 min.

Step 3:

After stripping the photo-resist with acetone, the wafer was immersed into a 40 wt.% potassium hydroxide (KOH) bath at 80°C for silicon etching. The etching was anisotropic, and the thickness of the remaining wafer was checked every 2

hours. Etching stopped when there were only $\sim 100\ \mu\text{m}$ of wafer left (original thickness of wafer was $\sim 520\ \mu\text{m}$).

Step 4:

A second patterning process (with a different mask and patterns) was applied on the other side of the wafer, using Step 1 – 3. The KOH etching was stopped when the cantilevers were formed.

4.2 Hardness and Elastic Modulus

The hardness results of the as-deposited a-C(Si) films with varying Si concentration are presented in Figure 4.1. Both hardness and elastic modulus decreased initially when the Si concentration was increased up to 10 to 15 at.%, and then increased with further increasing of the Si concentration and surpassed the original values of the undoped a-C at ~ 32.2 at.% Si. Although Si promotes sp^3 formation and suppresses sp^2 aromatic clusters as discussed earlier, the C-Si bond strength is weaker than the C-C sp^3 bond: 320 kJ/mol for the C-Si bond as compared to 411 kJ/mol for the C-C bond [81]. This ultimately translates to lower hardness and modulus when Si starts to get into the C network. Furthermore, when Si is introduced, the global density of the film decreases due to the mismatch of

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atomic size (Si – 2.92 Å, C – 1.82 Å) and bonding length (C-Si: 1.89 Å, C-C: 1.54 Å).

Figure 4.1| Hardness and elastic modulus with increasing Si concentration. The values decreased initially at low Si concentration range, and then increased when the concentration is further increased. The doping of Si causes a drop in the global density of the network because of its larger atomic size and longer bonding length with C, and hence the drop in hardness when a-C is doped. The elimination of two π bonds per substituted sp^2 bonded C atom by Si also eliminates the contribution of these weak bonds (bonding strength of 7 kJ/mol) to the hardness value. And combining with the deposition kinetics, the hardness and modulus increased at higher Si concentration.

Besides the inter-atomic effects, the deposition condition can influence properties at a macroscopic level. The kinetic energy of sputtered particles can be estimated by the following relationship [139]

$$U_k \propto \frac{D_w V_s}{P_g^{0.5}} \quad 4.2$$

Where U_k is the kinetic energy, D_w the target power density, V_s the substrate bias and P_g is the gas pressure. Since the substrate bias voltage and process pressure were not varied in our sputtering process, the contributing parameter was the target

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power density. From the laws of conservation of energy and momentum, the initial energy of the target particle, E_t , when it is sputtered out by the bombarding ion, can be derived as [140]

$$E_t = \frac{4M_i M_t \cos^2 \theta}{(M_i + M_t)^2} E_i \quad 4.3$$

where E_i is the energy of the incident particle, M_t and M_i are the mass of target and incident particle respectively, and θ is the angle of incidence taken from the line joining their centers of masses. Using the atomic mass of 40 amu for Ar (the incident particle), 28.1 amu for Si and 12 amu for C, taking the incident angle to be zero (i.e. maximum energy transferred), and expressing the energy of Ar sputtering Si to be a fraction of that sputtering C (due to different power density), the energy of the sputtered C, E_C is $0.71E_{Ar}$, and E_{Si} is $0.32E_{Ar}$ for the highest Si power density used. Therefore, the kinetic energies of the Si at all target power densities will be lower than that of the sputtered C. In the co-sputtering process, the sputtered species can gain or lose energy due to the momentum transfer during collision with each other (in addition to the interaction with Ar ions). The collision cannot be elastic, as some energy will be lost due to the generation of phonons, and hence energy is not conserved. At low Si target power density, the sputtered Si will have a much lower kinetic energy than the sputtered C. The impact will result in a decrease in energy for the C species. Since the implantation energy of C is lower, the a-C(Si) films with low Si concentration will have a lower atomic number density as compared to the undoped a-C. Although the energy of the sputtered Si

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will increase, the contribution will not be as significant as Si sputtered at a higher target power density (i.e. increased amount of sputtered atoms and increased initial kinetic energy). This deposition dependent phenomenon is apparent in Figure 4.2, where the surface roughness (R_{rms}) increases from 0.5 nm (0.0 at.% Si) to 2.0 nm (16.6 at.% Si): the rougher surface indicates lower density, matching well with the hardness and modulus measurements (c.f. Figure 4.1, data before 16.6 at.% Si).

Figure 4.2| a) Surface roughness with increasing Si concentration; b) Surface morphology of a-C(Si16.6at.%); c) Surface morphology of a-C(Si36.7at.%). The surface roughness increases initially due to the decrease in density as the incorporated Si have larger atomic size and bonding length with C. Also, the deposition species have lower kinetic energies, hence inducing less densification. The roughness decreases at higher Si concentration because of an increase in density. The depositing atoms have higher kinetic energies due to higher sputtering power, thereby densify the film. On the other hand, more C atoms are sp^3 bonded with the increasing Si; hence more long π bonds are eliminated.

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When the Si target power density is increased, the intensity of the momentum transfer is not as intense, as now the energy of the sputtered Si is higher. Both Si and C will bombard the film surface with higher energy, but the energy level is still lower than sputtering C alone. The density of the a-C(Si) with higher Si concentration will however increase due to the reduction in π bonds as the C=C (sp^2) component decreases. These π bonds have the longest bond length in the network (3.35 Å), and thus this decrease will cause an increase in density. The combination of higher energy depositing atoms and the removal of sp^2 -hybridized C bondings at higher Si concentration translate to a lowering of surface roughness (from 16.6 at.% Si onwards) and an increase in hardness and modulus (c.f. Figure 4.1). These results are similar to undoped a-C [41]. Note that because the films are sputtered at room temperature, atomic surface diffusion insignificantly affects the roughness.

Neglecting the contributions from C-O and Si-O, the major contribution to hardness comes from C-C (sp^3), C=C (sp^2) and C-Si (sp^3). The weakest link is the π bonds associated with C=C bondings. The strength of these van der Waals bonds is around 7 kJ/mol [141]. As Si is incorporated into the a-C, some of these π bonds will be eliminated (as discussed earlier) and replaced by stronger C-Si and/or C-C bonds. Therefore, when more Si is incorporated, it preferentially substitutes these sp^2 -hybridized C=C bonds (as verified and discussed earlier), removing more of these weak π bonds as the Si concentration is increased. This leads to an increase in the hardness and modulus in the a-C(Si) films as Si concentration increases.

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The transverse optic phonon peak of silicon carbide situated at 760-780 cm^{-1} Raman shift [142] is not detected. This shows that there is no formation of amorphous silicon carbide, thus the effect of this phase influencing the hardness and modulus is not present.

Comparing the hardness results of others (c.f. Figure 4.3), the result of this work has a similar trend as that of Kulikovsky *et al.* [15] and Papakonstantinou *et al.* [19] in the range they conducted their experiments. Although the films of Kulikovsky *et al.* and this work were fabricated through sputtering, Kulikovsky's hardness was much higher than what we obtained. As mentioned earlier, the sputtering parameters can affect the mechanical properties. Kulikovsky *et al.* used a substrate bias that was six times higher than ours, and their process pressure was almost ten times lower, thus their films had a higher density and hence higher hardness. However, the residual stress of their film was high, nearly four times as high as ours (comparing our samples with the highest Si concentration; results to be discussed later in §4.3).

Figure 4.3| Hardness of a-C:H(Si) and a-C(Si) films with increasing Si concentration.

The trend between this work and that of Kulikovskiy *et al.* [15] is similar. Both samples were synthesized by magnetron sputtering and unhydrogenated. The hardness of the hydrogenated samples are not showing sign of recovery (data from [19] cannot be confirmed). The formation of Si-H polymeric bonds weakens the structural and mechanical properties of a-C.

It is worth noting that the data provided from Ref. 14 and 19 in Figure 4.3 are for hydrogenated amorphous C containing Si, denoted as a-C:H(Si) in the plot, and the data from [15] is for hydrogen free a-C(Si) deposited by DC magnetron sputtering. Ref. 14 and 19 used silane and tetramethylsilane (TMS) as the Si source, respectively. Both precursors contain H. The Si concentration was increased by increasing the gas flow rate; therefore H concentration was also increased. In a-C:H(Si), H atoms are bonded to both carbon and silicon. Although C-H bonds (338.5 kJ/mol) are more stable than Si-H bonds (298.7 kJ/mol) [20], the different electronegativity of silicon (1.74) and carbon (2.50) strengthens the Si-H bonds and weakens the C-H if a silicon atom was bonded to a carbon atom. Upon Si incorporation, these polymeric structures could develop and weaken the

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structural and mechanical properties of the films. Another possible contribution is the presence of weak Si-C bridging bonds. In this regard, Si-C bridging would further weaken the structural integrity of the hydrogenated films. Therefore, although the incorporation of Si atoms into a-C:H can increase and stabilize the tetrahedral bonding (sp^3 bonding), it can also induce the development of a polymeric structure, which will reduce the hardness and scratch resistance of the film [143]. Some intra-atomic bonds like sp^3 can be strengthened while the overall inter-atomic structure is weakened. In contrast, in the unhydrogenated film, or a-C(Si) in this work and that of Kulikovsky *et al.* [15], the adverse effect caused by H is not present. As such and besides the deposition dependent mechanics, an optimum Si concentration seems to exist at which the effect on the reduction of the weak π bonds balances the decrease in global density caused by the Si and C atomic mismatch. The phenomenon can be true for sputtered unhydrogenated a-C(Si), and maybe also true for unhydrogenated a-C(Si) synthesized by other methods. In this work, the optimum Si concentration is ~32.3 at.% with ~15 % reduction in C=C (sp^2) bonding (c.f., Figure 3.3).

