## CHARACTERIZATION OF DIAMOND-LIKE CARBON THIN FILMS

#### EXPERIMENTAL CHARACTERIZATION AND THEORETICAL SIMULATION OF DIAMOND-LIKE CARBON THIN FILMS

By GARETH BELLINGER, B.ASc.

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AUTHOR:	Gareth Bellinger		
	B.ASc. (Engineering Physics)		
	Queen's University, Kingston, Canada		
SUPERVISOR:	Dr. Marek Niewczas		

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#### Lay Abstract

Thin films allow for modification of the properties of a variety of different materials from steels used in engine parts, glasses made for optical lenses, and components of solar cells. Diamond-like carbon is one example where it replicates the properties of diamond for a material it is applied to, i.e. the surface may become incredibly hard. The complex nature behind how the properties of these films may be controlled relies on characterizing their structure and how this varies with different processing conditions. This investigation underscores experimental and computational efforts to achieve an understanding between the processing conditions utilized to make diamond like carbon thin films and their desirable properties for emergent applications.

#### Abstract

Diamond-like carbon (DLC) films produced with radio-frequency plasma-enhanced chemical vapour deposition (PECVD) from two distinct hydrocarbon precursor gases were characterized to determine the effect of processing conditions on the structureproperty relationships exhibited by the films. The bias voltage was systematically varied and was shown to influence the hydrogen content, mechanical hardness, and chemical bonding. Films were produced with hydrogen contents between 25 to 30 at.%, graphite  $(sp^2)$  to diamond  $(sp^3)$  bonding near a 1 to 1 ratio, and indentation hardness reaching 24 GPa. Adhesion tests indicated that DLC was more strongly bonded to silicon than aluminum. Varying the bias voltage from 300 to 450 V was shown to decrease hydrogen content and increase the mechanical hardness, while the  $sp^2$  content remained unchanged. A mechanism was proposed to describe the structure evolution of the films with respect to the obtained results. The similarities in properties between films from distinct precursors suggested a similar dissociation of molecular species within the PECVD chamber. Separately, hydrogenated amorphous carbon (a-C:H) structures were prepared with molecular dynamics (MD) and translated to density functional theory (DFT) simulations for calculation of mechanical properties. The DFT results showed overlap with the experimental results and allowed for an estimation of the densities of the DLC films investigated between 2.0 and 2.6  $g\,cm^{-3}.$ 

To my family and friends

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# Declaration of Academic Achievement

I, Gareth Bellinger, declare this thesis and the work presented in it to be my own. The work described was completed between September 2022 and July 2024. Guidance was provided by my supervisor, Dr. Marek Niewczas, my supervisor committee member, Dr. Oleg Reubel, and by employees at Intlvac Thin Film, the industrial partner of the project throughout the duration of this project. The experiments, when possible, and data analyses were carried out independently by the author of this thesis.

### Chapter 1

### Introduction

Continued advancements in technology require research, development, and engineering of materials, components, and systems that significantly outperform the previous generation's. Over the past few decades, consideration of the natural world has become a fundamental engineering principle where new technology aims to implement sustainable processes that target the production of renewable energy or reduction of carbon emissions, among other objectives. Fulfilment of these goals has pushed materials engineering within the space of functional coatings and thin film systems for increased control and modification of surface properties at the micron- to subnanometre scale.

Thin films can enable the simultaneous tuning of optical, mechanical, electrical, and thermal properties. In this way, the application of thin film coatings has become common practice in the biomedical, automotive, and aerospace fields [1, 2]. A subset of technologically useful films are those consisting of disordered carbon. Unlike carbon's crystalline counterparts of diamond (fully sp<sup>3</sup> bonded) and graphite (fully sp<sup>2</sup> bonded), which themselves are equally technologically valuable, disordered carbon has an amorphous structure and is commonly referred to as diamond-like carbon (DLC) when deposited in thin film geometries. The novelty of DLC coatings stems from their ability to almost freely interpolate between the properties of diamond and graphite by changing the processing conditions at which they are deposited [2–4]. This allows DLC coatings to be engineered to exhibit semi-conducting to insulating behaviour and hardness approaching 80% that of diamond [2, 5]. Additional beneficial properties such as biocompatibility, hydrphobicity, and increased thermal stability may also be realized through the introduction of dopant atoms [6].

Currently, emergent applications of DLC include use as barrier coatings in hydrogen fuel cells, protective coatings on new-generation optical substrates, and use as dielectric layers in optoelectronic devices [7–12]. Prediction of DLC properties using both molecular dynamics (MD) and density functional theory (DFT) approaches is common for probing structure-property relationships for DLC [13–20]. The prevalence of utilizing data-driven approaches, including machine learning, has also expanded to the prediction of DLC properties [21–23]. Regardless of the theoretical technique used, material property exploration and verification through experimental characterization of DLC has tremendous opportunity to provide solutions for ideal processing conditions and expand the scope of applications. To ensure research and development (R&D) can proceed with informed decisions and that deposition conditions are optimized for new applications, DLC films must be characterized in a manner that is not overtly restrictive to industry with respect to cost and throughput.

#### **1.1** Research Objectives and Thesis Structure

There are two main objectives of this investigation. The first is to establish a connection between the processing condition of bias voltage and structure-property relationships exhibited by DLC films deposited by plasma-enhanced chemical vapour deposition (PECVD) through verification with trends shown in the literature. This goal is in pursuit of enhancing the research and development cycle of tailored DLC films for emergent applications for the industrial partner, Intlyac Thin Film Inc. The second objective aims to utilize theoretical simulations to further expand the body of knowledge with respect to the investigation of DLC films using a combined MD-DFT approach. Additionally, the analysis of theoretical results allows for direct comparison to experimental results to demonstrate the validity of the techniques applied to obtain accurate modelling of the structure and mechanical properties of DLC. To the extent of these two goals, this thesis is organized into six subsequent chapters. The nature of the separate experimental and theoretical investigations is manifested by distinct sections in each chapter. Although DLC refers to the wider range of amorphous carbons included in the ternary diagram described later in Section 2.1, herein DLC and a-C:H will be used interchangeably when describing the thin film samples investigated in this thesis.

Chapter 2 provides the necessary background information to understand the nature of DLC films in the context of the body of work completed in the early 2000s. In particular, an emphasis is placed on the use of Raman spectroscopy as the highestthroughput, most information-dense experimental method. A brief review of MD and DFT studies with commonly used protocols relating to amorphous carbon structures is detailed. The qualitative and quantitative techniques used to probe the structure and properties of a-C:H films are described in the experimental section of Chapter 3. Mechanical and tribological properties were examined using nanoindentation and scratch testing. Chemical bonding information was obtained using X-ray photoelectron spectroscopy (XPS) and X-ray excited auger electron spectrometry (XAES) methods in conjunction with Raman spectroscopy. Finally, elastic recoil detection analysis (ERDA) was used to quantify the hydrogen content of the films. A decision-tree flowchart is provided to visualize the design of the experiment used in the context of the bridged MD-DFT approach for the simulation of a-C:H. Additional explanations are provided in Chapter 4 to understand the data analysis techniques employed to analyze raw data obtained from Raman spectroscopy, MD, and DFT simulations.

Results are introduced concisely in Chapter 5 for further discussion in Chapter 6. Chapter 6 underscores the importance of Raman spectroscopy as it is cross-correlated with results obtained from quantitative methods including ERDA, nanoindentation, and XPS. Adhesion tests provide evidence that the bonding strength of DLC to different substrates can be estimated. Theoretical results show there exists a subset of simulated a-C:H structures that overlap with the mechanical properties exhibited by the experimentally investigated films. This allows an extension to describing the density of the films by comparison to the theoretical models. Improvements and next steps are incorporated into the discussions in Chapter 6.

Closing discussions and key insights are summarized in Chapter 7. These conclusions hopefully remain insightful in the context of upcoming projects at McMaster University in Professor Niewczas' research group targeting emergent DLC applications.

### Chapter 2

### Background

The complexity of DLC films is first described with respect to the bonding exhibited in the amorphous structure through comparisons to the well-understood allotropes of carbon: graphite and diamond. The Robertson model, along with experimental observations that reinforce the model's predominance in literature, is explained. Deposition techniques are also outlined, and PECVD is highlighted since it was used in the investigation. Among other characterization techniques, the interpretation of the Raman spectra of DLC is elaborated. Finally, theoretical modelling and protocols for MD and DFT studies of DLC are reported.

#### 2.1 Fundamental Aspects

Allotropes are materials composed of the same constituent element but differ by their respective crystal structures. Modification to the atomic bonding environment in the crystal structure allows carbon allotropes to exhibit distinct properties that span a wide range. Carbon exhibits the highest number of allotropes, stemming from its ability to form covalent networks with hybridized bonds. Valence bond theory explains that hybrid bonds are a geometric reorganization of atomic orbitals such that the bond strength is increased through orbital overlap between neighbouring atoms [24]. Thus, hybridization allows carbon to exhibit a wider range of bonding and crystal structures. The spherical 'S'-orbital overlapping with any of the three axial-lobed 'P'-orbitals produces  $sp^3$ ,  $sp^2$ , or sp hybridized bonds, dependent on the number of P-orbitals contributing to the hybridization [2, 24]. Examples of other carbon allotropes include zero-dimensional fullerenes, one-dimensional nanotubes, and two-dimensional graphene [2, 25]. Diamond contains purely sp<sup>3</sup> orbitals that form four tetrahedral  $\sigma$  bonds with neighbouring atoms, whereas graphite has only sp<sup>2</sup> orbitals, of which three are trigonal planar  $\sigma$  bonds and one is a de-localized  $\pi$  bond situated normal to the  $\sigma$  bonding plane [2]. Visualizations of diamond and graphite structures and their respective hybrid orbitals are provided in Figure 2.1 and Figure 2.2. The difference in optical, electrical, and mechanical properties exhibited by this change in bonding is illustrated in Table 2.1.



Figure 2.1: Visualization of (a) the tetrahedral bonding exhibited in diamond and (b) the trigonal planar bonding exhibited in graphite. Bond angles are shown where the angle between bonds in diamond is  $109.5^{\circ}$  whereas in graphite it is  $120^{\circ}$ .



**Figure 2.2:** Visualization of (a) sp<sup>3</sup> hybrid bonds in diamond and (b) sp<sup>2</sup> hybrid bonds in graphite. Note that the sp<sup>3</sup> hybrid bonds in diamond form four  $\sigma$  bonds whereas sp<sup>2</sup> hybrid bonds in graphite form three  $\sigma$  bonds and one  $\pi$  bond that is normal to the bonding plane.

**Table 2.1:** Properties of the carbon allotropes diamond and graphite compared on the basis of hybrid bonding character [2].

	Hybrid Bond Type	Band Gap $[eV]$	$\begin{array}{c} \mathbf{Density} \\ [g \ cm^{-3}] \end{array}$	Indentation Hardness [GPa]
Diamond	$\mathrm{sp}^3$	5.6 (insulator)	3.5	100
Graphite	$\mathrm{sp}^2$	0 (semi-metal)	2.2	≈1

Amorphous carbons and DLC are classified by the bonding ratio  $(sp^3 to sp^2)$  and amount of hydrogen content, as these dictate the properties that are exhibited [2]. The ternary diagram of DLC describing this structure-property relationship is shown in Figure 2.3 after adaptation from Ohtake [5].



**Figure 2.3:** Ternary diagram showing the different classifications of DLC and reliance on  $sp^2$ ,  $sp^3$ , and Hydrogen content. Adapted from Ohtake [5] under Creative Commons license 4.0

The nomenclature follows from definition by Ferrari and Robertson [26], where 'a-C' refers to amorphous carbon, 'ta' refers to tetrahedral, ':H' refers to hydrogenated films, and 'PLCH' is an amorphous hydrocarbon polymer that is not classified as

DLC [5]. ta-C and ta-C:H are distinct from a-C and a-C:H since the tetrahedral films have the highest sp<sup>3</sup> content and are most similar to diamond, exhibiting the characteristic hardness and transparency [2, 26]. Further categorization of a-C:H was made by Casiraghi [27], where films with high sp<sup>2</sup> bonding and low hydrogen content ( $\approx 20\%$ ) are called graphite-like a-C:H (GLCH). Table 2.2 shows an expanded version of Table 2.1 to include each DLC type, while diamond and graphite act as the bounding cases.

**Table 2.2:** Properties of diamond, graphite, and DLC types compared on the basis of hybrid bonding character. Following definitions from [2, 5, 27].

	${f sp}^3 \ [\%]$	Hydrogen Content [at.%]	Band Gap $[eV]$	$\begin{array}{c} \mathbf{Density} \\ [g \ cm^{-3}] \end{array}$	$\begin{array}{c} \textbf{Indentation} \\ \textbf{Hardness} \\ [GPa] \end{array}$
Diamond	100	0	5.6 (insulator)	3.5	100
ta-C	50-90	<5	0.2-1.7	2.6-3.5	25-90
a-C	10-50	<5	1.0-1.7	1.4-1.7	9-25
ta-C:H	50-90	5-50	1.0-2.5	2.0-2.6	9-35
a-C:H	20-50	5-50	0.5-2.0	1.4-2.0	9-25
GLCH	10-30	<20	<1.0	2.0-2.6	<10
Graphite	0	0	0 (semi-metal)	2.2	$\approx 1$

#### 2.1.1 The Cluster Model

Table 2.2 shows that DLC properties interpolate between the bounding cases of diamond and graphite. To describe the structural behaviour of these amorphous films in relation to their properties, a phenomenological model is required. The micro-structure of DLC can be described by the cluster model first proposed by Robertson

[28]. This model proposes that DLC (both hydrogenated and non-hydrogenated) consists of clusters of  $sp^2$  in a matrix, or backbone, of  $sp^3$  bonds [2, 28]. Concerning the energetics of the micro-structure, the cluster model proposes that [2, 28]:

- i) The sp<sup>2</sup> clusters attempt to form even-member rings since odd-member rings contribute a coordination defect from the unpaired state.
- ii) sp<sup>2</sup> sites maximize  $\pi$  orbital overlap through alignment similar to ethylene units (C=C).
- iii) Further energy minimization occurs if three C=C units form a six-fold ring (benzene-like structure).

Experimental evidence supporting the cluster model was shown by analysis of the optical properties of a-C:H. An increase to the  $sp^2$  fraction corresponded to a decreased optical band-gap as films progressed to the optical properties of graphite [4, 28]. While the graphitic phase controls the optical properties, the presence of  $sp^3$  bonds influence the mechanical properties. Strong evidence has been shown by Raman spectroscopy to support the cluster model since the characteristic peaks are those that correspond to six-member rings [26, 29, 30]. Further discussion of the interpretation of the Raman spectra of a-C:H is explained in Section 2.3.1.

#### 2.1.2 Growth Mechanisms

Lifshitz showed growth occurred at a sub-surface level by using auger depth profiling on DLC deposited on nickel substrates, and termed the growth mechanism of DLC sub-plantation [31]. The sub-plantation mechanism was then proposed as a general model to describe film growth by energetic species impinging on a substrate with energies between 1 to 1000 eV [31]. This ion energy range is observed in many thin film processes including plasma and ion beam deposition techniques. The difficulty in explaining the growth of DLC stems from providing a microscopic view of how the metastable sp<sup>3</sup> phase grows. The leading theory behind using sub-plantation to describe the growth of a-C films uses the following assumptions [2, 31]:

- Carbon ions that impinge an existing, restricted volume and interact at a subsurface level cause a metastable increase to the local density. This causes a change to the local bonding in favour of the sp<sup>3</sup> phase for the incident particle.
- 2) This phenomenon continues to increase in probability when ion energy is increased until a threshold is reached ( $\sim 100 \text{ eV}$ ) [3].
- 3) Past this threshold energy, excess energy is dissipated as heat and the surrounding metastable volume relaxes sp<sup>3</sup> back into sp<sup>2</sup>.

Recent evidence from Caro et al. has disproved sub-plantation in favour of a 'peening' mechanism through the use of ab-initio MD with a machine-learned potential trained on DFT data [18, 32]. The peening model **does not** discount that film growth occurs sub-surface, but it does clarify that incident atoms are deposited in sp<sup>2</sup> configuration rather than sp<sup>3</sup>, as proposed by sub-plantation [18, 32]. Instead of the perspective of a restricted volume, it was shown that impinging ions induce a pressure wave that travels radially outwards from the impact site. sp<sup>2</sup> growth occurs for the incident atoms at the impact site, but the pressure wave induces the metastable transition from sp<sup>2</sup> to sp<sup>3</sup> at further sub-surface levels [32]. Once incoming ions poses enough energy, sp<sup>3</sup> growth occurs at a faster rate. After a critical ion energy, the range of the sp<sup>2</sup> growth extends and sp<sup>2</sup> becomes the dominant bonding configuration as

the film grows [32]. The newer modelling also shows that if incident particles were responsible for sp<sup>3</sup> growth, films with only a maximum of 40% sp<sup>3</sup> could be realized. This inherently contrasts the existence of ta-C and ta-C:H films [32].

With respect to ion energy, both models share the same conclusions to describe the qualitative evolution of  $sp^2$  and  $sp^3$  bonding for the growth of a-C. Literature shows that for a-C:H films, the evolution of the  $sp^2$  and  $sp^3$  bonding fractions as a function of ion energy evolve as explained by either growth model [3, 4, 28, 33–35]. This enables a connection between the explanation of DLC properties by the cluster model to the structural evolution of DLC films as a function of ion energy which can be controlled as a process parameter. This facilitates the complete understanding of how DLC films can be engineered to exhibit specific properties primarily through tuning of the  $sp^3$  to  $sp^2$  ratio.

#### 2.2 Deposition Techniques

The deposition of DLC films can be accomplished by a variety of techniques. a-C:H is typically obtained from PECVD techniques while a-C films can be prepared from physical vapour deposition (PVD) methods such as magnetron sputtering or cathodic arc [2]. PECVD is an attractive technology for a-C:H deposition since it has a high deposition rate ( $\leq 10 \text{ nm/s}$ ) and can accommodate a variety of substrates since the deposition temperature remains low ( $\leq 100^{\circ}$ C) [1]. The most common implementation of PECVD is capacitively coupled radio-frequency (RF) for the deposition of DLC. The use of an RF power supply, compared to DC, enables an increase in the percent ionization of species in the plasma and allows for insulating films to be

deposited without a corresponding drop to applied bias since alternating current is used. A typical parallel plate RF-PECVD reactor is shown in Figure 2.4 **a**). The power supply applies an alternating current at 13.56 MHz to the cathode which capacitively couples to the plasma. The matching network is used for impedance matching. Plasma is formed when hydrocarbon gas is introduced into the chamber while under vacuum and application of the alternating RF current is applied. Highly energetic electrons dissociate molecular species producing ions and radicals, while some neutral species may remain depending on the degree of ionization (plasma density). RF PECVD operates in the weakly-ionized regime where typically less than 10% of the total species are ionized [36, 2]. Diffusion governs the transport of radicals and neutrals to the substrate interface[35]. Ions are transported by the electric field across the sheaths which is now explained.

The sheaths are regions of space between the plasma and electrode surfaces where there is an absence of plasma. Figure 2.4 b) models the sheaths as capacitors each with an associated potential difference. The anode and chamber walls are grounded, which translates to the areas of the capacitors being asymmetric where the powered sheath ( $C_A$ ) has a smaller area (smaller capacitance) than the grounded sheath ( $C_B$ ) with a larger capacitance. Since potential difference is inversely proportional to capacitance,  $V_A > V_B$ . By the circuit convention in Figure 2.4 b),  $V_{bias}$  is negative and a negative charge accumulates on the cathode. The blocking capacitor ( $C_{block}$ ) is used to prevent this charge from dissipating in the system. Accumulation of negative charge on the cathode ensures that ions produced in the plasma are attracted downward to the film, initiating film growth. Effectively, the parallel plate geometry confines the plasma to the centre of the chamber and substrates are placed on the cathode to be coated.



Figure 2.4: (a) RF-PECVD reactor schematic showing the basic components of the deposition system. Reprinted with permission from Advanced chemical vapor deposition silicon carbide barrier technology for ultralow permeability applications, Zambov et al., J. Vac. Sci. Tech. A, vol. 24, 2006. Copyright 2006, American Vacuum Society. (b) capacitive voltage divider model where sheaths are modelled as capacitors with DC voltages  $V_A$  and  $V_B$  and related to the DC bias voltage,  $V_{bias}$ .

The details of many derivations for plasma discharge models are provided by Lieberman [36]. In the context of this investigation, the important derivation is that the measurable, DC bias voltage ( $V_{bias}$ ), between the ground and powered electrode is proportional to the applied RF voltage amplitude and that it is negative. This is achieved by considering the RF voltage amplitude across one sheath is directly proportional to the time average of the potential difference across the same sheath. Including the relationship between the potential difference of each sheath and their area, it is possible to derive:

$$V_{bias} = -\alpha V_A \left[ 1 - \left(\frac{A_A}{A_B}\right)^q \right]$$
(2.2.1)

Where  $\alpha$  is approximately 5/6,  $V_A$  in this case is the RF amplitude across sheath A,  $A_A$  or  $A_B$  refer to the area of the respective sheath, and q is a scaling constant that differs for inclusion of different prevalent plasma phenomenon considered in the model. For clarification the reader is referred to Chapter 11 of Lieberman and specifically equations 11.2.22, 11.2.11, 11.4.1, and 11.4.2 and Table 11.1 [36]. Importantly, Equation 2.2.1 shows the relationship between the bias voltage and applied RF amplitude is directly proportional. Since  $A_A < A_B$ , Equation 2.2.1 shows that  $V_{bias}$  remains negative in sign, attracting positive ions from the plasma to the cathode. Equation 2.2.1 also shows an intrinsic limitation to the use of RF PECVD methods since the bias voltage ultimately depends on the geometry of the chamber through the ratio of areas of the cathode to anode. This limitation can be avoided if another AC power supply operating at a different frequency is used to bias the cathode.

Nevertheless, the bias voltage is the key processing condition that provides the potential necessary to accelerate ions in the plasma towards the substrate. In other words, the ion energy is directly proportional to the bias voltage. The pressure also dictates the mean free path, which also affects the energy that ions have after traversal of the sheath. Figure 2.5 shows the relationship between the sp<sup>3</sup> fraction, hydrogen content, density, and band-gap of a-C:H films as a function of bias voltage [2].



Figure 2.5: Evolution of a-C:H film properties as a function of bias voltage. Figure reprinted from J. Robertson, Diamond-like amorphous carbon, Mater. Sci. Eng. R, vol. 37, Page 211, Copyright 2002, with permission from Elsevier. Data originally from [4, 30, 37].

400

benzene

800

Bias, V

1200

2

1.6

1.2

0

This behaviour can be understood with the connection between bias voltage and ion

energy in the context of the growth mechanisms described in Section 2.1.2:

- a) Low bias voltages impart little energy to impinging ions. This reflects film growth by molecular ions and radicals with constituent hydrogen atoms, forming films with a large amount of hydrogen content.
- b) A maximum in density is reached when the carbon bonded sp<sup>3</sup> fraction is maximized. This regime corresponds to a critical ion energy range between 80-100 eV [3, 32].
- c) Film growth by high energy ions proceeds at higher bias voltages. This translates to an increase in formation of sp<sup>2</sup> fraction.

The trend for  $sp^3$  in Figure 2.5 shows the total fraction which is inclusive of carbonhydrogen bonding. Additionally the band-gap behaviour can be explained with reference to the cluster model description in Section 2.1.1 where this is linked to an increase in  $sp^2$  fraction. This is reinforced by the explanation that hydrogen acts as an etchant to the  $sp^2$  phase in plasma processes, which is supported by the method of CVD growth of diamond relying on a hydrogen rich environment [3]. Both the continual decrease of total  $sp^3$  and band-gap (increase of  $sp^2$ ) is then explained in connection to the continual decrease of hydrogen content. Schwarz et al. demonstrated that the index of refraction was strongly correlated to the bias voltage and developed qualitatively the same as the density[38]. Variation of the bias voltage therefore ensures the study of structure-property relationships for DLC films can be accomplished by changing only one processing parameter.
#### 2.2.1 CVD Growth Considerations for a-C:H

The growth mechanism by sub-plantation of a-C:H follow description from a physical deposition point of view. A description is still required to consider the complex behaviour of the chemical reactions occurring at the substrate interface when a-C:H is grown by PECVD. Possible interactions between incoming species and the film include adsorption, sputtering, fragmentation, and sub-plantation [36, 2, 35]. Depending on their respective sticking coefficient, incoming species may be incorporated into (high coefficient) or ejected from (low coefficient) the growing film. Closed-shell neutrals have low sticking coefficients ( $< 10^{-3}$ ), whereas ions and some radicals have high sticking coefficients approaching 1 due to their reactivity [36, 2, 35]. Evidence shows that the overall growth rates of a-C:H by PECVD exceed ion contribution, meaning that neutral and radicals both contribute to film growth. This is thought to occur by bonding to dangling bond sites which increases their sticking coefficient [36, 2, 35]. These dangling bond sites form at increased frequency when hydrogen is sputtered from C-H bonds at the surface by incoming ions. Atomic hydrogen present in the plasma may also abstract hydrogen in surface C-H bonds, causing it to desorb from the film [2]. The combined effect of forming dangling bonds and desorption of hydrogen from the film can be considered from an example of an incoming molecular ion  $(CH_3^+, etc.)$  that may fragment at the surface into carbon and atomic hydrogen. The atomic hydrogen can desorb hydrogen in surface C-H bonds, creating dangling bonds for incorporation of radicals into the growing film. The carbon atom may implant and dissipate remaining energy in sub-surface levels. Since hydrogen can only form one bond, it has a lower displacement energy than carbon [35]. This means the dissipation of energy from the sub-implanted carbon atom is more likely to displace hydrogen than carbon atoms, leading to a reduction in the hydrogen concentration in the film. Since the energy of the depositing ions scales proportionally with bias voltage, this translates to more energy dissipating by sub-implanted carbon atoms which explains the behaviour of hydrogen content decreasing as a function of increasing bias voltage.

### 2.3 Characterization Techniques

DLC films can be described structurally by their bonding ratio and the hydrogen content present (Figure 2.3). Characterization of the indentation hardness is desirable since DLC films are typically used for protective coatings in optics and tribology applications [1, 39]. Prominent characterization techniques include nuclear magnetic resonance (NMR), electron energy-loss spectroscopy (EELS), X-ray photoelectron spectroscopy (XPS), fourier-transform infrared spectroscopy (FTIR), spectroscopic ellipsometry, Raman spectroscopy, and elastic recoil detection analysis (ERDA). Nano-indentation and scratch testing are used to determine the indentation hardness and qualitative adhesion characteristics, respectively.

NMR has the unique capability to distinguish both the bonding ratio and the hydrogen content. Using proton decoupling has been shown to classify site-specific bonding ratios for a-C:H such as C-C and C-H sp<sup>2</sup> and sp<sup>3</sup> bonding fractions [40]. Unfortunately this technique requires tens of milligrams of material that is uniform and this is often impossible to obtain. EELS is highly capable of resolving the sp<sup>3</sup> and sp<sup>2</sup> bonding fractions however it is a destructive technique that typically requires focussed ion beam utilization to prepare samples in the thickness range of 10-20 nm [2]. FTIR is qualitative and is often used to estimate the hydrogen content of the films but has been shown to disagree with the more quantitative methods of NMR and ERDA [41, 42]. Accuracy of XPS, Raman, and spectroscopic ellipsometry rely heavily on the models used in data analysis for extraction of reliable information. Despite each technique having its own drawbacks, the relationship between structure and property of DLC is well understood, ensuring cross correlative studies can ascertain the hydrogen content and bonding ratios required for complete characterization.