The a-C(Si) films having a Si content of 36-38 at.% were subjected to two different thermal treatments. The hardness of the two sets of films was rather different. As shown in Figure 4.4, the hardness of a-C(Si) films deposited at high temperature decreased with the increasing substrate temperature, while the hardness of the post-deposition annealed a-C(Si) was constant with increasing

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temperature until 600 °C, but degraded drastically when the annealing temperature was increased further.

Figure 4.4| Hardness of a-C(Si37.6at.%) thermally treated at different temperature. Hardness decreased continuously with deposition temperature, but remained relatively unaltered with post-deposition annealing temperature. The activation energies for sp^2 clustering and $sp^3 \rightarrow sp^2$ conversion were higher during post annealing; therefore, the thermal stability was better.

As discussed in §3.4, the internal bonding evolution during the two different thermal treatments was different. High temperature deposited a-C(Si) has poor and deteriorating mechanical hardness with increasing deposition temperature while the same coating, room temperature deposited, was stable till ~600 °C annealing temperature. The stability comes from Si-induced deterrence of bonding conversion directly from sp^3 to sp^2 during annealing. This deterrence is not pronounced during high deposition temperature, where the activation energy is nearly three times lower. The activation energy of sp^2 clustering is much lower at high temperature deposition than post deposition annealing (about 1/5). At high

temperature deposition, the sp^2 -hybridized C are more favorably formed due to the dynamic annealing effect.

4.3 Residual Stress

The residual stresses of the room temperature deposited a-C(Si) films were calculated using Stoney's equation from the film/Si-substrate bimorph curvature change. The residual stresses were all compressive (negative). The residual stress as a function of increasing Si is presented in Figure 4.5. The stress decreased with the increase in Si atomic concentration. The substitution of Si for C atoms leads to strain relaxation by increasing the bond length, from 1.54 Å (C-C) to 1.89 Å (Si-C), in the adjacent sites of the incorporated Si atoms. From the calculation by Ferrari *et al.* [11], only 1 % strain variation is needed for a significant decrease in film stress. Jung *et al.* [81] also suggested that formation of C-Si plays a role in releasing the bond angle distortion.

Figure 4.6 illustrates the reduction in residual stress in a micro-machined cantilever: without doping, the a-C coated silicon cantilever undergoes severe bending due to large residual stress in the coating; with doping, however, the cantilever is almost unbent due to elimination of the residual stress.

Figure 4.5| Compressive stress decreases with increasing Si concentration. This is mainly due to the relaxation of strain within the network and releasing of bond angle distortion.

Figure 4.6| Micro-machined cantilevers illustrating the reduction of stress through Si doping of ~37.6at.%. SEM micrographs showing a) cantilever deposited with undoped a-C film; and b) cantilever deposited with a-C(Si37.6at.%) film. The micromachining procedure is illustrated in §4.1.4. The cantilever of a-C(Si37.6at%) film bends less as it has a lower compressive stress than the undoped a-C.

The as-deposited a-C(Si37.6at.%) film was still compressively stressed. To eliminate the stress, thermal annealing was needed. Figure 4.7 shows the stress evolution of the a-C(Si) film during thermal annealing. The result shows that the stress is nearly eliminated after annealing at temperature of 600 °C, and the temperature is similar to the complete stress relieve of ta-C [11]. There is an

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increase in C-Si bondings starting from 400 °C as shown in Figure 3.21b. This indicates that there will be an increase in strain relaxation through the increase in bond length, as well as releasing bond angle distortions, thereby relaxing the residual compressive stress.

Figure 4.7| Stress evolution during thermal annealing of a-C(Si37.6at.%). This is mainly due to strain relaxation and release of bond angle distortion through the increase in C-Si bondings. The strain relaxed is found to be around 0.3 %.

The changes in stress and strain in a thin film under biaxial stress are related by [144]

$$\Delta\sigma = \frac{E}{1-\nu}\Delta\varepsilon \quad 4.4$$

where σ is the stress, E is Young's modulus, ν is Poisson's ratio, and ε is the strain. Taking the change in film stress as $\Delta\sigma \sim 700$ MPa (from Figure 4.5 and Figure 4.7), $E \sim 180$ GPa (from Figure 4.1), and Poisson's ratio ~ 0.34 [145-147], the

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strain variation $\Delta\varepsilon$ is calculated to be $\sim 0.3\%$. Therefore, only a small change in the strain is needed to accomplish the observed stress relief.

There is actually a ~ 100 MPa (compressive) drop in stress when the a-C(Si37.6at.%) film is being cooled from $600 - 23^\circ\text{C}$. This is the thermal stress caused by the mismatch in coefficient of thermal expansion (CTE) between the film and the silicon substrate. The thermal stress variation is related by [148]

$$\Delta\sigma_{th} = \frac{E}{1-\nu}(\alpha_s - \alpha_f)\Delta T \quad 4.5$$

where σ_{th} is the thermal stress, E is Young's modulus, ν is Poisson's ratio, α_s is the CTE of $\text{Si}_{(100)}$ and α_f is the CTE of the film. The values of E and ν are the same as before and α_s is $2.8 \times 10^{-6}/^\circ\text{C}$. The CTE of a-C is dependent on the sp^2 concentration in the film [148]. From Figure 3.3, the sp^2 concentration of a-C(Si37.6at.%) is around 55 %; therefore, the CTE of the film, α_f , is estimated to be around $2.2 \times 10^{-6}/^\circ\text{C}$ (value taken from the plot in Ref. 148). As such, the calculated thermal stress during the cooling path is 94.4 MPa (compressive). This value is relatively close to the measured value in Figure 4.7.

4.4 Summary

The hardness and elastic modulus of a-C first decrease with increasing Si concentration, and then increase when the Si doping concentration is increased

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above 16.6at.%. This behavior is attributed to two causes: atomic bonding structure and deposition kinetics. Atomically, the doping with Si decreases the global density of the network because of Si's larger atomic size and longer bonding length with C, and hence decreases the hardness when a-C is doped. During sputter deposition, the kinetic energy of the Si at all target power densities will be lower than that of the sputtered C. At low Si target power density (i.e. producing a-C(Si) with lower Si concentration), the sputtered Si will have a much lower kinetic energy than the sputtered C. The impact upon interaction will decrease the energy of the C atoms. Therefore, the a-C(Si) films with low Si concentration will have a lower atomic number density than the undoped a-C. This deposition dependent phenomenon is manifested by the initial increase in the surface roughness with increasing Si doping, where a rougher surface indicates lower density. Hence, there is an initial decrease in hardness and elastic modulus.

When the Si concentration is increased, more C-Si sp^3 bonds will form, and since they are formed by preferentially bonding with sp^2 C, the softer sp^2 C clusters decrease. The elimination of two π bonds per substituted sp^2 bonded C atom by Si replaces the contribution to the hardness value of these weak bonds with higher bonds. When the Si target power density is increased to increase the Si concentration in the a-C film, both Si and C will bombard the film surface with higher energy. The density of the a-C(Si) with higher Si concentration will increase due to the reduction in π bonds as the sp^2 C component decreases. These π bonds have the longest bond length in the network (3.35 Å), and thus the

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decrease will increase the film density. The combination of higher energy deposition species and the removal of sp^2 -hybridized C bondings at higher Si concentration translate to a lowering of surface roughness (from 16.6 at.% Si onwards) and contribute to the increase in hardness and modulus. No amorphous silicon carbide was observed that could contribute to this increase.

This interesting behavior of the hardness and elastic modulus was only observed for unhydrogenated a-C(Si). In hydrogenated samples, the increase in Si concentration was always accompanied by an increase in the H concentration. This had a detrimental effect on the mechanical properties as there was enhanced formation of Si-H polymeric bonds. Thus, the hardness and modulus of hydrogenated a-C(Si) was not increased when the Si doping concentration was increased.

The hardness of a-C(Si) films deposited at high temperature decreases with the increasing substrate temperature, while the hardness of the post-annealed samples remained constant until 600 °C annealing temperature, and only degrades when the annealing temperature is increased further. As discussed in the §3.4.2, the thermal stability of a-C(Si) comes from Si-induced deterrence of bonding conversion directly from sp^3 to sp^2 during annealing. This deterrence is not pronounced during high temperature deposition, because the transition from sp^3 to sp^2 is much easier at high temperature deposition where disordering is hard to maintain due to the dynamic annealing effect.

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Residual compressive stress of a-C(Si) decreases with increasing Si concentration. This is attributed to the strain relaxation through the increase in bond length, from 1.54 Å (C-C) to 1.89 Å (Si-C), in the adjacent sites of the incorporated Si atoms, and the releasing of bond angle distortion through the formation of C-Si bonds. The residual stress of a-C(Si37.6at.%) can be eliminated completely by annealing at around 600 °C. The calculated strain that is being released is merely 0.3 %. Complete stress relief at 600 °C, also means that the atomic and mechanical properties are insignificantly altered when a-C(Si) is found to be thermally stable to the same temperature.