## 2.3.1 Raman Spectroscopy as the Basis for Cross Correlative Studies of DLC

Raman spectroscopy is a vibrational spectroscopic technique that utilizes a monochromatic light source (laser) to excite certain vibrational modes (phonons) of the sample under test. The incident photons can be elastically (Rayleigh) or inelastically (Stokes and anti-Stokes) scattered by phonons, as shown in Figure 2.6. Certain phonons may induce a change to the electrical polarizability of molecules involved and these vibrational modes are *Raman active* and inelastically scatter light at wavelengths shifted to the incident photons [29]. Utilizing a detector that can distinguish between different wavelengths, a Raman spectrum can be produced that showcases the wavenumber (units of cm<sup>-1</sup>) corresponding to Raman active vibrational modes.



**Figure 2.6:** Raman spectroscopy schematic showing elastic (Rayleigh) and inelastic (Stokes and anti-Stokes) scattering of light by a vibrational mode of a molecule. Image taken from Dey [43].

Among characterization techniques used to investigate DLC, Raman spectroscopy is by far the most utilized in literature. The Raman spectrum of disordered carbon materials has been extensively investigated to describe the micro-structure and extended to allow prediction into the hydrogen content and mechanical properties for a-C:H [27, 26, 29]. An important consideration in the Raman spectroscopy of amorphous materials is that the disorder destroys the concept of a conventional unit cell, reciprocal space, phonons as plane waves, and more (see [44]). This may be explained considering that a phonon may be confined to a defect which, by the Heisenberg uncertainty principle, de-localizes the momentum, relaxing a selection rule that restricts the Raman scattering of incident light in crystalline materials to a small range in reciprocal space [29]. Relaxing this selection rule increases the range of reciprocal space that an incoming photon can excite, expanding to the entire Brillouin zone. This means that the inelastic scattering of photons by phonons in amorphous materials resembles the vibrational density of states of the crystalline material.

Although not an exhaustive list, work completed from Ferrari, Robertson, and Casiraghi on the analysis of the Raman spectrum of a-C:H can be used to derive several key parameters of interest [27, 26]. The 'D peak' corresponds with an  $A_{1g}$  symmetric breathing mode due to sixfold (graphitic) sp<sup>2</sup> ring configurations whereas the 'G peak' is associated with  $E_{2g}$  symmetric stretching motion of sp<sup>2</sup> bonds in rings or chains [26]. It should be noted that visible wavelength Raman spectroscopy is not directly sensitive to sp<sup>3</sup> modes since visible photons excite  $\pi$  states (sp<sup>2</sup>) at a rate of almost three orders of magnitude over the excitation of  $\sigma$  states (sp<sup>3</sup>). This can be overcome with the use of higher energy excitation (UV wavelengths) which can excite  $\sigma$  states. The main characteristics (peak positions, widths, and intensities) of the Raman spectra are therefore dictated by sp<sup>2</sup> bonds and their disorder [26, 27]. The key parameters of interest typically investigated are:

- 1. The G peak position, Pos(G).
- 2. The full-width at half-maximum of the G peak, FWHM(G).
- 3. The intensity ratio of the D and G peak,  $I_D / I_G$ .
- 4. The ratio between a linear background slope and  $I_G$ ,  $I_G / m$ .

The following interpretations of the Raman spectra are based on using visible wavelength excitation. Pos(G) was first proposed by Ferrari and Robertson on the basis that it relates to a *Three Stage Model* that explains the amorphization trajectory of carbon materials to infer the presence of sp<sup>3</sup> bonding as a function of Pos(G) [26]. Later it was found that a-C can exhibit  $sp^2$  clustering changes independent of  $sp^3$  bonding, thus incorporating non-uniqueness into the amorphization trajectory [27]. In a-C:H, this non-uniqueness still exists but the presence of hydrogen simplifies the trend and thus higher Pos(G) values are generally attributed to higher  $sp^2$ content films [27]. Assuming a reference material of disordered  $sp^2$  bonded carbon, distortions to bond lengths and angles are represented by changes in the density of the material. Casiraghi et al. concluded that the FWHM(G) probed this structural disorder since the G peak widened as  $sp^2$  clusters were distorted [27]. Since density can be strongly correlated to Young's modulus and thus indentation hardness, the FWHM(G) can be used to predict the hardness of a-C:H films. Evidence of this correlation was also shown by Casiraghi [27]. Since the D peak is directly linked to the presence of sixfold rings, the  $I_D / I_G$  is able to approximate the relative amount of graphitic bonding in a-C:H. A higher value of  $I_D / I_G$  has been shown to correlate to a higher  $sp^2$  content [27]. This parameter is also used to predict the bonding ratio, even though the intensity of the G peak does not represent the amount of  $sp^3$  bonding. Marchon et al. showed that the background slope divided by the intensity of the G Peak  $(I_G / m)$  showed a strong correlation to the hydrogen content of the film measured by ERDA [45]. The background slope corresponds to photo-luminescence, which increases with the saturation of dangling bonds by hydrogen since the nonradiative combination sites from dangling bonds are quenched [45]. This means that DLC films with high hydrogen content show a large background that may overwhelm (at  $\sim 50$  at.% hydrogen) the signal from the D and G peaks whereas those with low hydrogen content show very pronounced D and G peaks [27]. This was first extended by Casiraghi et al. to produce an empirical equation that estimates the hydrogen content from these two parameters when characterizing a-C:H from visible Raman spectra [27]:

$$H[at.\%] = 21.7 + 16.6 \log_{10} \left(\frac{m}{I_G}[\mu m]\right)$$
(2.3.1)

where  $\frac{m}{I_G}$  is converted to units of µm. The intimacy of the relationship between these parameters derived from the Raman spectra and connection to the structural and mechanical properties of DLC provides proof of Raman as a vital technique for cross correlative studies on amorphous carbons.

#### Multi-wavelength Raman Studies

A more recent review of the Raman spectra of carbon materials by Merlen et al. summarizes the existing body of knowledge in the field and reinforces the use of multiwavelength Raman studies [29]. Multi-wavelength studies allow for dispersion of peak-positions to be shown in amorphous carbon materials. This is not an observable phenomenon in crystalline materials [29]. These types of studies are most informative with the use of visible and UV excitation wavelengths [27, 29, 46, 47]. The use of visible and IR wavelengths has also been attempted for multi-wavelength studies [48]. The G-peak shows dispersion characteristics that are sensitive to the size of aromatic clusters [27, 29]. The description of a *double resonance mechanism* is also provided in the review that can be understood from consideration of fourth-order perturbation theory which describes the origin and dispersion of the D-peak [29]. Dispersion behaviour of either the D or G peak both provide additional information in the context of disordered carbons [29]. Correlation of the dispersion of the G-peak in a-C:H has been shown to better predict the bonding fraction rather than using  $I_D / I_G$  [27, 29, 46, 47].

## 2.3.2 X-ray Photoelectron Spectroscopy and Auger Spectroscopy

X-ray photoelectron spectroscopy utilizes the photoelectric effect to study the chemical composition of a sample under test. Conducted at high vacuums, a sample is irradiated with monochromatic x-rays which induces emission of photoelectrons from the surface of the sample. Core electrons have much higher probability to interact with the x-rays (higher cross section) and thus, XPS cannot directly distinguish hydrogen or helium atoms due to both light elements being composed of only valence electrons. Core electrons that absorb the high energy photons (x-rays) overcome their binding to the nucleus and become freed. Since the binding energies of electrons at different energy levels varies per element, the analysis of the leftover energy (kinetic energy) of the freed electrons allow chemical identification of the elements present in the sample. A schematic of the XPS mechanism is provided in Figure 2.7. Auger electron spectroscopy induced from x-rays (XAES) is a complementary technique. In auger emission, as the core electron is freed, energy emitted as an outer shell electron fills the core-hole is absorbed by another outer shell electron which overcomes its binding energy and may be detected at much lower kinetic energy. The auger process naming convention is distinguished by the energy levels (orbitals) that the core electron and the two outer shell electrons originate from. The auger process occurs at higher frequency in low-atomic number elements.



Figure 2.7: X-ray spectroscopy schematic illustrating the photoelectric effect, characteristic x-ray, and auger electron emission mechanisms. Image taken from Moller [49].

#### 2.3.3**Elastic Recoil Detection Analysis**

Elastic recoil detection analysis is an ion beam technique where an incident beam of particles at a shallow incident angle forward-scatters lighter elements from the sample under test. For a beam of He<sup>++</sup> ions, large momentum may be transferred to hydrogen, but not to heavier elements. The momentum transfer to hydrogen elastically scatters it in the forward direction and can be collected by a detector. The detector is commonly a PN junction, silicon detector covered in a thin ( $\sim 10 \ \mu m$ ) aluminum foil which preserves hydrogen reaching the detector but stops  $He^{++}$  ions. The atomic concentration of hydrogen can be obtained if data is calibrated based on a standard material that has a stoichiometric amount of hydrogen, such as Kapton. A schematic diagram of ERDA is shown in Figure 2.8.



**Figure 2.8:** Elastic recoil detection analysis schematic illustrating the incident beam, sample, and detector set up. Note that Rutherford backscattering (RBS) is a complimentary technique that was not utilized during this investigation. Image taken from Fager [50].

#### 2.3.4 Nano-indentation and Scratch Testing

Indentation uses an ultrahard material, such as diamond, shaped into a specific geometry with radius on the order of nanometers to micrometers, depending on the specimen's dimensions. A maximum applied load or maximum depth is specified, typically along with a loading rate and hold time. The indenter contacts the specimen and is loaded until the maximum load or depth condition is reached. Depending on the ductility of the specimen and indenter parameter selection, elastic deformation occurs before the onset of plastic deformation. This behaviour produces the archetypical load-unload curve. Assumption of a poisson ratio, with geometrical information obtained from the indenter tip allows for the method of Oliver and Pharr to be used to estimate the hardness and elastic modulus. The analysis technique of Oliver and Pharr is included alongside a typical load-unload curve in Figure 2.9.



Figure 2.9: Nano-indentation load-unload curve schematic alongside Oliver and Pharr analysis method and calculations.

Scratch testing methods are used to estimate the coefficient of friction, wear rate, and assess the quality of adhesion between film and substrate. Scratch testing employs a hard tip that is loaded while moving perpendicular to the loading direction, along a chosen distance on the surface of the specimen. With a fixed scratch length, a loading rate (units of force/time) or scan speed (units of length/time) can be specified. Different scratch modes include constant load, progressive load, and multipass, where the latter can be used to infer wear resistance information [51]. To estimate the adhesion strength, critical loads are assigned at instances where there is a pronounced visual difference in appearance of the scratch, increase to the measured friction force, or detected acoustic signal. The mechanisms of delamination and thus assignments of critical loading points may manifest in a variety of different ways such as cracking, spalling, buckling, fracturing, or complete failure of the film [52].

### 2.4 Theoretical Models

The following sections introduce a brief overview of background information relevant to the theoretical modelling that was applied during the investigation. These sections are not an exhaustive source nor adequate collection of background information on the subjects of molecular dynamics and density functional theory. The reader is urged to consult the popular Frenkel and Smit [53] for a guide to MD while the text by Thijssen [54] or review article by Jones [55] may assist with DFT fundamentals.

#### 2.4.1 Molecular Dynamics

Molecular dynamics has been used as a standard framework to investigate classical many-body systems for structural, dynamical, and thermodynamic properties for over 60 years [53, 56]. Statistical mechanics allows for microscopic states to confer macroscopic properties with utilization of the thermodynamic laws. Utilization of these principles in conjunction with reliance on Newton's equations of motion allow for numerical methods that control thermodynamic quantities (ensembles), enabling a model that can describe a classical system. Integration of Newton's equations of motion allow for classical systems to be described dynamically. Implementation of these equations in an efficient manner is achieved through the use of the Störmer-Verlet-Leapfrog method and enables systems of several million atoms to be modelled numerically [57]. This method chooses that velocity is evaluated at half-steps or a staggered grid  $v_{i+\frac{1}{2}}$  compared to evaluation of position  $r_{i+1}$  at regular intervals:

$$v_{i+\frac{1}{2}} = v_{i-\frac{1}{2}} + \Delta t \, a(r_i) \tag{2.4.1}$$

$$r_{i+1} = r_i + \Delta t \, v_{i+\frac{1}{2}} \tag{2.4.2}$$

This method is more efficient and numerically stable than the standard Verlet which integrates using two previous positions [57]. Use of Equation 2.4.1 and Equation 2.4.2 ensures the system evolves symmetrically and is time reversible [57]. After specification of initial boundary conditions, commonly obtained from the MD ensemble, the acceleration a(r(t)) is evaluated from the force, obtained from a conservative potential  $F(r(t)) = ma(r(t)) = -\nabla_{r_i}U(r(t))$  that is chosen to best describe the interactions of specific systems under investigation. The development of these force-fields is a primary subject of investigation in the field of molecular modelling to further increase the agreement between theory and experiment.

Ensembles are utilized to denote the relation between thermodynamic state variables (number of particles, energy, pressure, temperature, volume, chemical potential, etc.) and measured quantities of interest. These ensembles also prescribe how the numerical method applies boundary conditions to ensure the simulation remains at the correct temperature, pressure, or chemical potential. This is typically accomplished by using a reservoir that is connected to the simulation 'box' that is sufficiently large such that it allows exchange of temperature (heat bath), pressure (barostat), or particles [53]. Consequently, simulations can follow constant-NVE, constant-NVT, constant-NPT, or constant- $\mu$ VT ensembles [53]. Therefore, typical MD simulations follow protocol similar to [53]:

- i) The system is prepared by specifying particle number, position, density (through simulation box size), magnitude of time step for integration, initial temperature, and force-field.
- ii) Velocities are initialized, typically from a distribution dependent on the initial temperature.
- iii) Forces are computed, and a numerical method is used to integrate Newton's equations of motion.
- iv) Boundary conditions are enforced to ensure the simulation does not deviate from the ensemble's restrictions. This can be in the form of using a thermostat, barostat, or particle exchange.
  - (a) steps ii) to iv) are repeated for the duration of the simulation length (specified in number of time steps) to model the dynamics of the system adequately.
- v) Average measured quantities of interest are calculated following the thermodynamic variables of state specified by the ensemble in use.

The MD simulation of amorphous systems typically begins with the preparation of

the structure achieved with a liquid-quench protocol. Simulations start at temperatures above the melting temperature and cool rapidly to room temperature. This ensures that the system does not have time to relax into the lowest energy structure and that the final system is representative of a 'frozen-in' liquid structure, exemplifying a metastable amorphous solid [44]. For a-C and a-C:H systems, the structure can then be analyzed for the number of nearest neighbours within a certain cut-off distance for each particle. This provides and estimation into the coordination number and thus provides information relating to the  $sp^3$  to  $sp^2$  ratio. Investigations into the effect of the empirical force field, quench rate, hydrogen content, or starting density of the system on the bonding ratio are typically undertaken to comprehend what parameter set best matches experimental data |15, 58, 19, 59-62|. Alternative techniques to prepare a-C and a-C:H structures attempt to model the experimental deposition techniques by simulating impacting species from an ion beam [63, 60, 64-66. Although more complex to implement in simulation, this method does allow investigation of impinging ion energies which the resulting structures have been shown to provide excellent agreement to experimental results when appropriate force fields are used |66|.

#### 2.4.2 Density Functional Theory

The utility of density functional theory arises from its ability to determine physical and chemical properties by treatment of quantum many-body systems using an electric density,  $n(\mathbf{r})$  [67–69]. This is achieved by utilizing the Hohenberg-Kohn theorems that states [68]:

i) The energy of a many-body electron system is a functional of the electronic

charge density.

$$E[n(\mathbf{r})] = F[n(\mathbf{r})] + \int v^{ext}(\mathbf{r})n(\mathbf{r}) \, d\mathbf{r}$$
(2.4.3)

where  $F[n(\mathbf{r})]$  is a universal functional, meaning it is valid for any form of the external potential,  $v^{ext}(\mathbf{r})$ .

ii) The energy,  $E[n(\mathbf{r})]$ , follows the variational principle and has a minimum equal to the ground state energy if appropriate choice of  $n(\mathbf{r})$  is found.

Additionally,  $F[n(\mathbf{r})]$  contains terms corresponding to kinetic energy, exchange-correlation energy, and coulomb-interactions, denoted by  $T[n(\mathbf{r})]$ ,  $E_{xe}[n(\mathbf{r})]$ , and  $\iint \frac{n(\mathbf{r})n(\mathbf{r'})}{|\mathbf{r}-\mathbf{r'}|} d\mathbf{r} d\mathbf{r'}$ , respectively [67, 69]. These two key principles along with the formulation of the Kohn-Sham Hamiltonian allow the many-body electron problem to be reduced into requiring a tangible numerical method [69]. This method is achieved by selection of an initial  $n(\mathbf{r})$ , calculation of  $F[n(\mathbf{r})]$ , and then solving the Kohn-Sham Hamiltonian which produces Kohn-Sham wave-functions allowing for recalculation of  $n(\mathbf{r})$ . These steps are repeated, self consistently, until the changes in  $n(\mathbf{r})$  fall below a threshold [54]. For distinct systems of atoms, molecules, or solids to be investigated, the specification of the approximation to describe  $E_{xe}[n(\mathbf{r})]$  is required. Commonly used are the Local Density Approximation (LDA), Generalized Gradient Approximation (GGA), or hybrid functionals [55, 54].

Within the context of modelling DLC systems, DFT allows for the prediction of elastic constants and electronic properties as a function of structural parameters such as sp<sup>3</sup> or density [13, 19, 20, 70–72]. Investigation into the effects of dopant atoms on magnetism or diffusion have also been achieved [20, 72, 73]. The most common application of theoretical modelling for a-C systems is determination of how the sp<sup>3</sup>

fraction modifies the bulk and Young's moduli [16]. The goal of these simulations is to show increasing sp<sup>3</sup> fractions (and densities) lead to higher Young's modulus values as a-C systems trend towards diamond. A simplified method to achieve this can be realized through calculation of the bulk modulus through application of isotropic volume deformation [16]. If a Poisson's ratio ( $\nu$ ) is assumed for the a-C systems, the use of the isotropic solid assumption leads to [74]:

$$E[GPa] = 3K(1 - 2\nu) \tag{2.4.4}$$

Since diamond has the highest known bulk modulus ( $K \approx 443$  GPa) and Equation 2.4.4 shows that the Young's modulus (E) is directly proportional to the bulk modulus, a-C systems with higher sp<sup>3</sup> indeed show a monotonic increase of bulk and Young's moduli [16]. An additional crude assumption can be made to infer the indentation hardness of the system. Since DLC often exhibit characteristic values of the quotient between hardness and Young's modulus ( $\frac{H}{E}$ ) within the range 0.1 and 0.16 [2, 75], Equation 2.4.4 can be expanded to:

$$H[GPa] \approx \frac{H}{E} [3K(1-2\nu)] \tag{2.4.5}$$

Equation 2.4.5 produces the reasonable value of indentation hardness ( $\approx 100$  GPa) for diamond assuming K of 443 GPa,  $\nu$  of 0.08, and  $\frac{H}{E}$  of 0.09.

#### Scarcity of a-C:H DFT Exploration

It is peculiar to note that investigation of a-C:H systems is seldom completed solely within the framework of DFT. MD or ab-initio MD (AIMD) methods are more commonly found to probe the characteristics of a-C:H typically examined by proxy a-C systems [17, 62, 63, 58, 76, 77]. Although some parametric studies of different hydrogen content and densities were conducted [17, 20, 72], there is a distinct focus on ta-C:H rather than on an extended range of a-C:H.

## Chapter 3

## Methods

The process parameters that were used during deposition of DLC with the RF-PECVD chamber is described. Since the processes used to deposit the DLC are intellectual property of the industrial partner, Intlvac Thin Film Inc., the hydrocarbon gas and deposition pressures have been obfuscated. This should not distract from the goal of showing the connection between processing conditions and the structure-property relationship exhibited by the DLC. The methods utilized for the characterization techniques of nano-indentation, scratch testing, XPS, ERDA, and Raman spectroscopy are provided. The MD and DFT simulation framework that was utilized is detailed.

### 3.1 Experimental Methods

An industrial-sized RF-PECVD reactor was utilized to deposit DLC films. The investigation varied the bias voltage which was identified as the key processing parameter for DLC deposited by RF-PECVD (see Section 2.2). The details of the characterization techniques are provided. XPS and Raman provided information on the  $sp^3$  to  $sp^2$  ratio. Nano-indentation and scratch testing examined the mechanical hardness and adhesion of the coatings, respectively. ERDA allowed the quantitative study of hydrogen content.

#### 3.1.1 Sample preparation

Single-side polished (001) silicon (Si) wafers diced into squares with side lengths of  $\sim 25.4$  mm were used as substrates. Substrates coated with  $\sim 300$  nm of aluminum were used for adhesion studies. One Al-Si, one Si, and one Si sample that allowed stylus profilometry measurements (KLA Tencor P16+) were used per deposition. Substrates were cleaned with isopropyl alcohol prior to loading into the PECVD reactor. The PECVD reactor used to deposit the DLC films was an Intlvac Aegis system capable of controlling processing conditions including deposition temperature, vacuum pressure, deposition time, bias voltage, precursor gases, and usage of background gases [78]. The 500 mm diameter cathode was connected to a 13.56 MHz (RF), 1 kW power source and matching network. A turbo-molecular pump was used to reach a base pressure of  $1 \times 10^{-3}$  Pa ( $1 \times 10^{-5}$  torr). An argon plasma was initiated for 10 minutes with bias voltage of 250 V to clean residual surface contaminants on the substrates prior to DLC deposition. Two distinct hydrocarbon gases, herein referred to as A and B, were used to deposit two sets of a-C:H films while the self-bias was varied from 300 to 450 V. The pressure was also varied for each deposition. The deposition of each film took 60 minutes which corresponded to  $\sim 1 \ \mu m$  thickness. Table 3.1 shows the deposition parameters for these eight films. Note that these

films were the primary focus of this thesis with respect to full characterization.

Table 3.1: Deposition parameters for the main films investigated. \* note that the film here de-laminated upon venting the chamber on the Al-Si substrate. Correspondingly, there is no data corresponding to adhesion testing for B at 300 V.

Hydrocarbon Gas	$\begin{array}{c} \mathbf{Bias} \\ \mathbf{Voltage} \ [V] \end{array}$	Chamber Pressure	$\begin{array}{c} \mathbf{Thickness} \\ [\mu m] \end{array}$	
А	300	High	0.98	
	340	Medium	0.93	
	380	Medium	0.89	
	450	Low	0.73	
В	300*	$\mathrm{High}^*$	1.31*	
	340	Medium	1.02	
	380	Medium	1.12	
	450	Low	0.77	

Additional A-films were deposited on Si substrates over the course of the investigation and were studied exclusively using Raman spectroscopy. The deposition parameters used for these additional films are shown in Table 3.2.

Hydrocarbon Gas	$\begin{array}{c} \mathbf{Bias} \\ \mathbf{Voltage} \ [V] \end{array}$	Chamber Pressure	$\begin{array}{c} \mathbf{Thickness} \\ [\mu m] \end{array}$	
А	600*	Medium*	1.23*	
	600	Medium	1.22	
	530	Medium	1.18	
	450	Medium	0.96	
	450	Medium	1.07	

**Table 3.2:** Deposition parameters for additional A-films that were characterized with Raman spectroscopy exclusively. \* note that this film was characterized additionally by ERDA.

Films deposited from a different hydrocarbon gas, herein referred to as C, several years before the start of the investigation were investigated using Raman spectroscopy to expand the parameter space of DLC. The deposition parameters used for these additional films are shown in Table 3.3.

Hydrocarbon Gas	$\begin{array}{c} \mathbf{Bias} \\ \mathbf{Voltage} \ [V] \end{array}$	Chamber Pressure
$\mathbf{C}$	195	Medium
	195	Medium
	130	Medium
	130	Medium
	92	Medium
	90	Medium

**Table 3.3:** Deposition parameters for films deposited several years ago from distincthydrocarbon gas. Films were characterized with Raman spectroscopy exclusively.

### 3.1.2 Nano-indentation

Nano-indentation (Micro Materials Nano Test Platform 3) was conducted to determine the hardness and Young's modulus. A linear loading scheme was used with a maximum load of 1 mN, load rate of 2 mN/s, and hold-time of 2 s. These parameters were used to ensure penetration depths did not exceed 10% of the film thickness, following the ISO14577-4 general guideline to prevent substrate contribution [79]. A minimum of 10 data points were collected for each film, but up to four outliers for every 10 data points were discarded. Data analysis was completed using the methodology of Oliver and Pharr [80].

#### 3.1.3 Scratch testing

Adhesion (Anton Paar Revetest Scratch Tester) was studied by comparison of scratch tests for films in Table 3.1 with and without the aluminum interlayer. A progressive load from 0.5 N to 10 N was applied over a length of 5 mm with a speed of 4 mm/min (loading rate of 7.6 N/min). Two to three scratch tests were conducted on each sample. Critical loads and associated mechanisms of fracture were assigned based on ASTM Standard C1624-22 [52].

## 3.1.4 X-ray photoelectron spectroscopy and x-ray excited Auger spectroscopy

XPS data was obtained with Al K $\alpha$  (1456.6 eV) x-rays as the primary beam (Phi Quantera II Scanning XPS Microprobe). Survey data was collected with step size of 0.8 eV and pass energy of 224 eV. C1s, O1s, and C-KLL (C KVV) spectra were obtained with step sizes of 0.1 eV and pass energy of 26 eV. Where noted, surface contamination was eliminated using argon ion sputtering at 250 V for 300 s. C1s data was fit using the commercial software CasaXPS to determine the contributions from sp<sup>3</sup> and sp<sup>2</sup> bonding. The method outlined by Lascovich was used to analyze the C-KLL spectrum for an alternative method that determined sp<sup>2</sup> content and is described in Section 4.2 [81].

#### 3.1.5 Raman spectroscopy

Raman spectroscopy (Renishaw inVia confocal microscope) was conducted using 532 nm wavelength excitation using 25 mW power and data collection between 900 to

 $1900 \text{ cm}^{-1}$ . Each film was sampled at eight different locations which ensured statistical analysis. Different methods were tested with respect to data analysis techniques which are outlined in Section 4.1.

#### 3.1.6 Elastic recoil detection analysis

A 2.8 MeV, He<sup>++</sup> beam at 75° incidence was used while a silicon detector with an aluminum coated 12.6  $\mu$ m mylar range foil was placed at a 30° exit angle. Data was collected twice for each film where a dose of 1.5  $\mu$ C was used to ensure adequate ion collection. Kapton was utilized as a standard to correlate sample data to a known hydrogen concentration. The simulation software, SIMNRA, was used to model experimental data and determine the hydrogen concentration present in each film [82].

### 3.2 Theoretical Methods

A bridged approach was undertaken where MD simulations prepared amorphous structures and DFT was used to relax the structures and calculate the bulk-modulus. Similar types of combined studies have been attempted before but most use ab initio MD (AIMD) [77, 62, 76]. Since DFT is computationally expensive compared to MD, simulations were restricted to 128 particles. Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) was used for the MD steps whereas Vienna Ab initio Simulation Package (VASP) was used for the DFT studies [83, 84]. The approach taken for the theoretical method can be visualized in Figure 3.1.



Figure 3.1: Visualization of the combined MD-DFT approach taken for the simulation and analysis of a-C:H. Following Table 3.4, 5100 structures were simulated for MD while 151 structures were selected for DFT simulation.

The parameter space explored with MD simulation is shown in Table 3.4. Simulation box sizes were first calculated for pure a-C systems with densities ranging between 2.0 to 2.6  $g cm^{-3}$  with increments of 0.1  $g cm^{-3}$ . Hydrogen was added into the systems in increments of 6.25% (8 atoms), specifying a new parameter set. This occurred until the density of the system fell below the experimentally observed limit for a-C:H [2, 5]. The bounds for valid a-C:H simulations with respect to density were between 1.4 and 2.6  $g \, cm^{-3}$ .