High compressive stress could increase the hardness slightly. However, the main contributor of the hardness is the density and the harder phases (sp^3 C-C and C-Si bonds). It has been found that the stress is not necessary to stabilize the sp^3 bonds and thus the hardness is not altered when the stress is relaxed at 600 °C. The hardness decreases because of the onset of the graphitization when annealing temperature is above 600 °C.

CHAPTER 5 ~ SURFACE ENERGY OF AMORPHOUS CARBON CONTAINING SILICON

5.1 Surface Energy

Surface energy of a biomaterial surface affects its biological response, that is, the adsorption and interaction with biological matters (e.g. proteins, cells, blood platelets, etc.). As discussed in §2.4.1 and §2.6.3, the bondings in a-C films influence their surface energies. The basic factor that affects the surface property is the sp^3 fraction in the films. The works discussed in the two sections failed to address the secondary influence of a dopant, which in this case is silicon. In this work, a more comprehensive study was carried out to understand the relationship between the bonding and the surface energy, as well as the role of silicon in the modification of the surface energy.

The surface free energy of the films was determined by contact angle measurements. The Lifshitz-van der Waals / acid-base (van Oss) approach [149] was employed to interpret the contact angle measurements. In this method, the surface tension is differentiated into three components: the apolar Lifshitz-van der Waals (LW) component, the polar acid (+) and the base (-) components. The “acid” component is also called the acceptor because it is positively charged, thus is ready to accept electrons; the “base” component is also called donor because it is negatively charged, thus has extra electrons to give away. The total surface tension is given by

$$\gamma_i = \gamma_i^{LW} + 2\sqrt{\gamma_i^+ \gamma_i^-} \quad 5.1$$

Where i denotes either the solid or liquid phase and γ^+ is the acceptor and γ^- the donor part of the surface energy. The interfacial tension was postulated both of solid-liquid and liquid-liquid systems as

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1^{LW} \gamma_2^{LW}} - 2\sqrt{\gamma_1^+ \gamma_2^-} - 2\sqrt{\gamma_1^- \gamma_2^+} \quad 5.2$$

Taking Young's equation: $\gamma_l \cos \theta = \gamma_s - \gamma_{sl}$ [150] into consideration (where θ is the measured contact angle, γ_l , γ_s and γ_{sl} are the liquid-vapor, solid-vapor and solid-liquid interfacial tension respectively), the Lifshitz-van der Waals / acid-base equation can be written as follows

$$\gamma_l(1 + \cos \theta) = 2\sqrt{\gamma_l^{LW} \gamma_s^{LW}} + 2\sqrt{\gamma_l^+ \gamma_s^-} + 2\sqrt{\gamma_l^- \gamma_s^+} \quad 5.3$$

Equation 5.3 can be used to determine the three surface tension components (γ_s^{LW} , γ_s^- and γ_s^+) by measuring contact angles and solving three simultaneous equations. To do this, three liquids of known surface tension are required. Deionized water, formamide and diiodomethane were the selected test liquids. Liquids with different surface tension components are preferred. Deionized water has the highest polar component, diiodomethane has the highest dispersive component (and no polar component) and formamide has a near-balanced dispersive and polar component of its surface energy. The surface tension values [151] of these liquids are presented in Table 5.1. Contact angle measurements

were conducted using the sessile drop technique with *First Ten Angstroms 200 Goniometer*.

Table 5.1| Surface free energy constants for test liquids. [151]

Liquid	$\gamma_{\text{tot.}}$	γ^{LW}	γ^+	γ^-
DI Water	71.8	21.8	25.5	25.5
Formamide	58	39	2.28	39.6
Diiodomethane	50.8	50.8	0	0

5.2 Effect of Silicon Concentration

Figure 5.1 shows the changes in the contact angles of the three test liquids with Si concentration. The corresponding surface energies are presented in Figure 5.2. The dispersive component of the surface energy initially decreased with Si concentration and reached a minimum at a Si concentration of ~16.6 at.%, and then increased as the Si concentration was further increased. The polar component, on the other hand, increased with Si concentration.

Figure 5.1| Contact angles of DI water, formamide and diiodomethane with increasing Si concentration.

Figure 5.2| Dispersive and polar components of the surface energy with increasing Si concentration. Polar component increases due to an increase in the surface O concentration. Both Si-O and C-O bonds are polar in nature, thus increasing O promotes the increment of polar component. The dispersive component is related to the density of the film.

In hydrogenated a-C, there are relatively fewer dangling bonds at the surface when most are terminated by H, which has only one electron available for bonding. This reduces the tendency for the surface atoms to bond with other atoms

in the atmosphere. Unlike hydrogenated a-C, the surface atoms of hydrogen-free a-C films are not fused and are free to bond with atoms in the atmosphere, especially oxygen. With this surface adsorption of atmospheric oxygen, polarity increases because Si-O and C-O bonds are polar in nature. The greater difference in electronegativities between oxygen (~ 3.5) and silicon (~ 1.8) as compared to carbon (~ 2.5) implies that there is a higher affinity of oxygen with silicon. Therefore, there is an increase in the surface oxygen level when the Si concentration was increased (as indicated in Figure 5.3 – XPS analysis without ion etching), hence resulting in a greater polar component. The oxygen concentration seems to plateau after 16.6at.% Si. This might be caused by the increase in inter-Si bondings as more Si atoms are at the surface, hence reducing the number of Si unfused bonds that are able to bond with oxygen.

Figure 5.3| Surface oxygen concentration with increasing Si concentration. Since there is a greater difference in electronegativities between O and Si as compared to C, the surface oxygen level increases when Si concentration is increased.

The dispersive component is directly related to the dispersive or induced dipole-to-dipole forces of the atoms in the films, and this force is governed by the following relationship [152];

$$F \propto \frac{\alpha}{r^3} \left[\frac{d}{dr} \left(\frac{1}{r^3} \right) \right] \quad 5.4$$

where α is the polarizability and r the inter-atomic distance. It may be apparent that the dispersive component is affected by the surface roughness, but study has shown independency of wetting and surface morphology when the roughness is below 100 nm [153]. Therefore, the dispersive component is very much related to the density of the film, since the roughest surface is much lower than 100 nm. As discussed earlier, the density is low at Si concentration below ~16.6at.% and increases as the Si concentration is increased. The drop in density means an increase in the inter-atomic distance. Since the dispersive force is inversely proportional to the inter-atomic distance, the increase in the inter-atomic distance thus decreased the dispersive forces and ultimately the dispersive component of the surface energy (c.f. Figure 4.2a and Figure 5.2 for Si below 16.6 at.%). The increment of the dispersive component above Si atomic concentration of 16.6 at.% is caused by an increase in density. In this case, more Si atoms bond with the sp^2 -hybridized C atoms, hence turning them into sp^3 -configured C-Si and/or C-C bondings. This eliminated more of the longer bond length π -bonds (3.35 Å), thereby increasing the global density and resulting in a smaller inter-atomic distance as the Si concentration increased.

5.3 Effect of Temperature

Figure 5.4 shows the changes in the contact angles of the three test liquids with annealing temperature. The corresponding surface energies are presented in Figure 5.5. Since the bonding structure of a-C(Si) films remains relatively unaltered within the annealing temperature range, the change of the surface energy components (dispersive and polar) was minimal.

The dispersive component of the surface energy is directly related to the dispersive or induced dipole-to-dipole forces of the atoms in the films as discussed earlier. From the Raman spectroscopy results, there is no large-scale transformation of sp^3 -configured atoms (C-Si with bonding length of 1.89 Å and C-C with bonding length of 1.54 Å) into sp^2 -configured atoms (C=C). Although, the σ -bond in sp^2 -configured C atoms is 1.42 Å, shorter than that of an sp^3 -configured C, each sp^2 -configured C has a pair of $p\pi$ -bond, each having a bonding length of 3.35 Å. Therefore, if the nucleation and clustering of the sp^2 -configured C takes place, the average inter-atomic bonding length of the film will increase. This will cause the dispersive force and ultimately the dispersive component of the surface energy to decrease. Since the Si atoms retard the graphitization process during thermal treatment, the dispersive component of the film will not be affected much. The dispersive component is between 44.5 – 45 mN/m. This is also why the contact angle of the films with diiodomethane (that only has dispersive component; refer to Table 5.1) is not largely affected.

Figure 5.4| Contact angles of DI water, formamide and diiodomethane on a-C(Si37.6at.%) film annealed at different temperatures.

Figure 5.5| Dispersive and polar components of the surface energy of a-C(Si) film annealed at different temperatures. Dispersive component is relatively unaltered as the internal bonding structure is stable under the annealing temperature range; i.e. no change in film density. Polar component decreases as the O on the surface and sub-surface outgas during high temperature annealing, thus reducing the amount of polar Si-O and C-O bonds.

The polar component on the other hand decreased from 5.1 mN/m to 2.2 mN/m at 600 °C annealing. When atmospheric oxygen is adsorbed onto the film

surface, it will diffuse into the sub-surface layer of the film over some time. During annealing, the oxygen could be released from the film surface. Maybe that is why there are changes in the surface roughness of the films. The roughness increased as annealing temperature increased, as shown in Figure 5.6a. A typical morphology is presented in Figure 5.6b. There is an increase in the surface oxygen level when Si concentration is increased. From the XPS analysis of as-deposited a-C(Si) and a-C films, the surface oxygen level of the Si-incorporated film is 26.5at.% compared to 9.3at.% of pure a-C (c.f. Figure 5.3). The atmospheric oxygen is bonded to the dangling bonds of surface Si and surface C atoms as well. During thermal treatment, the adsorbed oxygen could gain enough energy to break its bond with the surface Si and C and outgas as O_2 and/or to react with the weakly bonded C (with lower coordination number) and outgas as CO or CO_2 . The slight increase in surface roughness could be the result of the vacating of spaces once occupied by the C atoms.

However, at higher annealing temperature, more energy could be imparted to the atoms in the sub-surface layer, causing the oxygen in this level to back-diffuse to the top surface and outgases as atoms or molecules (including molecules with C). Therefore, the a-C(Si) film treated at higher temperature could have a lower sub-surface oxygen level as compared to the films treated at lower temperature. The polar component of the films is mainly affected by the C-O and Si-O bonds, as they are polar in nature. If the sub-surface oxygen level was lower

in films annealed at higher temperature, the polar component will be affected and therefore decreased.

Figure 5.6| a) Average surface roughness; b) Surface morphology of a-C(Si37.6at.%) film annealed at 600 °C. The roughness increases due to the outgasing of gaseous CO or CO₂ during high temperature annealing, after the weakly bonded surface C reacts with O.

5.4 Summary

The surface energies were determined from the contact angles from three different liquids: DI water, formamide and diiodomethane. The dispersive component of the surface energy is related to the density of the a-C(Si) films. The drop in density with increasing Si concentration means a decrease in the dispersive forces and ultimately the dispersive component of the surface energy (for Si below 16.6 at.%). The increment of the dispersive component above Si atomic concentration of 16.6 at.% is caused by an increase in density. As discussed in the previous two sections, more Si atoms bond with the sp^2 -hybridized C atoms, hence turning them into sp^3 -configured C-Si and/or C-C bondings. This will get rid of more of the longer bond length π -bonds. The increase in Si target power density during sputter deposition will increase the kinetic energy of the sputtered specie. Therefore, the global density will increase and result in a smaller inter-atomic distance as the Si concentration increased. The dispersive force is thus increase, and so is the dispersive component.

The polar component, on the other hand, always increases when the Si concentration is increased. The surface atoms of are not fused and are free to bond with atoms in the atmosphere, especially oxygen. With this surface adsorption of atmospheric oxygen, polarity increases because Si-O and C-O bonds are polar in nature. Since there is a greater difference in electronegativities between oxygen and silicon as compared to carbon, there will be a higher affinity of oxygen with

silicon. Therefore, there is an increase in the surface oxygen level when Si concentration is increased; resulting in a greater polar component.

After thermal annealing of a-C(Si37.6at.%) film, there is no significant change to the dispersive component as the atomic configuration (and hence the density) is not altered too much within this temperature range. The polar component however, decreases when the annealing temperature increases. During thermal treatment, the adsorped oxygen could be energetic enough to break its bond with the surface Si and C and outgas as O₂ and/or to react with the weakly bonded C and outgas as CO or CO₂. Therefore, the a-C(Si) film treated at higher temperature could have a lower sub-surface oxygen level. Since the polar component of the films is mainly affected by the polar C-O and Si-O bonds, which could be reduced, the polar component of the surface energy is affected and therefore decreased.

CHAPTER 6 ~ BIOLOGICAL PROPERTIES OF AMORPHOUS CARBON CONTAINING SILICON

6.1 Human Blood Platelet Adhesion Assay

The interaction of a foreign material with blood stimulates platelet activation, coagulation and thrombus formation. Therefore, a less blood compatible material attracts more blood platelets to adhere on its surface and subsequently forming into clots. The human blood platelet adhesion assay was used to characterize the blood compatibility of a-C(Si) films. Platelet counts were determined and their morphologies were observed and study was carried out in term of the different silicon concentration and thermal treatments.

6.1.1 Platelet-Rich-Plasma Preparation, Incubation and Fixation

450 ml of human whole blood from a drug-free donor was drawn and mixed with tri-sodium citrate. The ratio of blood to tri-sodium citrate was 9 to 1. To prepare the platelet-rich-plasma (PRP), the blood was centrifuged at 3200 rpm for 10 min to separate the blood corpuscles. The plasma was extracted and centrifuged again at 3200 rpm for 15 min. Platelet clumps were obtained, and were allowed to redistribute back into the plasma, which was then 30 ml after draining away the excess. The platelet count in the PRP was determined by flow cytometry to be 1.6×10^6 cells/ μ L. The plasma was then held in a 37 °C water bath for 30 minutes to allow the platelets to return to their original shape. After cleaning (ultrasonic cleaning in acetone) and sterilization (4-hour UV exposure) processes, the PRP

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was seeded onto the surfaces of the a-C(Si) coated substrates placed in a petri dish. Incubation was carried out at 37 °C in 5% CO₂ for 30 minutes. Afterwards, the supernatant was discarded, and the samples were rinsed twice with phosphate buffered saline (PBS) to remove the proteins and non-adherent platelets. The cells on the specimens were fixed with 2.5% glutaraldehyde for 30 minutes, followed by 1% osmium tetroxide on ice for 45 minutes. After the fixation, the samples were washed and dehydrated in a graded ethanol series of 50%, 70%, 80%, 95% and 100% (twice) for 10 minutes each.

6.1.2 Platelet Count and Morphology

A Leica S360 scanning electron microscope was used to observe the platelets on the a-C(Si) films. The samples were coated with ~15 nm of gold using a Polaron SC 7640 coating unit to prevent surface charging. An average platelet count using the mean of six non-repeating selected areas of size 125µm x 90µm was conducted on each sample. Results were expressed as counts/unit area and standard error. The statistical analysis used was one-way analysis of variance (ANOVA) on an average of three replicates to compare data between different periods of culture, and Student's *t*-test was carried out to compare the culture data between coatings on each count. Statistical significance was considered at $p < 0.05$. The morphological shape changes were categorized according to Goodman *et al.* [154], and are illustrated in Table 6.1. There are five types of platelet morphologies. Unactivated platelets of Type I are ~ 2 µm in diameter and don't have a pseudopod. With increasing activation, the platelets develop pseudopodial

extensions, which eventually become hyaloplasm at the highest state of activation (Type V). The platelets then can have a size up to $\sim 5 \mu\text{m}$.

Table 6.1| Five types of platelet morphologies in relation to their activation level upon adhesion to foreign surfaces. [154]

Type	Morphology Description	
I		Round and discoid - <i>No pseudopodia</i>
II		Dendritic - <i>Early pseudopodial with no flattening</i>
III		Spread-Dentritic - <i>Intermediate pseudopodia with one or more pseudopodia flattened, no hyaloplasm between pseudopodia</i>
IV		Spreading - <i>Late pseudopodial with hyaloplasm spreading</i>
V		Fully Spread - <i>Hyaloplasm fully spread with no distinct pseudopodia</i>

6.2 Cell Culture

The study of cellular behavior on biomaterials surface *in vitro* is an important aspect in determining the biocompatibility of the material. The healthy

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growth/proliferation and morphology of the biological cells on the material surface is an important pre-requisite for compatibility.

Two types of cell-lines were used in this study: African green monkey kidney fibroblast COS7; and human osteosarcoma MG63. Both cell-lines were obtained from the American Type Culture Collection (ATCC, Rockwell, MD). Cells were cultured at 37 °C in a humidified 5% CO₂ atmosphere. The standard medium used for culturing COS7 was Dulbecco's modified eagle's medium (DMEM, ATCC) supplemented by 10 % fetal calf serum (FCS, ATCC) and 1 % penicillin (ATCC), while for MG63 was Eagle's minimum essential medium (EMEM, ATCC) was used, also supplemented by 10 % fetal calf serum (FCS, ATCC) and 1 % penicillin (ATCC). For cell assay, the a-C samples were diced into 10 × 10 mm segments and exposed to UV for 4 hours. After which, the samples are placed in a 24-well culture dish, and both cell-lines were seeded at a density of 4 × 10⁴ cells/ml and cultured up to 6 days. After each culture period (1, 3 and 6 days), the samples were rinsed twice with phosphate buffered saline solution, then the cells were detached using trypsin/ETDA. The detached cells were stained with trypan blue, and the living cells were counted using a haemocytometer (Becton Dickinson, Germany). The statistics of the cellular tests were conducted using one-way analysis of variance (ANOVA) on an average of three replicates, to compare data between different periods of culture. Student's *t*-test was carried out to compare the culture data between coatings from each count. Statistical significance was considered at *p*<0.05. For cellular morphology

observation, culture wells were deposited with 100 nm of a-C(Si). The films were optically transparent, therefore facilitating optical observation during 6 hours of culturing (for initial attachment), and 6 days of culturing (for colonization).

6.3 Haemocompatibility

6.3.1 Effect of Silicon Concentration

The number of adhered platelets and the fraction of unactivated platelets are presented in Figure 6.1. From a *t*-test, there is no significant difference between the count on a-C(Si7.4at.%) and a-C, while the rest are significantly different (having a *p*-value smaller than 0.05, especially a-C(Si37.6at.%) with $p < 0.001$). In addition, the result from ANOVA shows that Si concentration in a-C indeed influenced the number of adhering platelets. The results clearly show a decrease in the number of adhering platelets as well as in the fraction of activated platelets as the Si concentration in the film is increased. The decrement is comparable to Raman spectroscopy results, suggesting the increasing Si concentration and sp^3/sp^2 ratio improves the haemocompatibility of the film. However, the evolution of the surface properties of these films is not directly related to the platelet count. There is a decrease in the total surface energy until the Si concentration of 16.6 at.%. The decrease in the platelet count with decreasing total surface energy in the low Si concentration region is also shown by Okpalugo *et al.* [17] on hydrogenated a-C films. The results of film with higher Si concentration cannot be compared, as there is currently no haemocompatibility study done on such a-C films, whether hydrogenated or not. In this case, there is an increase in the surface energy when

Si concentration is increased further, and it is attributed by the increased in the polar component (as shown in Figure 5.2).