**Table 3.4:** Parameter set utilized in the theoretical investigation of a-C and a-C:H structures. Shows relationship between the density and hydrogen content where each column shares the same simulation box volume calculated from a pure a-C system for 128 particles total.

${f a-C} {f system density} \ [gcm^{-3}]$	2.60	2.50	2.40	2.30	2.20	2.10	2.00	Number of H-Atoms
a-C:H system density $[gcm^{-3}]$	2.45	2.36	2.26	2.17	2.07	1.98	1.89	8
	2.30	2.21	2.13	2.04	1.95	1.86	1.77	16
	2.15	2.07	1.99	1.90	1.82	1.74	1.66	24
	2.00	1.93	1.85	1.77	1.70	1.62	1.54	32
	1.86	1.78	1.71	1.64	1.57	1.50	1.43	40
	1.71	1.64	1.58	1.51	1.44	1.38	1.31	48
	1.56	1.50	1.44	1.38	1.32	1.26	1.20	56
	1.41	1.35	1.30	1.25	1.19	1.14	1.08	64

Data analysis employed custom python programming where the packages NumPy, Matplotlib, OVITO, freud, Atomic Simulation Environment (ASE), SciPy, and LMfit were used [85–91]. Additional information can be found in Section 4.3 and appendices A and B.

#### 3.2.1 Molecular dynamics

Simulations were initialized at 6000 K to ensure a liquid state was reached. The charge implicit reactive force field (ci-ReaxFF) was used to model particle interactions [92]. After 5 ps of equilibration in the liquid state, a linear quench rate of

1000  $K ps^{-1}$  was used to reach 300 K to freeze-in an amorphous state. Finally, the system was held at 300 K for another 5 ps. The NVT ensemble was used throughout the simulations, thus the structure was not relaxed after it was quenched. 100 simulations, each corresponding to a unique *seed*, were repeated for each set of parameters in Table 3.4 to ensure a statistical treatment of the amorphous structures. This meant 5100 simulations were completed.

#### **3.2.2** Density functional theory

Three structures were chosen, for each unique parameter set out of 100 seeds, to be transferred to undergo DFT calculations. This totalled 153 structures. These three structures were selected on the basis that they exhibited the same number of  $sp^3$ bonds, within  $\pm 1$ , of the mean of the 100 seeds. The Perdew-Burke-Ernzerhof GGA functional was used as the exchange-correlation functional [93]. Structures were relaxed by moving atomic positions and changing the volume and shape of the structure. Small displacements ( $\pm 1$  to  $\pm 5\%$ ) to the relaxed structures were imposed to isotropically lengthen or shorten the structure volume to mimic application of hydrostatic strain. An energy-volume relationship was derived and the Birch-Murnaghan equation of state was used to obtain the bulk modulus for a given structure [94]. Figure 3.2 shows an example for three a-C MD structures for starting densities of 2.0, 2.3, and 2.6  $g\,cm^{-3}$ , and their associated relaxed DFT structure with colours visualizing the total number of first nearest neighbour bonds. Figure 3.3 shows the same information but for three a-C:H structures for densities of 1.7, 2.0, and 2.3  $q \, cm^{-3}$  where these structures correspond to those containing 48, 32, and 16 hydrogen atoms for the column of a-C that started with 2.6  $q \, cm^{-3}$  in Table 3.4.



**Figure 3.2:** Visualization of a-C MD and DFT structures and their respective number of first nearest neighbours for starting densities of 2.0, 2.3, and 2.6  $g \, cm^{-3}$ .



**Figure 3.3:** Visualization of a-C:H MD and DFT structures and their respective number of first nearest neighbours for starting densities of 1.7, 2.0, and 2.3  $g \, cm^{-3}$ . Note that these structures correspond to those with matching density in the column corresponding to a-C at 2.6  $g \, cm^{-3}$  but with 48, 32, and 16 hydrogen atoms in Table 3.4.

## Chapter 4

# Analysis

The design and implementation of python and bash scripts made to analyze raw data obtained from Raman spectroscopy, MD, and DFT simulations is first described. The details of an investigation into peak fitting XPS data using CasaXPS is also conveyed.

### 4.1 Raman Techniques

This section covers the python program used to obtain the key parameters of interest from the Raman spectra. Ba et al. performed a more intensive statistical approach for a similar investigation [95].

Raw data was truncated by restricting the wavenumber range to between 900 and  $1900 \text{ cm}^{-1}$ . This was replicated from the article by Marchon et al. during the original investigation between background slope of a-C:H and hydrogen content [45]. An investigation was carried out to determine the best method to use to fit the linear

background slope. This was completed because there was a possibility of fitting a linear slope that over- or underestimated the background slope. Four methods were investigated. Method A2 chose 40 datapoints at the start of the data (onwards from  $\sim 900 \ {\rm cm^{-1}}$ ) and 40 datapoints at the end of the data (backwards from  $\sim$ 1900  $\rm cm^{-1}$ ). Method B2 first identified the minimums to the left(right) of the D and G peak regions. Then 40 datapoints were chosen before(after) the left(right) minimum. Method C2 used the protocol employed by Casiraghi et al. and Ba et al. where the datapoints closest to 1050 and 1800  $\rm cm^{-1}$  were chosen [27, 95]. Finally, method D2 chose 30 datapoints centred on the left(right) minima before(after) the D and G peak region. After datapoints were specified, the Levenberg-Marquardt minimization algorithm was used from the LMfit package to fit a linear background. This linear background slope was the m parameter used in Equation 2.3.1 to estimate the hydrogen content. The linear background was then subtracted from the raw data and the background subtracted data was then fit with two gaussian profiles for the D and G peaks to obtain the positions, intensities, and FWHMs. This method was repeated for each datafile, for each film. Based on the parameter of interest, a coefficient of variance was obtained for each film. These coefficients of variances were then summed together to demonstrate which method (A2, B2, C2, D2) was most appropriate. Method A2 performed best for A and B films, while method B2 was best for C films. Figures 4.1 and 4.2 visualize the background subtraction and the D and G peak fitting for a single data file from B(450). It should be noted that the total variance between each method did not change dramatically and this investigation proved rather superfluous.



Figure 4.1: Linear background fitted with method A2 for the Raman spectrum data for a datafile from B(450). The slope of the linear background is a parameter of interest as it is used in Equation 2.3.1 to estimate the hydrogen content in DLC films.



Figure 4.2: D and G peaks fitted with gaussian profiles visualized on the linear background subtracted Raman spectrum data for a datafile from B(450). Method A2 was used for the linear background subtraction as shown in Figure 4.1.

To summarize, multiple Raman spectra (datafiles) were obtained at different locations on each DLC film. Data analysis yielded the parameters of interest described in Section 2.3.1, each with a corresponding uncertainty. This uncertainty corresponded to an average taken from the group of datafiles for a given sample. Each uncertainty was first taken from the numerical fitting error obtained from the LMfit covariance matrix. This error was then propagated to each parameter of interest using the method of quadrature.

### 4.2 XPS/XAES Techniques

Many articles describe approaches for peak fitting XPS core emission spectra [96–99]. Notable considerations include the method for charge correction of binding energies, use of appropriate background models, and use of correct lineshapes to model peaks. Charge correction by shifting the binding energies to the C1s spectrum peak position has been shown to be unreliable [100]. A rigorous charge correction method was not utilized since this was not necessary to obtain sp<sup>2</sup> and sp<sup>3</sup> bonding fractions. The background model chosen was a Shirley background since spectra showed an increase in intensity at higher binding energies after emission peaks, following assignment from Figure 9 b) of Engelhard et al. [101]. The lineshapes used to model the sp<sup>2</sup> and sp<sup>3</sup> differed. Since graphite shows asymmetric tails towards the higher binding energy side, sp<sup>2</sup> components are recommended to be fit with a lineshape that accounts for this behaviour [99, 98].

The  $sp^2$  and  $sp^3$  bonding fractions were obtained from the C1s spectrum of DLC films utilizing the following method. CasaXPS software was used where a Shirley

background was first used in the C1s region for a range of 8 eV. An asymmetric-Lorentzian (LA) lineshape was used to model the  $sp^3$  component with input parameters (1,1,800) which ensured the lineshape was a symmetric Voigt function (convolution of a Lorentzian with Gaussian) [98]. If argon cleaning was not used and oxygen was present in the survey spectrum of a sample, the same LA lineshape was used to account for carbon-oxygen bonds (C-O or C=O) at higher binding energies. A finite-Lorentzian (LF) lineshape with input parameters (0.85, 1.8, 50, 100) was used to model the  $sp^2$  component as this lineshape accounted for the asymmetry present in a reference sample of graphite that was investigated and shown in Figure 4.3. More information on the input parameters is provided in sections 3.3 and 3.4 of the article by Major et al. [98]. The  $sp^2$  component was first constrained by its position to be located 0.5 eV prior to the  $sp^3$  peak. The  $sp^2$  total area was initially constrained to be less than 40% of the total area since it was expected that the significant hydrogen content in these films would have promoted  $sp^3$  bonding over  $sp^2$ . The fit proceeded using a Levenberg-Marquardt algorithm. After the peaks were fit, the constraints were lifted from the  $sp^2$  component and fit again. If the residual standard deviation decreased after the constraints were lifted, the new fit was kept, if it increased, the fit was reverted. The binding energy was calibrated by shifting the fitted  $sp^2$  peak position to 284.5 eV which was the binding energy of the reference graphite sample C1s peak. The  $sp^2$  and  $sp^3$  bonding fractions were obtained by the area fraction percentage that each component contributed to the total fit. An example C1s core spectrum for A(340) before argon cleaning is shown in Figure 4.4.



**Figure 4.3:** XPS spectrum of graphite sample fit using the finite-lorenztian function available in CasaXPS. A Shirley background was used and no constraints were placed on the fit.


**Figure 4.4:** XPS spectrum of as-deposited A(340) fit with sp<sup>2</sup>, sp<sup>3</sup>, and C-O bonding peaks. Note that C-O was included to attempt to match the oxygen concentration present in the survey spectrum.

The C-KLL auger spectrum can be analyzed in carbon materials to obtain an estimation on the sp<sup>2</sup> bonding fraction as an alternative from the C1s method. Lascovich et al. showed that the derivative of the C-KLL spectral region showed a well defined maxima and minima where the distance (D parameter) between them widened with an increase of sp<sup>2</sup> bonding [81]. The D parameter of diamond (0% sp<sup>2</sup>) was found to be 13.2 eV whereas graphite (100% sp<sup>2</sup>) showed a value of 22.5 eV. These bounds allowed for interpolation and estimation of the sp<sup>2</sup> percentage. An example of this result for as-deposited (without argon sputter cleaning) A(340) film is shown in Figure 4.5. The derivative of the C-KLL spectra was obtained by first fitting a order 32 polynomial to the C-KLL spectrum between binding energies of 1245 to 1195 eV, then differentiating to obtain a smooth curve. D parameters were obtained for each film, but some difficulty was incurred (see Sections 5.1.3 and 6.2).



Figure 4.5: C-KLL spectrum data for as-deposited A(340) film shown with overlay of order 32 polynomial fit and derivative. The D-parameter is obtained by taking the difference between the maximum and minimum of the derivative. In this case a D parameter of 16.2 corresponds to a value of approximately 32% sp<sup>2</sup>.

### 4.3 Theoretical Techniques

Determination of the bonding fractions required implementation of a nearest neighbour analysis technique. Previous experience utilizing the Freud python package allowed for a program to be constructed that analyzed individual frames of MD simulations and counted the number of nearest neighbours for each particle [90]. This program could be employed to determine the time-average evolution of the bonding, but was primarily used to analyze the last simulation frame only. Given an input simulation, the Freud package was used to obtain a radial distribution function (RDF) corresponding to the configuration in the last timestep of a given simulation. The RDF was used to determine the cut-off distances necessary to query only the first nearest neighbours. An example RDF is shown in Figure 4.6 and in general, RDFs describe the probability of finding a neighbour particle within a certain distance away from any given particle in a system [53]. The methodology employed with Freud was transferred over to OVITO since OVITO allowed for easier implementation to differentiate between carbon-carbon (C-C) and carbon-hydrogen (C-H) bonding [88]. Namely, OVITO can produce *partial RDFs* which only probe certain pairs of particles differentiated by their type. In this case, C-C, C-H, and H-H RDFs could be produced to obtain the corresponding first nearest neighbour distances as is shown in Figure 4.7.



**Figure 4.6:** Example of a total RDF produced using OVITO analysis technique for a system matching starting density 2.6  $g \, cm^{-3}$  and 12.5 at% hydrogen concentration. The cutoff distances are also visualized for the analysis of individual C-C and C-H neighbours. RDF corresponded to a time average of the last 50 frames of the simulation, corresponding to the quenched a-C:H structure.



**Figure 4.7:** Example of partial RDFs produced using OVITO analysis technique for a system matching starting density 2.6  $g \, cm^{-3}$  and 12.5 at% hydrogen concentration. The cutoff distances are also visualized for the analysis of individual C-C and C-H neighbours. RDF corresponded to a time average of the last 50 frames of the simulation, corresponding to the quenched a-C:H structure.

A cut-off distance of 1.8 and 1.2 were used for C-C and C-H bonds, respectively. Specification of the cut-off distance enabled the systems to be queried for nearest neighbours where neighbours were found within a sphere of radius equal to the cut-off distance. A filter was applied to ensure only the bonds of interest were analyzed for nearest neighbour contribution, meaning that although C-H bonds existed in the 1.8 cutoff meant for C-C, those bonds were automatically filtered out by identification of the elements that constituted the bonds. This produced a list where for each particle, the number of C-C and *total* bonded neighbours could be specified by  $sp^2$  (three total neighbours) and  $sp^3$  (four total neighbours) bonds. Herein, total bonds refers to the sum of C-C and C-H bonds for a given particle. This program was agnostic to the file structure and thus was used to analyze the systems resulting from MD and DFT simulations. For a given MD dataset with 100 simulations, this program was used to calculate the bonding fractions of interest and produce a standard deviation which was used as the magnitude of the errorbars in Section 5.2.1 figures. Since the POSCAR file in DFT was representative of the final frame of MD simulations, the program was calculated the bonding fractions from POSCAR and CONTCAR files. This meant that for the datafiles translated to DFT simulation, the bonding fractions were averaged together across these three datafiles and MD results were shown from POSCAR results while DFT results were obtained using CONTCAR files. This is shown in Section 5.2.2 figures where there are no errorbars present since each datapoint corresponded to an average of only 3 datafile results.