Figure 6.1| The number of adherent platelets and percentage of unactivated platelets with increasing Si concentration. The values are mean of six replicates, while the error bars denote the standard error. ANOVA was conducted, and the effect of Si concentration on the number of adherent platelet was significant, $F(5,30)=23.05$, $p=1.89 \times 10^{-9}$.

The amount of adhered platelets and activation on the film surfaces is inversely proportional to the ratio of albumin to fibrinogen adhesion on the surfaces [53,54]. This is because the adhesion of albumin (a water-soluble protein in the blood plasma) on the film can prevent the adhesion of platelets. While fibrinogen is a protein that can enhance the adhesion and activation of platelets, and hence a thrombus when it is converted into fibrin by the action of the enzyme thrombin. The surface tensions of both albumin and fibrinogen are found to be similar at 65 mN/m [155], and the polar component of fibrinogen is higher than that of albumin; 40.3 mN/m as compared to 33.6 mN/m. The Lifshitz–van der Waals / acid-base approach allows a more in-depth analysis of the polar

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component. The polar component can further be differentiated into base (electron donor) and acid (electron acceptor) components, and from Table 6.2, it is shown that the base components for all the films are very much larger than the acid component, indicating the polar component of the surfaces is predominantly negatively charged. This is beneficial towards haemocompatibility as the platelets and proteins tend to have a net negative zeta-potential of -8 to -13 mV [156]. In other words, there will not be any preferential adsorption of any of the proteins and platelets due to electrostatic interaction. Computing the relative contribution of the respective surface energy components, it is found that the polar to dispersive ratio increases as the Si concentration is increased (c.f. Figure 6.2). Therefore, the repulsion between the film surface and proteins should increase as the Si concentration increases. Albumin is also repelled, but the effect should be less intense than with fibrinogen due to its lower polar component. Furthermore, the dispersive component of all the films is relatively very much larger than the polar component; therefore reflecting the interaction is predominantly based on dispersive forces. Since albumin has a higher dispersive component, it should have a more stable interaction with the film surfaces.

Table 6.2| The base (-) and acid (+) contribution to the polar component of a-C(Si) films with increasing Si concentration.

Si at. %	0	7.4	16.6	24.9	32.3	37.6
γ^- (mN/m)	26.45	13.28	10.85	19.96	23.65	21.28
γ^+ (mN/m)	0.01	0.03	0.06	0.07	0.23	0.30

Figure 6.2| Polar to dispersive ratio with increasing Si concentration. The ratio increase is mainly due to the increase in the polar component. Since there is a higher surface O concentration when Si concentration is increased, polar bonds like Si-O and C-O also increase, thereby causing the increment of polar component of the surface energy.

The phenomenon can be justified in Figure 6.1 where the amount of activated platelets decreases as the Si concentration is increased. The discouragement of fibrinogen adsorption is also evidential from the evolution of platelet morphology. As shown in Figure 6.3, the platelets on a-C film are mainly Type 3 - 5, while mainly Type 1 - 3 for platelets on a-C(Si37.6at.%) film (the platelet activation level is presented in Table 6.1). This shows that the doping of Si not only reduces the number of adherent platelets, it can also deter their activation. The undoped a-C film although causes a higher state of platelet activation, but there is no evidence of any aggregation. Unlike the coated Si wafer, the bare Si surface (not chemically treated, i.e., there will be a presence of a native oxide layer) not only had a higher number of adherent platelets and activation, but there were also numerous aggregation sites. This marks the initial stage of thrombus formation.

Figure 6.3| SEM micrographs of the adherent platelets on: a) & b) uncoated Si wafer, c) & d) undoped a-C film, e) & f) a-C(Si37.6at.%) film. The number of adherent blood platelets decreases when Si concentration is increased. The platelet activation type for a-C is mainly Type 3-5, while for a-C(Si37.6at.%) is mainly Type 1-3. Numerous platelet aggregation sites are found on bare wafer, which marks the initial stage of thrombus formation.

6.3.2 Effect of Temperature

The number of adhered platelets and the fraction of unactivated platelets are presented in Figure 6.4 as a function of annealing temperature. The number of adherent platelets increases when the annealing temperature was increased (all films were deposited at room temperature and annealing performed thereafter).

Although this may be viewed as a degradation of blood compatibility of the films, only the platelets with a higher state of activation contribute significantly to the formation of thrombus. Figure 6.5 presents the micrographs of the platelet morphologies adhering onto the film surface. Type 5 platelets are present on all a-C(Si) films annealed at different temperature, but there are a fraction of Type 1 - 3 platelets when the film is annealed at higher temperature. From Figure 6.4 and Figure 6.5, the fraction of activated platelets decreases with increasing annealing temperature.

Figure 6.4| The number of adherent platelets and percentage of unactivated platelets on a-C(Si37.6at.%) film annealed at different temperatures. The values are mean of six replicates, while the error bars denote the standard error. ANOVA was conducted, and the effect of annealing temperature on the number of adherent platelet was significant, $F(3,20)=6.435$, $p=0.003$.

Figure 6.5| SEM micrographs of the adherent platelets on a-C(Si) films of 37.6at.%Si: a) as-deposited; b) annealed at 200 °C; c) annealed at 400 °C and d) annealed at 600 °C. Type 5 platelets can be found on all sample surfaces, but Type 1-3 platelets seem to have a slight increase when the annealing temperature is increased. Although platelet activation level is a little lower on sample annealed at 600 °C, there seem to have an increase in aggregation sites.

Besides the surface chemistry, the surface morphology is another factor influencing the wetting behavior and blood compatibility of a solid-state material. The surface morphology can impart conformation changes to the protein, hence rendering it inactive [157]. Although there is an increase in the surface roughness when annealing temperature is increased, the maximum attained surface roughness value at 600 °C is about 0.76 nm (R_{rms}). This roughness value is still too low to affect the wetting and thus surface energy (i.e. $\ll 100$ nm [153]). Even though the total surface area has increased, at such a low roughness value, no significant

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influence is expected for the adsorption of platelets since the platelets size is about 2 μm . Proteins have similar size, i.e. a few nanometers. For instance, albumin globule has a triangular shape of about 8 nm on the sides and 3 nm in thickness [158]. Therefore, the roughness ($R_{\text{rms}} \sim 0.76 \text{ nm}$), though low, might have a certain effect on the adsorption of the proteins through mechanical interlocking. The changes in the number of adherent platelets and activation fraction are not likely to be affected by the changes in the internal bonding structure of the films. From results presented and discussed earlier in §3.4.2, the films are thermally stable up to 600 °C.

From Table 6.3, it is shown that the base components for all the films are again very much larger than the acid component, indicating that the polar component of the surface is predominantly negatively charged. Therefore, as discussed earlier, there will not be any preferential adsorption of any of the proteins and platelets due to electrostatic interaction if the polar component is increased. However, computing the relative contribution of the respective surface energy component reveals that the polar to dispersive ratio decreased as annealing temperature was increased (c.f. Figure 6.6). Therefore, the repulsion between the film surface and proteins decreases as the annealing temperature increases. The adsorption of both albumin and fibrinogen will now increase, with a slightly stronger effect on fibrinogen since it has a higher polar component. The result is a higher count of adherent platelets on the a-C(Si) annealed at higher temperature. On the other hand, since the dispersive component of the films is much larger than

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the polar component (c.f. Figure 5.5), the interaction is predominantly based on dispersive forces. Since albumin has a higher dispersive component, it will have a more stable interaction with the film surfaces, whereby contributing to the decrease fraction of activated platelets.

Table 6.3| The base (-) and acid (+) contribution to the polar component of a-C(Si37.6at.%) with increasing annealing temperature.

	As-Deposited	200 °C	400 °C	600 °C
γ^- (mN/m)	21.3	20.5	17.7	14.9
γ^+ (mN/m)	0.30	0.32	0.36	0.08

Figure 6.6| Ratio of polar to dispersive surface energy component on a-C(Si37.6at.%) film annealed at different temperatures. The ratio decrease at high annealing temperature is mainly due to the decrease in the polar component. Since there is a decrease in surface and sub-surface O level after thermal treatment, polar bonds like Si-O and C-O also decrease, thereby causing the decrement of polar component of the surface energy.

6.4 Cellular Response

The number of attached COS7 fibroblast and MG63 osteoblast-like cells are presented in Figure 6.7. ANOVA has shown significance of $p < 0.001$, implying the cells are growing and proliferating well on both a-C and a-C(Si) films. The t -test has shown significant difference of cell count between a-C(Si37.6at.%) and a-C (lower count) for both cell-lines on the sixth day of incubation.

Both COS7 and MG63 seem to proliferate better on a-C film with the highest Si concentration (~37.6at.%). Amorphous carbon containing 37.6at.% Si had the highest polar/dispersive component ratio (c.f. Figure 6.2), and also has the highest surface energy (c.f. Figure 5.2) among the three films. The result suggests that both cell-types prefer a more hydrophilic surface. In a physiological environment, protein adsorption always precedes cellular adhesion. Pre-adsorbed proteins, in combination with proteins produced by the cell, and depending on the coating properties, determine the strength and type of adhesion. There exist several proteins in a physiological environment and *in vitro* culture media, i.e. albumin, fibronectin, vitronectin, globulin, etc. For example, if fibronectin is present on either the cellular or the solid surface, adhesion and spreading of cells will exponentially increase. Cell spreading is a combined process of continuing adhesion and cytoplasmic contractile meshwork activity. At first, lamellar protrusions are formed, and microfilaments can always be observed in these lamellae. In a later stage, cytoplasmic flaps in between the protrusions also expand, completing the cell spreading. Figure 6.8 shows the living cells morphology on a-

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C(Si37.6at.%). The long and fine cytoplasmic extensions in multiple directions show that there is excellent adhesion of the cells to the film. The cells also exhibit long lamellipodes indicating active cell migration leading to homogenous colonization (c.f. Figure 6.8b and d).

Cell adhesion and spreading are influenced by the physicochemical characteristics of the underlying solid surface. The substrate surface free energy can affect the cell spreading. Poor spreading on hydrophobic surface and good spreading on hydrophilic surface can be observed in both the absence and presence of pre-adsorbed serum proteins [159]. Therefore, the substrate characteristics extend through the adsorbed proteins and affect cell adhesion and spreading. Cells can reach the underlying substrate by pseudopodia protruding through the pre-adsorbed protein layer, cells can consume pre-adsorbed proteins to make direct contact, and/or the substrate characteristics are reflected in the composition and conformation of adsorbed proteins, thus presenting different molecular groups to adhering and spreading cells. All proteins have NH_2 and COOH groups at their ends. The NH_2 tends to be positively charged and the COOH groups negatively charged [160]. a-C(Si) include C-O and Si-O bonds at the surface and are polarized due to the difference in electronegativity between each element. Thus, the proteins can electrostatically bond with the film surface. Since a-C(Si37.6at.%) has the highest polar component of the surface energy, it has better affinity with the proteins; and in turn attracts more cells to adhere, spread and proliferate.

Figure 6.7| Cell attachment number of (a) COS7 fibroblast; and (b) MG63 osteoblast-like cells. The values are mean of three replicates, while the error bars denote the standard error. ANOVA shows that both cell-types proliferated on a-C and a-C(Si) with $p < 0.001$. * denotes significant difference between COS7 count on a-C(Si37.6at.%) and a-C (* $p < 0.001$); and ** denotes significant difference between MG63 count on a-C(Si37.6at.%) and a-C (** $p < 0.05$).

Figure 6.8| Optical micrographs of (a, b) COS7; and (c, d) MG63 on a-C(Si37.6at.%). The cells exhibit long lamellipodes indicating active cell migration. The long and fine cytoplasmic extensions indicated that there is good adhesion of the cells to the film; thus good initial attachment. On the sixth day of culturing, complete colonization of both cell lines are observed.

6.5 Summary

The haemocompatibility of a-C(Si) is improved when the Si concentration is increased. This is manifested by the decrease in the adhered blood platelets, as well as the decrease in platelet activation level. At first glance, this phenomenon is closely related to the increase in sp^3/sp^2 fraction as the surface energy will decrease and thus improves haemocompatibility (as suggested by other research groups). However, when the Si concentration is increased, there is an increased in the

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surface energy. This is mainly due to the increase in the polar component. A more in-depth study shows that the polar component is predominantly negatively charged. Since platelets and proteins tend to have a net negative zeta-potential, there will not be any preferential adsorption of any of the proteins and platelets due to electrostatic interaction. Furthermore, the dispersive component of all the films is much larger than the polar component; therefore the interaction should be predominantly based on dispersive forces. Since albumin has a higher dispersive component, it will have a more stable interaction with the film surfaces rather than fibrinogen, a protein that will cause the formation of thrombin (a precursor of blood clog).

Thermal annealing of the a-C(Si37.6at.%) films increases the adhered platelet count and hence decreases the haemocompatibility. The negatively charged polar component decreases when the annealing temperature is increased (by a mechanism discussed in the previous section). This means that the repulsion between the film surface and proteins decreases, and the adsorption of both albumin and fibrinogen increases, with a slightly stronger effect on fibrinogen since it has a higher polar component. This causes the increase in the number of adhered platelets. But, the surface interaction is still largely based on dispersive forces, so albumin, with its higher dispersive component will have a more stable interaction with the surface. This contributes to a slightly decreased activation level of the adhered platelets.

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COS7 fibroblasts and MG63 osteoblastic cells proliferate better on a-C film with the highest Si concentration (~37.6at.%). Amorphous carbon containing 37.6at.% Si has the highest polar/dispersive component ratio and also the highest surface energy. The result thus suggests that both cell-types prefer a more hydrophilic surface. The cell morphologies indicate good initial attachment on the film surface, as well as healthy growth leading to colonization.

CHAPTER 7 ~ NITINOL/AMORPHOUS CARBON MICRO-CAGE

7.1 Micro System

Microgrippers, microtweezers and microcages are important microtools with great potential for biomedical applications, such as the biopsy of cancerous tumors or the capture and manipulation of cells for dissection. There are some basic requirements for these biological micro-tools: small size, low operation temperature, low power consumption and biocompatibility. A microgripper actuated by high temperature or high voltage will damage or even kill living cells, limiting its applications. Several efforts have been made to fabricate high performance microgrippers [161 - 165]. Microtweezers are one type of microgripper, typically made using thin film technology, however due to thickness limitations, they are incapable of confining microobjects out of plane [161-164]. Also microtweezers, which capture micro-objects by applying a force directly to the object, may damage the object. A microcage with multiple fingers with a bimorph structure is another type of microgripper [164,165], which has the advantage of confining and manipulating micro-objects without applying a force directly to the object. However these devices are normally open. A constant power or applied pressure is required to keep the microcage closed during operation. This will increase the temperature of the microcage and the surrounding environment and could damage living cells in a biological experiment. To close these normally open microcages by thermal actuation, extremely high temperatures or very long

fingers are needed. In this project, a normally closed microcage was fabricated and studied. This chapter describes the characterization and performance of the these microcage.

7.2 Microfabrication

7.2.1 Micro-cantilever (Design 2)

The second design of micro-cantilever will be used for demonstrating the concept of a normally closed film structure. The micromachining steps are illustrated in the following:

Step 1:

A bilayer film was deposited sequentially. The deposition parameters for the a-C film were mentioned in §3.1.1. The time was changed so as to deposit 100 nm films. Next, a 50 nm Al film was deposited at 3.3 W/cm² power density (RF) for 5 min.

Step 2:

The patterns of the cantilevers were programmed into a laser micromachining system (*New-Wave QuikLaze, USA*). The patterns were transferred onto the sample by a solid-state YAG ultraviolet laser (355 nm). The laser power was 50 W, and the focused laser spot had a dimension of $5 \times 5 \mu\text{m}$. Frequency used was 50 Hz, and the scan rate was $20 \mu\text{m/s}$.

Step3:

The Si substrate beneath the bilayer film was etched with SF_6 plasma. The gas pressure during etching was 100 mTorr, gas flow rate was 70 sccm, and the plasma power was 100 W and the frequency of the power supply is 13.56 MHz.

7.2.2 Micro-cage

The micromachining steps for fabricating a normally close microcage are illustrated in the following:

Step 1:

A trilayer film was deposited sequentially. The deposition parameters for the a-C films were mentioned in §3.1.1. The time was changed so as to deposit 50 nm films. The TiNi layer was co-deposited using one stoichiometric TiNi target and one Ti target. The sputtering target power densities for the TiNi and Ti targets were 10 W/cm² (RF) and 1.5 W/cm² (DC) respectively to produce a stoichiometric film. Ar flow rate was 20 sccm, and the process pressure was 1 mTorr. Substrate rotation was ~ 16 rpm. The deposition time was 1.7 hour to produce a film thickness of 1.5 µm. After finishing the trilayer deposition, the film was annealed *in vacuo* to crystallize the TiNi. The annealing pressure, temperature and time were 1×10⁻⁷ Torr, 600 °C and 1 hour respectively.

Step 2:

AZ9260 photo-resist was first spin coated using a *Karl Suss Delta 80BM Coater* at a rotational speed of 2000 rpm for 25 sec. The resulting thickness was approximately 7 μm . The wafer was then baked on a hotplate at 110 $^{\circ}\text{C}$ for 4 min to cure the photo-resist. The wafer was loaded into the *Karl Suss MA6 Mask Aligner* ready for UV exposure. The patterns were on a chrome-plated glass mask, and were transferred onto the wafer by UV exposure of the photo-resist. The exposure time was 25 sec. The wafer was then developed in AZ 421K developer until the exposed areas were dissolved. The wafer was then rinsed with deionized water and blown dry.

Step 3:

First, the top a-C film was etched by Ar plasma. The Ar flow was 80 sccm, process pressure is 10 mTorr, bias voltage was -300 V, and time was 15 min. Secondly, the TiNi layer was etched with a $\text{HF}:\text{HNO}_3:\text{H}_2\text{O}$ (1:1:20) solution. The etching time was within a minute. Once the layer was etched, the wafer was immediately rinsed with DI water and spin-dried. Finally, the bottom a-C(Si) layer will be etched with the same condition as the top a-C layer. The photo-resist was stripped after all the etching processes.