## Chapter 5

# Results

Results provided in this chapter serve to illustrate those necessary for further discussion in Chapter 6. Tables and figures may refer to specific films by a naming convention: Hydrocarbon Gas(Bias Voltage). For example, the film deposited with hydrocarbon gas A at bias voltage 450 V would be A(450). When further distinction is necessary, other deposition parameters are included.

## 5.1 Experimental

Raman spectroscopy results are presented first followed by results from ERDA, XPS, nano-indentation and scratch tests.

### 5.1.1 Raman Spectroscopy

Figure 5.1 shows the results for the parameters of interest for the eight main films in Table 3.1 and the  $A(600^*)$  film from Table 3.2. Figures 5.2 and 5.3 show the

results for the parameters of interest for DLC deposited on Al coated Si for the main films in Table 3.1. Figure 5.4 shows the parameters of interest for films deposited from hydrocarbon A at the same pressure (black datapoints) and three datapoints at 450 V to show utilization of pressure as the key processing parameter. Figures 5.5 and 5.6 show replication of Figures 5 and 26 from Casiraghi et al. with the data from Tables 3.1 to 3.3, illustrating verification of the methods used for Raman spectra data analysis described in Section 4.1 [27].



**Figure 5.1:** Raman results corresponding to films in Table 3.1 and A(600) showing **a**)  $I_D / I_G$ , **b**) FWHM(G), **c**) hydrogen content, and **d**) Pos(G) trends as a function of bias voltage.



Figure 5.2: Raman results for comparison between DLC-Si and DLC-Al-Si films from hydrocarbon A showing a)  $I_D / I_G$ , b) FWHM(G), c) hydrogen content, and d) Pos(G) trends as a function of bias voltage.



Figure 5.3: Raman results for comparison between DLC-Si and DLC-Al-Si films from hydrocarbon B showing a)  $I_D / I_G$ , b) FWHM(G), c) hydrogen content, and d) Pos(G) trends as a function of bias voltage.



Figure 5.4: Shows differences in a)  $I_D / I_G$ , b) FWHM(G), c) hydrogen content, and d) Pos(G) parameters for a constant (black data) or changing (coloured data) pressure for illustration that bias voltage modified the properties of the films more than pressure.

Bias Voltage [V]



**Figure 5.5:** Verification of Raman spectroscopy method through replication of a literature article figure (Casiraghi Fig 5) [27].



**Figure 5.6:** Verification of Raman spectroscopy method through replication of a literature article figure (Casiraghi Fig 26) [27].

#### 5.1.2 ERDA

Figure 5.7 shows an example of the results obtained for ERDA where the software SIMNRA was used to model the DLC being composed of purely carbon and hydrogen. Quantitative estimates of the hydrogen content were possible after calibration of the model to data obtained from kapton tape ( $C_{22}H_{10}N_2O_5$ ) with the known hydrogen content of 25.64 at%. Small amounts of oxygen (<10 at%) was included in an alternative model, but it was shown not to impact the results and since there should only be oxygen due to surface contamination with atmosphere, this model was discarded. The similarities between using Oxygen to model the hydrogen content is shown in the last column of Table 5.1. Each datapoint in Table 5.1 represents an average between two datapoints taken on each sample with the exception of B(380) where only one datapoint was collected.



Figure 5.7: ERDA data visualized with SIMNRA software showing agreement of experimental data and model. Data corresponds to A(450).

Sample Description	Hydrogen Content [at.%] (Modelled with C,H)	Hydrogen Content [at.%] (Modelled with C,H,O)
A(600)	25.69	26.08
A(450)	29.32	29.72
A(380)	29.96	30.39
A(340)	31.38	31.94
A(300)	30.72	30.98
B(450)	29.12	28.75
$B(380)^{*}$	31.16*	30.66*
B(340)	29.29	28.80
B(300)	30.91	30.52

**Table 5.1:** Hydrogen content obtained from ERDA results after simulation with SIMNRA software and utilization of a model that included and excluded oxygen. \* only one datapoint was collected for B(380) sample.

#### 5.1.3 XPS XAES

Further details of the data analysis and investigations involved are described in Section 4.2. The amount of  $sp^2$  and  $sp^3$  bonds for each film obtained from analysis of the C1s spectrum, for data collection with argon cleaning, are shown in Table 5.2. The D-parameter and associated  $sp^2$  amount, calculated from the method of Lascovich [81], is presented in Table 5.2 where the reference of 100%  $sp^2$  was taken at a D parameter of 22.5 eV, 100%  $sp^3$  was taken at a value of 13.2 eV. The graphite sample and A(340) were used to compare the difference in C1s and C-KLL results before argon cleaning was used. The results are shown in Table 5.3. Comparisons between the C1s and C-KLL spectrum shapes for A(340) and the graphite reference sample are shown in Figures 5.8 to 5.11.

**Table 5.2:** XPS results showing  $sp^2$  and  $sp^3$  results from area percentage contributions of the C1s spectrum and  $sp^2$  also calculated from D parameter.

Sample Description	${{ m sp}^3} \ [\%] \ { m (C1s)}$	${{ m sp}^2}[\%] \ { m (C1s)}$	sp <sup>2</sup> [%] (C-KLL D parameter)
A(450)	71.4	28.6	90.3 (21.6)
A(380)	74.6	25.4	>100 (23.5)
A(340)	69.6	30.4	>100 (24.0)
A(300)	57.4	42.6	>100 (22.8)
B(450)	65.2	34.8	>100 (23.6)
B(380)	71.9	28.1	>100 (23.2)
B(340)	67.9	32.1	>100 (24.2)
B(300)	35.6	64.4	95.7(22.1)
Graphite	0	100	55.9(18.4)

**Table 5.3:** Oxygen is included in the DLC C1s fit since there was approximately 8 at.% showing in the survey spectrum whereas graphite showed less than 1 at.%.

Sample Description	${{ m sp}^3} \ [\%] \ ({ m C1s})$	${{ m sp}^2} \ [\%] \ ({ m C1s} \ )$	C-O [%] (C1s)	sp <sup>2</sup> [%] (C-KLL D parameter)
A(340)	57.9	36.1	6.0	32.3 (16.2)
Graphite	0	100	0	>100 (22.7)



**Figure 5.8:** XPS C1s spectrum comparing utilization of argon cleaning for A(340) sample. Note the small peak exhibited by the bump around 288 eV is typical for C-O or C=O bonds.



**Figure 5.9:** XPS C-KLL spectrum comparing utilization of argon cleaning for A(340) sample. Note the large shift in the width of the peak that significantly impacts the associated D parameter.



**Figure 5.10:** XPS C1s spectrum comparing utilization of argon cleaning for graphite sample. Note the widening introduced by using argon cleaning.



Figure 5.11: XPS C-KLL spectrum comparing utilization of argon cleaning for graphite sample. Note the similarities between the two spectra, in contrast to comparisons in Figure 5.9. The difference in D parameters in Table 5.2 and Table 5.3 is more subtle to identify but is caused by the changes in slope in the regions around 1235 and 1210 eV which produce shifts in the maxima and minima of the derivative spectra for calculation of the D parameter.

#### 5.1.4 Mechanical Properties

Nano-indentation results are tabulated in Table 5.4 following automatic analysis utilizing the Oliver and Pharr method with a Poisson's ratio of 0.3. The max depth of the indentation was normalized to the thickness of the samples to more clearly show agreement to the guide of indenting to less than 10% of the thickness of films see ISO-14577, [79]. Each datapoint corresponded to the average of a set of indentations on a given sample where the error was assigned by the standard deviation of the set of indentations. The Young's modulus was calculated assuming a indenter of diamond with Young's modulus 1141 GPa and poisson ratio of 0.07. A panoramic stitch of the scratch track is shown in Figure 5.12 for B(340) to exemplify the distinct cohesive and adhesive failures occurring on the DLC-Si and DLC-Al-Si systems investigated. The mean critical load values obtained from scratch testing DLC-Si and DLC-Al-Si are provided in Table 5.5 and Table 5.6, respectively. As is shown in Figure 5.12, it was difficult to determine the location of  $L_{c_1}$  on DLC-Al-Si systems due to their rather immediate fracture at a given load. Thus,  $L_{c_1}$  are taken as the initial load of 0.5 N for the DLC-Al-Si results in Table 5.6 as it was assumed that cohesive failure occurred on impact with the indenter.

Sample Description	Indentation Hardness [GPa]	Young's Modulus [GPa]	Max Indentation Depth [%] (normalized to thickness)
A(450)	$24.9 \pm 1.0$	$230.5 \pm 6.4$	$4.3 \pm 0.1$
A(380)	$21.4 \pm 1.9$	$211.6\pm9.0$	$4.8\pm0.1$
A(340)	$21.2 \pm 1.0$	$180.0\pm6.7$	$5.3\pm0.1$
A(300)	$18.6\pm1.8$	$170.5 \pm 7.3$	$6.8\pm0.3$
B(450)	$23.2 \pm 1.4$	$191.8 \pm 30.0$	$3.5\pm0.2$
B(380)	$21.7 \pm 1.6$	$179.3 \pm 14.1$	$4.6\pm0.1$
B(340)	$21.4 \pm 1.3$	$166.6\pm6.5$	$4.4\pm0.1$
B(300)	$15.4\pm0.9$	$133.3 \pm 5.2$	$7.4\pm0.2$

**Table 5.4:** Nano-indentation results obtained after analysis with the Oliver andPharr method.



Figure 5.12: Ending portion of panoramic stitch of the scratch tracks for DLC-Si and DLC-Al-Si samples from B(340). The green, orange, and red circles draw attention to where critical loads  $L_{c_1}, L_{c_2}$ , and  $L_{c_3}$  were assigned, respectively.

**Table 5.5:** Scratch test results for DLC-Si samples investigated. Results show that  $L_{c_1}$  typically occurs between 5 to 6 N whereas  $L_{c_3}$  is between 8 to 9 N. Note that assignment of  $L_{c_1}$  was particularly difficult since the resolution of the panoramic images did not allow for precise identification of the first location of cohesive failure.

Sample Description [DLC-Si]	$\mathbf{L}_{c_1} \; [\mathbf{N}]$	$\mathbf{L}_{c_2} \; [\mathbf{N}]$	$\mathbf{L}_{c_3} \; [\mathbf{N}]$
A(450)	5.87	7.36	8.50
A(380)	5.60	7.22	8.43
A(340)	5.56	7.41	9.03
A(300)	6.79	7.80	8.50
B(450)	5.88	6.60	8.6
B(380)	5.82	6.84	8.22
B(340)	5.70	6.59	7.66

**Table 5.6:** Scratch test results for DLC-Al-Si samples investigated. Much lower  $L_{c_2}$  and  $L_{c_3}$  values were obtained compared to results in Table 5.5 showing that the adhesion for DLC-Al-Si systems is not as strong as it is for DLC-Si systems.

Sample Description [DLC-Al-Si]	$\mathbf{L}_{c_1}$ [N]	$\mathbf{L}_{c_2} \; [\mathbf{N}]$	$\mathbf{L}_{c_3} \; [\mathbf{N}]$
A(450)	0.5	4.15	4.53
A(380)	0.5	3.39	3.71
A(340)	0.5	3.76	4.06
A(300)	0.5	2.83	3.31
B(450)	0.5	3.35	3.83
B(380)	0.5	1.68	3.08
B(340)	0.5	3.68	3.89

#### 5.1.5 Cross Correlations to Raman Results

Presented below are studies comparing the results obtained from Raman (Equation 2.3.1) spectroscopy to the other quantitative methods of ERDA, nano-indentation, and XPS. Overlaying the results from ERDA Table 5.1 onto Figure 5.1 (c), Figure 5.13 is produced, while Figure 5.14 produced an equation similar to Casiraghi's (Equation 2.3.1) to derive a hydrogen content relationship between the Raman parameter of interest and the ERDA results. The linear fit is produced:

$$H[at.\%] = 25.4 + 11.8 \log_{10} \left(\frac{m}{I_G}[\mu m]\right)$$
(5.1.1)



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Figure 5.13: Data from ERDA and Raman spectroscopy for estimation into the hydrogen content of A and B films. The qualitative trend produced by Raman is verified by ERDA. The Raman also correctly estimates the range of atomic percentage of hydrogen from ERDA.



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**Figure 5.14:** Data from ERDA plotted against  $\log(m/I_G)$  from Raman spectroscopy results. Linear fit produced  $H[at.\%] = 25.4 + 11.8 \log_{10} \left(\frac{m}{I_G}[\mu m]\right)$  while Casiraghi's Equation 2.3.1 is plotted for direct comparison.

Figure 5.15 shows the FWHM(G) parameter from Raman plotted against the nanoindentation results while Figure 5.16 produced an equation to model the hardness as a function of FWHM(G):

$$H_{IT}[GPa] = 1.0 * FWHM(G) - 166.4$$
 (5.1.2)



Figure 5.15: Data from nano-indentation and Raman spectroscopy for estimation into indentation hardness of A and B films. The qualitative trend produced by the FWHM(G) parameter from Raman is verified by nano-indentation. Results show that a higher FWHM(G) predicts characteristically harder films.



Figure 5.16: Nano-indentation hardness data plotted against Raman FWHM(G) parameter. Linear fit produced  $H_{IT}[GPa] = 1.0 * FWHM(G) - 166.4$  showing that the hardness evolves directly with the FWHM(G) parameter.

Finally, Figure 5.17 shows  $I_D / I_G$  plotted alongside the percent area of the sp<sup>2</sup> fitted peak from the C1s core spectrum of XPS.



**Figure 5.17:** Data from XPS and Raman spectroscopy for estimation into  $sp^2$  bonding character of A and B films. Note that the values  $I_D / I_G$  being close to 0.3 are not representative of  $sp^2$  fraction of 0.3. The qualitative trend produced by the  $I_D / I_G$  parameter from Raman is **not** verified by XPS results. Further discussion of results and additional considerations are provided in Section 6.1.

## 5.2 Theoretical

The methods and analysis used to obtain the following results were described in Section 3.2.2 and Section 4.3. MD results are presented first, then followed by DFT results where some figures show direct comparison to MD results. Some figures show relationships drawn against the bonding fractions of carbon, denoted by (C), while others utilize the total number of bonds, denoted by (tot). A *descriptor* was chosen as the quotient of hydrogen content and density with units  $\frac{at.\%}{g\,cm^{-3}}$ . The choice of this descriptor was spontaneous but was used to make the relationship to hydrogen content be more continuous rather than at discrete intervals of 6.25 at.%. Note that whenever both MD and DFT results are shown on the same figure with density as a variable, the density for MD results refer to that obtained after the MD simulation protocol, before relaxation with DFT methods. The density for DFT results refer to the value after the structural relaxation occurred in the DFT simulation protocol.

#### 5.2.1 Molecular Dynamics Results

Figures 5.18 and 5.19 show the variation in  $sp^2(C)$ ,  $sp^3(C)$ , and  $sp^3(tot)$ , respectively as a function of density. Figures 5.21 to 5.24 show the variation in  $sp^2(C)$ ,  $sp^3(C)$ ,  $sp^2(tot)$ , and  $sp^3(tot)$ , respectively as a function of hydrogen content. Figure 5.25 shows the the variation in the relative ratio of  $sp^3(tot)$  as a function of hydrogen content. Figures 5.26 and 5.27 show the variation in  $sp^2(C)$  and  $sp^3(C)$ , respectively as a function of the descriptor.



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**Figure 5.18:**  $sp^2(C)$  obtained from MD simulations shown as a function of density. The amount of  $sp^2(C)$  bonds saturate at high densities and for a-C structures simulated. There appears to be different slopes that can be distinguished with respect to a-C:H system  $sp^2(C)$  evolution with density which also terminate at different a-C system  $sp^2(C)$  values.



**Figure 5.19:**  $sp^{3}(C)$  obtained from MD simulations shown as a function of density. The amount of  $sp^{3}(C)$  bonding looks to increase exponentially at higher densities.



Figure 5.20:  $sp^{3}(tot)$  obtained from MD simulations shown as a function of density. An increase in the amount of  $sp^{3}(tot)$  bonding is insignificant until the highest density a-C:H system where there is a significant jump from by  $\sim 5\%$ .



**Figure 5.21:**  $sp^2(C)$  obtained from MD simulations shown as a function of hydrogen content. The trend shows that increasing the hydrogen in the system continues to decrease the number of C-C  $sp^2$  bonds.



**Figure 5.22:**  $sp^{3}(C)$  obtained from MD simulations shown as a function of hydrogen content. The trend shows that increasing the hydrogen in the system continues to lower the number of C-C  $sp^{3}$  bonds to almost 0 at a hydrogen content of 50 at.%.



**Figure 5.23:**  $sp^2(tot)$  obtained from MD simulations shown as a function of hydrogen content. The trend shows that increasing the hydrogen in the system continues to decrease the number of  $sp^2$  bonds. This correlates to the experimental understanding that hydrogen 'selectively sputters' graphitic bonds.



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**Figure 5.24:**  $sp^{3}(tot)$  obtained from MD simulations shown as a function of hydrogen content. The trend shows that increasing the hydrogen in the system first lowers the  $sp^{3}$  bonding but then saturates. The trend at high hydrogen concentration shows that  $sp^{3}(tot)$  saturates (not the same trend as Figure 5.22) and no longer decreases since enough hydrogen is present in the system to saturate the bonding to favour  $sp^{3}$  configuration.



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**Figure 5.25:**  $sp^{3}(tot)$  bonding ratio obtained from MD simulations shown as a function of hydrogen content. The trend at high hydrogen concentration shows that the bonding ratio trends upwards to favour  $sp^{3}$  configuration. This is observed in films similar to PLCH where a high hydrogen content but low density film corresponds to a structure composed of C-H  $sp^{3}$  bonds.


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**Figure 5.26:**  $sp^2(C)$  obtained from MD simulations as a function of the descriptor variable.  $sp^2(C)$  decreases with increasing values of the descriptor, representative of the trends in density and hydrogen content shown in Figures 5.18 and 5.21. There appears to be different slopes that can be distinguished that show relationship to similar systems that vary only by the starting density that was chosen.

Hydrogen Content / Density [at. % /g cm<sup>-3</sup>]



**Figure 5.27:**  $sp^{3}(C)$  obtained from MD simulations as a function of the descriptor variable.  $sp^{3}(C)$  decreases sharply with increasing values of the descriptor, representative of the trends in density and hydrogen content shown in Figures 5.19 and 5.22.

#### 5.2.2 Density Functional Theory Results

Figures 5.28 to 5.30 show the variation in  $sp^2(C)$ ,  $sp^3(C)$ , and  $sp^3(tot)$  respectively as a function of density. Exponential fits applied separately to the MD Equation 5.2.1 and DFT Equation 5.2.2 data for  $sp^3(C)[\%]$  as a function of density ( $\rho$ ) in Figure 5.29 produced:

$$sp^{3}(C)[\%] = 0.060 * 10.6^{\rho}$$
 (5.2.1)

$$\operatorname{sp}^{3}(C)[\%] = 0.013 * 15.4^{\rho}$$
 (5.2.2)

Figures 5.31 to 5.34 show the variation in  $sp^2(C)$ ,  $sp^3(C)$ ,  $sp^2(tot)$ , and  $sp^3(tot)$ , respectively as a function of hydrogen content. Figure 5.35 shows the variation in

the relative ratio of  $sp^3(tot)$  as a function of hydrogen content. Figures 5.36 and 5.37 show the variation in bulk modulus as a function of density and  $sp^3(C)$ , respectively. The value of H/E used in Equation 2.4.5 for Figure 5.36 to obtain the estimated hardness was 0.11 and was chosen based on the average of results in Table 5.4. A linear fit applied to the data in Figure 5.36 produced:

$$K[GPa] = 126\rho - 124 \tag{5.2.3}$$

$$H[GPa] \approx \frac{H}{E}[3(126\rho - 124)(1 - 2\nu)]$$
 (5.2.4)

Finally, Figures 5.38 to 5.40 show the variation in  $sp^2(C)$ ,  $sp^3(C)$ , and bulk modulus as a function of the descriptor, respectively.





**Figure 5.28:**  $sp^2(C)$  obtained from MD and DFT simulations shown as a function of density. The DFT results show some 'correction' taking place especially for the a-C systems where the structures relaxed with DFT are decreasing their  $sp^2(C)$  bonds in favour of  $sp^3(C)$  compared to those simulated with MD. This is explained by the ReaxFF force-field overestimating the preference of  $sp^2(C)$  bonding and thus utilizing DFT has altered these structures to be more representative of a physical structure. Note that simulations below 1.4  $g \, cm^{-3}$  are not representative of DLC systems.



Figure 5.29: sp<sup>3</sup>(C) obtained from MD and DFT simulations shown as a function of density. The DFT results show some 'correction' taking place where the structures relaxed with DFT have higher sp<sup>3</sup>(C) content than those simulated with MD. This is explained by the ReaxFF force-field significantly underestimating sp<sup>3</sup>(C) bonding and thus utilizing DFT has altered these structures to be more representative of a physical structure. Note that simulations below 1.4  $g \, cm^{-3}$  are not representative of DLC systems. Fitting the DFT data with an exponential function yielded: sp<sup>3</sup>(C)[at.%] = 0.060 \* 10.6<sup> $\rho$ </sup> where density is  $\rho$  in units of  $g \, cm^{-3}$ . Similarly, the MD data fit provided: sp<sup>3</sup>(C)[at.%] = 0.013 \* 15.4<sup> $\rho$ </sup>.



**Figure 5.30:**  $sp^3(tot)$  obtained from MD and DFT simulations shown as a function of density. Note that simulations below 1.4  $g \, cm^{-3}$  are not representative of DLC systems.



**Figure 5.31:**  $sp^2(C)$  obtained from MD and DFT simulations shown as a function of hydrogen content. The trend shows that increasing the hydrogen in the system continues to decrease the number of C-C  $sp^2$  bonds.





**Figure 5.32:**  $sp^3(C)$  obtained from MD and DFT simulations shown as a function of hydrogen content. The trend shows that increasing the hydrogen in the system continues to lower the number of C-C  $sp^3$  bonds to almost 0 at a hydrogen content of 50 at.%.



**Figure 5.33:**  $sp^2(tot)$  obtained from MD and DFT simulations shown as a function of hydrogen content. The trend shows that increasing the hydrogen in the system continues to decrease the number of  $sp^2$  bonds. This correlates to the experimental understanding that hydrogen 'selectively sputters' graphitic bonds.



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**Figure 5.34:**  $sp^{3}(tot)$  obtained from MD and DFT simulations shown as a function of hydrogen content. The trend at high hydrogen concentration shows that  $sp^{3}(tot)$  saturates and no longer decreases since enough hydrogen is present in the system to saturate the bonding to favour  $sp^{3}$  configuration.



**Figure 5.35:**  $sp^{3}(tot)$  bonding ratio obtained from MD and DFT simulations shown as a function of hydrogen content. The trend at high hydrogen concentration shows that the bonding ratio trends upwards to favour  $sp^{3}$  configuration. This is observed in films similar to PLCH where a high hydrogen content but low density film corresponds to a structure composed of C-H  $sp^{3}$  bonds.



Figure 5.36: Bulk modulus and estimated hardness obtained from DFT simulations as a function of density. A linear trend is observed and the key result highlights that estimated hardness values are comparable to those obtained experimentally with nano-indentation Table 5.4. Note that simulations below 1.4  $g \, cm^{-3}$  are not representative of DLC systems. The value of H/E used in Equation 2.4.5 to obtain the estimated hardness was 0.11 and was chosen based on the average of results in Table 5.4. Fitted with a linear function produced:  $K[GPa] = 126\rho - 124$  where density is  $\rho$  in units of  $g \, cm^{-3}$ .



**Figure 5.37:** Bulk modulus obtained from DFT simulations as a function of  $sp^3(C)$ . The trend closely follows that shown in Figure 5.29 since the bulk modulus varies linearly with density as shown in Figure 5.36.



**Figure 5.38:**  $sp^2(C)$  obtained from DFT and MD simulations as a function of the descriptor variable.  $sp^2(C)$  decreases with increasing values of the descriptor, representative of the trends in density and hydrogen content shown in Figures 5.28 and 5.31



**Figure 5.39:**  $sp^{3}(C)$  obtained from DFT and MD simulations as a function of the descriptor variable.  $sp^{3}(C)$  sharply decreases with increasing values of the descriptor, similar in trend to Figure 5.29.



**Figure 5.40:** Bulk modulus obtained from DFT simulations as a function of the descriptor variable. The bulk modulus decreases with increasing values of the descriptor, similar in trend to Figure 5.38.

## Chapter 6

# Discussion

Results presented in Chapter 5 are discussed where ERDA and nano-indentation agree well with the trends observed from the key parameters obtained from Raman spectroscopy. The reliability of XPS for characterization of sp<sup>2</sup> and sp<sup>3</sup> fractions for a-C:H is noted. Adhesion results are explained with connection to utilization of DLC-Si in thin film processes. MD results are discussed in the context of the effectiveness of the ReaxFF potential to model a-C:H systems. DFT results show improvements in describing a-C:H systems. Improvements or alternatives to the methods used in this investigation are mentioned alongside each section of discussion.

### 6.1 Raman Spectroscopy

Figures 5.5 and 5.6 show that the qualitative trends demonstrated by Casiraghi et al. in Figures 5 and 26 are reproduced closely by the films examined in this investigation for key parameters obtained from the Raman spectra [27]. This result reinforces

the data analysis techniques for the Raman spectra detailed in Section 4.1 and supports the interpretation of the key parameters for insights into hydrogen content, bonding fraction, and indentation hardness in following discussions. The C films investigated in Table 3.3 show characteristics of PLCH including low Pos(G) (<1520) cm<sup>-1</sup>), low FWHM(G) (<165 cm<sup>-1</sup>), and low  $I_D / I_G$  (<0.3) with high hydrogen content approaching  $\sim 40$  at.%. From Robertson's definition, if this combination of key parameters matches PLCH films, then the films in Table 3.3 have indentation hardness lower than 10 GPa, large optical band gaps of up to 4 eV, and mainly C-H sp<sup>3</sup> bonding with bonding fraction approaching 70% [2]. Figure 5.1 shows that  $I_D \,/\, I_G$  is rather insensitive to detect changes in the sp<sup>2</sup> bonding ratios for the main eight films investigated in Table 3.1. This result suggests that these films have very similar  $sp^2$  bonding fractions, even though their FWHM(G), Pos(G), and hydrogen content are different in Figure 5.1. Inclusion of A(600) in Figure 5.1 shows that at a bias voltage of 600 V, the FWHM(G) decreasing with a noticeable increase in  $I_D / I_G$ is characteristic of DLC deposited by PECVD after the critical ion energy is reached (see Section 2.1.2). The A(600) film in this case is assumed to correspond to be progressing towards the GLCH definition and may have a higher  $sp^2$  fraction than  $sp^3$  with a corresponding decrease in hardness denoted by the low FWHM(G).

Figures 5.2 and 5.3 show comparison between DLC-Si and DLC-Al-Si systems which were investigated for adhesion properties in Section 6.4. Similar hydrogen content is observed but a noticeably lower FWHM(G) and higher Pos(G) is observed for DLC-Al-Si compared to DLC-Si systems. A lower FWHM(G) in this case is representative of softer films. This could be indicative of the results in Tables 5.5 and 5.6 where the DLC-Si systems with higher FWHM(G) were shown to have much greater adhesion strength than DLC-Al-Si systems with lower FWHM(G).