Step 4:

A STS ICP deep reactive ion etching system (DRIE) was used to isotropically etch the silicon substrate. No passivation step was used. The gas used was SF_6 with a flow rate of 70 sccm, and a pressure of 72 mTorr. The coil and platen powers were 50 W and 100 W respectively. The etching time for full release of the fingers was about 16 min. The coil ionizes the reactive gas, and platen attracts the ions toward the substrate. The powers and working conditions were optimized to create more chemical etching rather than physical etching (mentioned in §2.3.1). Si under the trilayer film was etched mainly by the chemical part of the etching. The fingers of the microcage were very thin and thus were released first before the center structure (having larger surface area) connecting the fingers.

7.3 Demonstration of Concept

While most researchers studied the nominal stress of Si substrate/film system, the differential stress of the film system is used in this case. Differential stress is responsible for the bending of a free-standing film. Comparing with a normally-open microcage, a normally-closed microcage is more advantageous in biological applications as there is no need for a constant supply of power or pressure, and the temperature raise near the microcage can be minimized. The microcage captures a

micro-object by confining or trapping it without applying a force directly on it, thus avoiding potential damage to bio-cells.

What is desired of the film system used for the microcage is upward curling once it is released from the substrate. It is known that a-C is compressively stressed; therefore the curling/bending is downward (as shown in Figure 4.25). However, it is possible to make use of this compressive stress for a normally-closed microcage in a bimorph structure (bilayered film). Figure 7.1 shows the upward curling of an a-C/Al bimorph cantilever.

Figure 7.1| Deformation morphology of Al/a-C cantilever. The micromachining procedure is illustrated in §7.2.1. The highly compressively stressed a-C bottom layer stretches when being released from the substrate, thereby curling the bimorph upwards.

The bimorph structure was made up of a 100 nm a-C with 60 nm of Al sputter deposited on top of it. The a-C film had a compressive stress of around 1 GPa, and the Al film had a low tensile stress of around 260 MPa. The cantilevers were patterned using a laser micromachining system, and the underlying Si substrate was etched using reactive ion etching with SF₆ plasma. After the

bimorph structure was released from the Si substrate, the a-C layer stretches due to its large intrinsic stress, and bent the bimorph layer upwards to form a curved structure. These cantilevers can be actuated using thermal heating or electrical heating. Al has a relatively large coefficient of thermal expansion (CTE), $\sim 21 \times 10^{-6}/^{\circ}\text{C}$, as compared to that of a-C that has a CTE of around $2 \times 10^{-6}/^{\circ}\text{C}$. During actuation, the Al layer expands more than the a-C layer, and generates a compressive thermal stress on the top side of the bilayer, thus leading to the uncurling of the cantilevers.

7.4 Nitinol/a-C Hybrid Micro-cage

TiNi based thin film shape memory alloy (SMA) has been recognized as a promising and high performance material MEMS applications [166-169]. The advantages of SMAs are their high power to weight ratio, large recovery stress and strain and certain degree of biocompatibility. The work output per volume of thin film TiNi exceeds those of the other micro-actuation mechanisms. Application of TiNi films in MEMS also facilitates simplification of mechanisms with flexibility of design. Therefore, instead of depending only on the difference in CTE of the materials to induce the actuation, using TiNi alloy can be more efficient in terms of actuation power and speed. Once a designed microcage structure is released from the substrate, the opening/closing performance of the microcage upon thermal cycling is not only determined by thermal effect; i.e., temperature change and the

difference in the CTE of the two materials, but also the shape memory effect of TiNi will play a role.

The hybrid micro-cage system consisted of three layers. Firstly, a 50 nm a-C(Si37.6at.%) film was deposited, followed by a 1500 nm TiNi film; the top layer was pure a-C. The concept of this trilayer is slightly different from the bilayer system discussed earlier; where the highly stressed a-C is first deposited so as to induce the upward curling once the bimorph is released. In order to realize the shape memory effect, the TiNi film needed to be crystallized. Therefore, annealing was required. The annealing was carried out at 600 °C *in vacuo*. At this temperature, the residual stress of both amorphous carbon layers should be relaxed. However, structural change is expected for pure a-C. Graphitization takes place, and the hardness and elastic modulus decreases. At 600 °C, a-C(Si37.6at.%) does not exhibit noticeable structural changes, but the stress can be successfully relaxed. Therefore, the bottom a-C(Si) layer will have a higher stiffness than the TiNi and the top a-C layer. In addition, it will have the lowest CTE among the three layers. The a-C layer was graphitized after the annealing process, thus the CTE increased. During thermal actuation, the TiNi expanded more than the other two layers. Since the bottom a-C(Si) layer was stiffer and had a lower CTE, the cage opened. This effect, however was not very significant as both amorphous carbon layers were very thin. The more significant effect of the actuation (cage opening) was the shape memory effect of the TiNi layer.

The main purpose of sandwiching TiNi between the amorphous carbon layers was to impart better haemo- and bio-compatibility to the micro-system. However, it is a concern that the haemocompatibility of the amorphous carbon layers could deteriorate when they are annealed at 600 °C. Though the biological issues are important, the fabrication of the trilayer microcage in this project serves as a demonstration for the compatibility of a-C(Si) with the current MEMS micromachining technique. It is in no way a finished device ready for practical application, so the biological aspects remain an area to be explored in any future study.

Figure 7.2 shows the XRD pattern of TiNi after annealing. Since it was scanned at room temperature, the structure is B19' (martensite phase). In order to quantify the power and efficiency of the TiNi film during thermal actuation, it was necessary to determine the recovery stress (σ_R). This stress is the maximum stress generated by the film during thermal cycling. Figure 7.3 shows the hysteresis loops of the trilayer film and a TiNi monolayer. These hysteresis loops are determined through *in situ* stress measurement during temperature ramping and cooling (method described in §4.1.2, ramping and cooling set at 1 °C/min). The recovery stress of the trilayer film was double of that of a single layer of TiNi. This shows that the actuation power of the trilayer film system was higher than a single layer of TiNi. The reasons are twofold. First, it is due to the difference in elastic modulus and CTE among the layers, which can generate a differential stress during thermal cycling; second, the a-C layer prevents TiNi from oxidizing (by

oxygen species outgassed from within the chamber) during thermal annealing, thus preventing the loss of the shape memory effect.

Figure 7.2| XRD pattern of TiNi at room temperature. The phases are all martensite, B19', which is a low temperature phase of TiNi. The pattern shows a predominant (111) texture.

Figure 7.3| Hysteresis loop of a-C(Si)/TiNi/a-C trilayer and TiNi monolayer films. The trilayer film exhibited a recovery stress, σ_R that was twice as high as that of a single layer of TiNi. This shows that the actuation power or force is higher for the trilayer film. There are two reasons for this improvement. First, it is the generation of a differential stress during thermal cycling induced by the mismatch in elastic modulus and CTE between the layers. Second, the a-C layers prevented the TiNi from oxidizing during thermal annealing, thus protecting the shape memory effect.

Differentiated stress or stress rate as a function of temperature can be derived from the hysteresis loops. From Figure 7.4, it is obvious that the stress rate of the trilayer system ($> 30 \text{ MPa/}^\circ\text{C}$) was much higher than the TiNi single layer ($< 13 \text{ MPa/}^\circ\text{C}$). Furthermore, the phase transformation hysteresis between the martensite and austenite phases of the trilayer film ($12 \text{ }^\circ\text{C}$) was smaller than that of the TiNi single layer ($21 \text{ }^\circ\text{C}$). Both phenomena indicate a faster response from the trilayer film system during thermal actuation. These improvements are again due to the extra differential stress induced by the elastic modulus and CTE mismatch between the layers, and the better shape memory effect when the TiNi layer is being protected from oxidation during annealing.

Figure 7.4| Stress rate as a function of temperature of a) a-C(Si)/TiNi/a-C trilayer film; b) TiNi monolayer film. The stress rate of the trilayer film is around three times as high as the single layer film, and the phase transformation hysteresis between martensite, M and austenite, A is smaller than the single layer film. The results indicate the trilayer film has a faster response during actuation.

There were several microcage designs. Figure 7.5 shows two of the trilayer microcages after micromachining. Each individual cantilever curled upward as expected. However, the curl radius was not small enough to form a truly normally-closed cage. Since the bottom a-C(Si) layer was nearly stress free (top a-C as well), the curling depended mainly on the residual stress of the TiNi layer. The nominal stress of the trilayer was around 158 MPa tensile, which is rather low to cause substantiate curling.

Figure 7.5| SEM micrographs of the a-C(Si)/TiNi/a-C trilayer microcages. The micromachining procedure is illustrated in §7.2.2. The cages are not fully closed due to the removal of residual of the a-C layers.

Figure 7.6 illustrates the opening of the trilayer microcage. There was a slow and constant opening from 20 °C – 50 °C, and a sudden increase in opening speed between 60 °C and 70 °C. Referring to Figure 7.4a, 60-70 °C is the temperature range where the bulk of the austenite transformation takes place, and also a temperature region of rapid stress rate. The cage was fully open at around 90 °C, which is also the temperature where the martensite to austenite phase transformation is completed.

Figure 7.6| Optical images showing the opening of a-C(Si)/TiNi/a-C trilayer microcage through thermal actuation. The opening was constant from 20-50 °C and speeded up around 60-70 °C, where the bulk of the austenite transformation occurs. The opening was completed around 90 °C, where all martensite was transformed into austenite.

7.5 Summary

The concept of differential stress was used for the fabrication of a normally-close micro-cage. This concept was proven using an a-C/Al bimorph film, where the film cured upward once it was released from the Si substrate. This upward curl was caused by the stretching of the bottom a-C layer that is highly compressively stressed. The top Al layer expanded more than the a-C layer during thermal actuation due to a larger CTE, thereby uncurling the cantilevers.

Instead of using only the differential stress generated, TiNi shape memory alloy was employed as the metallic layer for its shape memory effect, which induced additional stress upon actuation. The TiNi layer was sandwiched between the bottom a-C(Si37.6at.%) layer and the top a-C layer. These a-C layers not only impart haemo- and bio-compatibility to the microsystem, they also contribute to the differential stress that aids actuation. The TiNi layer needed to be annealed at 600 °C *in vacuo* to be crystallized (hence having shape memory effect). The residual stresses of both amorphous carbon layers relaxed. At this temperature, a-C layer will graphitize, and its hardness and elastic modulus will decrease, but there will not be much significant change to the a-C(Si37.6at.%) layer. During thermal actuation, the TiNi expanded more than the other two layers. Since the bottom a-C(Si) layer was stiffer and had lower CTE, the cage opened. But, the more significant effect of the cage opening was the shape memory effect of the TiNi layer.

The recovery stress of the trilayer film was doubled that of a single layer of TiNi. This implies that the actuation power or force was higher for the trilayer microcage. Besides the enhanced recovery stress, the stress rate of the trilayer film was also higher, and the phase transformation hysteresis between martensite and austenite was smaller than the single layer film. The results indicate that the trilayer film had a faster response during actuation. These improvements were due to the extra differential stress induced by the mismatch of elastic modulus and CTE between the layers, and a better preserved shape memory effect when the TiNi layer was protected from oxidizing during annealing by the a-C layers.

The fingers on the micromachine trilayer microcage were not fully closed. Since, the annealing process relaxed the stress of the bottom a-C(Si) layer, the stretching was not sufficient to fully curl the structure upwards. The curling will depend on the residual stress of the TiNi layer. The nominal stress of the trilayer was found to be around 158 MPa tensile, which is rather low to cause substantiate curling. Differential stress might not have acted on the initial upward curl (normally-close); it aided the actuation of the microcage. The microcage was able to partially open and close through thermal cycling between room temperature and $\sim 90\text{ }^{\circ}\text{C}$.

CHAPTER 8 ~ CONCLUSIONS & RECOMMENDATIONS

8.1 Conclusions

Amorphous carbon films containing different Si concentrations have been deposited by magnetron sputtering. The atomic bonding characteristics after Si incorporation have been investigated, and are found to greatly affect the mechanical and biological properties of the films. Mechanical properties: hardness, elastic modulus and residual stress, and biological properties: haemocompatibility and cellular responses; are all characterized.

Based on the experimental results obtained, the major conclusions are as follow:

1. Incorporation of Si into the a-C network alters the atomic bonding configurations. C-Si sp^3 bonds form through breaking up C=C sp^2 aromatic ring bonding structures. As a result, with increasing Si, C-Si bond concentration increases while that of C=C bond decreases. C-C sp^3 concentration is relatively unaltered. Amorphous carbon film containing ~37at.% Si is found to have the highest sp^3 bonding fraction.
 2. During post-deposition annealing, a-C(Si37.6at.%) exhibit better thermal stability than the undoped a-C. The undoped a-C starts to graphitize (conversion from C $sp^3 \rightarrow$ C sp^2 and C sp^2 clustering) as early as 200 °C, while the atomic structure of a-C(Si) is stable until at least 600 °C. The stability
-

comes from Si-induced deterrence of bonding conversion directly from sp^3 to sp^2 during annealing. This deterrence is not pronounced during high deposition temperature, where the activation energy is nearly three times lower. The activation energy of sp^2 clustering is much lower during high temperature deposition than post deposition annealing (about 1/5), because the sp^2 -hybridized C are more favorably formed at high temperature deposition when disordering is hard to maintain due to dynamic annealing effect.

3. As Si is incorporated in a-C, hardness and elastic modulus are found to first decrease, and then increase from ~16at.% Si. The initial reduction in hardness and modulus is attributed to the decrease in film density from the mismatch in atomic size and bond strength in Si and C. When more than 16at.% Si is incorporated, the increase in higher strength C-Si and C-C bonds and decrease in the weak π bonds eventually compensates the initial decrease in film density, and hardness and modulus both increase. High temperature deposited a-C(Si) has poor and deteriorating mechanical hardness with increasing deposition temperature while the same coatings deposited at room temperature are stable till ~600 °C post-annealing. This is due to higher activation energies for graphitization processes during post-annealing (as explained in the previous point).
4. The residual stress of a-C is compressive, and decreases appreciatively with Si concentration due to the relaxation of the atomic strain through increase in

inter-atomic bonding length between C and Si, and the releasing of bond angle distortion through the formation of C-Si bonds. The residual stress of a-C(Si37.6at.%) can be eliminated completely by annealing at around 600 °C with a release of 0.3 % strain.

5. The dispersive component of the surface energy is related to the density of the a-C(Si) films. As Si is incorporated in a-C, the dispersive component of the surface energy first decreases and then starts to increase from ~16at.% Si. The polar component, on the other hands, always increases when the Si concentration is increased, as a result of the increase of Si-O and C-O polar bonds on the film surface. After thermal annealing of a-C(Si37.6at.%) film, there is no significant change in the dispersive component as the atomic configuration (hence density) is not altered significantly. The polar component however, decreases when the annealing temperature increases as the probable outgasing of O species could decrease the surface polar C-O and Si-O bonds.
6. The haemocompatibility of a-C(Si) is improved when the Si concentration is increased - the number of adhered blood platelets, as well as platelet activation level, decrease. The total surface energy decreases until ~16.6at.% Si. Below this concentration, the haemocompatibility improves due to the increase in sp^3 fraction. Beyond this concentration, increase in Si increases the polar to dispersive component ratio of the surface energy. The negatively charged polar component will discourage preferred affinity of platelets and proteins; as

a result, haemocompatibility is also improved at high Si concentration. When a a-C(Si37.6at.%) film is subjected to thermal annealing, haemocompatibility deteriorates in terms of adhered platelet counts. The negatively charged polar component decreases when the annealing temperature is increased, causing the repulsion between the film surface and proteins to decrease, thereby increasing the number of adhered platelets.

7. Although there is a decrease in C sp²-hybridized bondings with the incorporation of Si, it does not translate to a more hydrophobic surface, due to the polar Si-O and C-O bonds on the surface. The films become more hydrophilic, and with higher polar to dispersive surface energy component ratio when Si concentration is increased. Both COS7 and MG63 can adhere, spread and proliferate well on a-C and a-C(Si) films. The more hydrophilic film, a-C(Si37.6at.%), is more conducive for cellular growth - the cell count is highest at the end of the incubation period among Si concentration tested. The cell morphologies also indicate good initial attachment on the film surface, as well as a healthy growth leading to colonization.
8. The actuation power or force for a a-C(Si)/TiNi/a-C trilayer film is higher than that of a monolayer TiNi as manifested by the doubling of recovery stress during thermal cycling. The stress rate of the trilayer film is also higher, and the phase transformation hysteresis between martensite and austenite is smaller than the single layer film, indicating that the trilayer film has a faster response

during actuation. The fingers on a micromachined trilayer microcage were not fully closed as the annealing process has relaxed the stress of the bottom a-C(Si) layer, so the stretching is not sufficient to curl the structure upwards. The microcage is able to partially open and close through thermal cycling between room temperature and $\sim 90^\circ\text{C}$.

8.2 Recommendations

The research findings from this project have shown a-C(Si) films to be a strong candidate for biomedical and MEMS applications. There are still a number of unexplored aspects that can be investigated to gain a more thorough understanding of this material.

1. Toughness of a-C(Si) films should be evaluated. Although a-C(Si_{37.6at.%}) is found to be hard, hardness does have an inverse relationship with toughness. For a film to be feasible for any application, toughness is important as it expresses the resistance to shock load and crack propagation. This property can be characterized using several techniques such as bending, buckling, indentation and tensile methods, and quantitatively through the determination of fracture toughness.
2. Endothelial cells can be seeded to substantiate the haemocompatibility findings for a-C(Si). They are the cells inside the blood vessel wall. If these cells exhibit healthy growth characteristics on the film, then it shows that the film is

indeed blood compatible. Protein (e.g. albumin, fibrinogen, vitronectin, globulin etc.) adhesion characteristics on the a-C(Si) should be investigated to determine the mechanism behind cellular response and blood platelet adhesion in more detail. In addition, the static corrosion properties of a-C(Si) in simulated body fluid, gastric and intestinal juices should be studied to understand the film behavior under physiological environment.

3. The reactivity of a-C(Si) with various Si etching solutions used in conventional micromachining technique should be studied to determine the passivation properties. Although there is no clear evidence that the a-C(Si) film was etched during the wet micromachining procedures used in this project, it would be helpful to obtain quantitative proof of its inert behavior, so as to aid machining design for BioMEMS.
4. A more thorough theoretical analysis should be done to study the working of the trilayer microcage. The analysis can involve the quantification of the curvature/bend of the microcage fingers, once they are released from silicon substrate and their angle change during thermal actuation. The study should take into account two effects: 1) thermal effect, which is caused by the different coefficient of thermal expansion of the various layers; and 2) shape memory effect, an intrinsic property of TiNi that could assist the actuation.

Appendix

An overview of the entire experimental process:

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