Figure 5.4 shows an investigation into pressure as the key processing parameter for A(450) films. The A(450) film deposited at the lowest pressure shows higher FWHM(G) with the lowest  $I_D / I_G$  and Pos(G). The A(450) film deposited at the highest pressure shows the inverse trend in key parameters and approach the key parameter values for the A(530) film. These results show that when utilized as the key processing parameter, a lower pressure leads to higher energy incoming ions responsible for film growth via an increased inelastic mean free path and this densifies the film leading to harder, more C-C sp<sup>3</sup> characteristics. Figure 5.4 also more easily shows the trend of an increase in bias voltage past 450 V leading to a decrease in FWHM(G) and increase to  $I_D / I_G$ , characteristic of surpassing the critical ion energy and developing films with GLCH quality at 530 and 600 V.

### 6.2 XPS and XAES

Table 5.2 shows sp<sup>2</sup> and sp<sup>3</sup> bonding fractions obtained from C1s and C-KLL analysis of argon cleaned samples. The D parameters of all films exceeded 22.5 which is the reference value commonly used as 100% sp<sup>2</sup> bonding [102–105, 81]. The graphite D parameter was significantly less than the DLC films, indicating that it was composed of less sp<sup>2</sup> bonds than the films. These results are not interpretable. Table 5.3 showed C1s and C-KLL results before argon ion bombardment was used to determine if the cleaning method contributed to the unusual D parameter values. The results from Table 5.3 are more consistent between C1s and C-KLL methods and show that argon ion bombardment has a significant impact on XPS spectra. This effect

is seldom reported in literature but the effect of ion bombardment on the C-KLL spectrum of graphite samples is discussed by Morgan [106]. Usually, higher energy argon ions are used to clean samples and there are no cited changes in the C1s or C-KLL spectra [107, 102, 103]. Calliara described the differences in auger and core electron emission for a-C and a-C:H films [108]. Although agreement between C1s and C-KLL methods is common for a-C systems, Calliara attributed the disagreement observed between C1s and C-KLL results for a-C:H samples originating from the complexity of hydrogen interactions with the disordered carbon micro-structure [108]. The presence of oxygen is known to decrease the width of the C-KLL peak, lowering the D parameter [108]. Although the results in Table 5.3 show better agreement, the decrease in D parameter from results in Table 5.2 is most likely due to the presence of oxygen from surface contamination in the as-deposited film. Cleaning the graphite sample both significantly widened the C1s spectrum in Figure 5.10 and lowered the D parameter in Figure 5.11, both effects which are not typically observed [106, 108]. Since there was surface contamination on A(340) ( $\approx 6$  at.% oxygen), it becomes increasingly difficult to determine if the results in Table 5.3 are characteristic of the film or of adsorbed atmospheric species since the inelastic mean free path of C-KLL electrons is 6 to 9 Å [109]. The difference in information depths of C1s and C-KLL spectra is occasionally used in literature to describe differences in results [108]. The inability to establish the behaviour of the bonding fractions was compounded by the high C1s sp<sup>2</sup> fractions from Table 5.2 at bias voltages of 300 V that are not expected since these films are the most hydrogenated and should primary consist of sp<sup>3</sup> C-H bonding. The lack of consistency between C-KLL and C1s results in addition to disagreement to other characterization results show that the XPS results reported in Tables 5.2 and 5.3 are invalid. The a-C:H type DLC investigated here is not well suited to be studied using XPS and XAES methods for sp<sup>2</sup> and sp<sup>3</sup> bonding fractions due to the simultaneous complexity of hydrogen and disorder that are still not well understood with respect to the core and auger emission electrons. Other techniques such as EELS, NMR, or a multiwavelength Raman spectroscopy study should be used to confidently ascertain the bonding fractions present in a-C:H films[27, 29, 46].

### 6.3 Nano-indentation

Table 5.4 shows that higher bias voltage corresponded to harder films for the main films investigated in in Table 3.1. The films deposited at 450 V have hardnesses approaching 25 GPa, one fourth the indentation hardness of diamond. Overall improvements to the investigation of the mechanical properties of DLC films can be achieved through the use of alternative nano-indentation procedures. Through application of combined linear loading and cyclic loading, the depth dependence of hardness and Young's modulus can be obtained. This is exceedingly important since hard-on-soft systems (for example DLC on Si) show distinct regions where the hardness can be identified to be representative of the film (at low depths), then show influence of the substrate (at depths  $\geq 10\%$  thickness of coating), and finally transition to the hardness of the substrate (at depths exceeding the film thickness) [51]. Additionally, the Young's modulus values obtained in Table 5.4 are not representative of the true Young's modulus since the elastic stress field is known to extend considerably far past the indentation depth and is usually influenced by the substrate at all depths of indentation [51]. Further improvements to the accuracy of the Young's modulus can be obtained if it is plotted against depth and linearly extrapolated backwards to a depth of 0 [51].

### 6.4 Adhesion

Adhesion was studied qualitatively using scratch tests where the critical loads  $L_{c_1}$ ,  $L_{c_2}$ , and  $L_{c_3}$  were assigned to describe initial crack formation, initial delamination (either inside or outside the track), and full delamination of the film, respectively [52, 110]. Scratch testing has been shown to be very sensitive to film thickness, roughness, hardness, friction coefficient, and internal stresses [111]. Since DLC thickness changed between processes (see Section 3.1), comparisons are made only between DLC deposited on Si or Al-Si with the same DLC process and not between different DLC processes. In addition to the difficulty in locating the  $L_{c_1}$  on DLC-Al-Si systems (see Section 5.1.4),  $L_{c_1}$  was difficult to assign on DLC-Si systems due to the contrast and resolution of the panoramic photos taken of the scratch tracks. This meant precise identification of  $L_{c_1}$ , in general, was not possible and therefore the onset of cohesive failure cannot not be accurately described. Comparisons of  $L_{c_2}$  and  $L_{c_3}$ can be made clearly between DLC-Si and DLC-Al-Si systems. The DLC-Si systems reliably exhibited adhesive failure at  $L_{c_2}$  values more than twice of the DLC-Al-Si systems. The same trend is shown in comparison of  $L_{c_3}$  values. This behaviour can be attributed to the strong bonding exhibited between DLC-Si interfaces. The proposed mechanism responsible for this is Si forming tetrahedral covalent bonds to the carbon in DLC and forming DLC-Si complexes consisting of amorphous SiC. This is in juxtaposition to the poor bond formation expected between aluminum (metallic bonds) and DLC (covalent bonds). In practice, DLC-Si interlayers are commonly

deposited first on substrates using either tetramethylsilane (TMS) or hexamethyldisiloxane (HMDSO) [112–115]. This interface layer ensures adhesion is achieved to the substrate and is proceeded by subsequent DLC deposition where the targeted properties can be achieved. In the context of the scratch testing results of this investigation, the results reinforce the use of DLC-Si for stronger adhesion than the use of DLC-Al-Si. Additionally, the surface energy differences between aluminum and silicon could provide an alternative explanation [116, 117]. High energy surfaces allow for improved wetting. Since silicon has a higher surface energy than aluminum, this could translate into enhancing the growth of DLC as molecular species may have a lower energy barrier to overcome and adsorb onto a silicon surface rather than on aluminum. Further investigation of adhesion characteristics could be achieved through identification of interlayers that reduce residual stresses present in DLC films since it is usually high stress that causes DLC to delaminate and limit the thickness of coatings. This could be examined on the basis of utilizing different interlayers or graded processes to obtain near stress-free films that remain mechanical hard which could then be tested with the scratch testing procedures used in this investigation to show if adhesion can be improved.

#### 6.5 Cross Correlations

Figure 5.13 shows ERDA results for hydrogen content compared against predictions made by Raman results using Equation 2.3.1 plotted as a function of bias voltage. Importantly, the hydrogen content estimation from the Raman results reproduced the same range of hydrogen content across all films investigated with ERDA. Figure 5.13 also shows agreement to the trend discussed in Section 2.2 and Figure 2.5 that an increases to bias voltage, decreases hydrogen content in a-C:H films [2, 27, 30, 46]. The closeness in hydrogen content over the range of bias voltage investigated for two distinct hydrocarbon precursors may suggest a similar dissociation mechanism occurred in the plasma during deposition. Fitting the ERDA results to the Raman parameter  $\log m/I_G$  in Figure 5.14 produced Equation 5.1.1 which shows a larger slope compared to Casiraghi's empirical equation (Equation 2.3.1) and more closely follows the empirical equation derived by Pardanaud [118].

Figure 5.15 shows a higher bias voltage corresponded to higher FWHM(G) and harder films within the range investigated. These results agree with the description given by Casiraghi et al., where the FWHM(G) provides prediction into topological disorder and allows estimation of the density and thereby mechanical properties of a-C:H films [27, 30, 46]. This can be explained with reference to the growth mechanism described in Section 2.1.2 and trends in properties for a-C:H described in Section 2.2. Films deposited by low bias voltage have higher hydrogen content, making softer films. Increasing the bias voltage increases the energy of incoming ions and decreases the hydrogen content (shown in Figure 5.13) while promoting C-C  $sp^3$  bonds, densifying the films. For the films investigated in Figure 5.15, there is no decrease to the FWHM(G) or hardness and thus the critical ion energy threshold was not expected to have been exceeded. Evidence of exceeding the critical ion energy is shown in Figure 5.4 where further increasing the bias voltage to 530 or 600 V for films deposited by hydrocarbon A decreases the FWHM(G). These films are expected to exhibit promotion of  $sp^2$  over  $sp^3$  bonding and lead to GLCH films that are softer. This could be verified by using nano-indentation on the 530 and 600 V films. Alternatively, since the relationships in Figure 5.16 and Equation 5.1.2 describes the evolution of nano-indentation hardness as a function of FWHM(G), the determination of this critical bias voltage could be determined by optimization of the FWHM(G) for films deposited by A or B precursors. This should be achieved to ensure a-C:H films can be engineered for a given application with confidence of their mechanical properties.

Figure 5.17 shows comparison of the  $I_D / I_G$  to the XPS results from Table 5.2. Discussion of the XPS results has been detailed in Section 6.2 and comparison to the Raman results do not help to show verification of either method for the bonding fractions for the main films investigated in Table 3.1. The trends explained in Section 2.2 show that increasing the bias voltage should correlate to an increase in  $sp^2$ bonding fraction in the films. The  $I_D / I_G$  results in Figure 5.17 do not show this, and instead suggest very similar  $sp^2$  contents. The author proposes the following competing mechanism to provide an approximate idea on how the  $I_D / I_G$  are practically the same but the films show different hydrogen contents and indentation hardnesses. An increase in bias voltage and a decrease in pressure was followed for the deposition of the main eight films investigated (see Table 3.1). Both increasing the bias voltage and decreasing the pressure leads to increasing the ion energy, leading to promotion of C-C  $sp^3$  bonds and denser films. This is reinforced by FWHM(G) variation while at constant voltage and varying pressure and vice versa in Figure 5.4. The hydrogen content in the films is a function of bias voltage and does not change for variations in pressure (see Figure 5.4). Hydrogen selectively etches  $sp^2$  bonds, thus a larger hydrogen content should be representative of lower sp<sup>2</sup> films [2, 1]. Increasing the bias voltage should promote  $sp^2$  bonds at a constant rate, but increasing the bias voltage while decreasing the pressure promotes  $sp^3$  C-C bonds at a faster rate than sp<sup>2</sup> bonds. Thus, following the deposition conditions of Table 3.1 and results shown in Figure 5.1, the trend exhibited by the main eight films show an increase in sp<sup>3</sup> C-C bonds evolving from sp<sup>3</sup> C-H bonds while the hydrogen content decreases and the sp<sup>2</sup> bonding remains approximately unchanged. This is reinforced by increased FWHM(G) and nano-indentation while the hydrogen content decreased and the  $I_D / I_G$  remained roughly the same. This proposed mechanism could be verified if the optical gap of the films was obtained by spectrophotometry. Agreement to the proposed mechanism would be obtained if each film exhibited similar optical gaps, since this translates to the same sp<sup>2</sup> content [2].

### 6.6 Molecular Dynamics

Figure 5.18 shows a-C:H structures increasing in  $sp^2(C)$  bonding fraction with an increase in density. Saturation of  $sp^2(C)$  appears to occur at ~80% for a-C systems. Figure 5.18 shows that a-C:H systems can be grouped into the different columns shown in Table 3.4 by their respective slopes shown in the figure. For example, systems starting with a-C at a density of 2.6  $g \, cm^{-3}$  (last column of Table 3.4), appear to be grouped into datapoints on the far right of Figure 5.18 in a line. The trend in Figure 5.19 shows that a-C:H systems start with almost 0% sp<sup>3</sup>(C) bonding at the lowest densities before sp<sup>3</sup>(C) bonding increases exponentially at densities higher than 2.0  $g \, cm^{-3}$ . Figure 5.20 does not show significant trend in relationship to the total sp<sup>3</sup> bonds for a-C:H systems except for the highest density a-C:H system simulated where it appears there is an onset of increase to sp<sup>3</sup>(tot) with increasing density above 2.4  $g \, cm^{-3}$ . Results presented in Figures 5.18 and 5.19 for a-C systems are shown to agree to simulations reported in literature with the ReaxFF potential in LAMMPS over similar density ranges [59, 14, 15]. Tomas et al. and Liu et al. presented a comparison of different interatomic potentials for the simulation of a-C and showed that ReaxFF significantly over estimates the presence of  $sp^2(C)$ across densities from 2.0 to 3.2  $g cm^{-3}$  [15, 59]. Investigations using an alternative interaction potential for MD simulation of a-C:H have been completed by Titantah et al. and Fraunheim et al. [62, 77]. The sp<sup>3</sup> fractions simulated by these authors is assumed to represent sp<sup>3</sup>(tot) as no distinction is made to explicitly count C-C bonds. The sp<sup>3</sup>(tot) results in Figure 5.20 are significantly lower than those presented by Titantah and Fraunheim over the entire density range investigated by either author. This is attributed to the difference in interaction potentials.

Figures 5.21 and 5.22 show a significant decrease in C-C bonds as the systems become saturated with hydrogen. At  $\geq 40$  at.% hydrogen, the systems have less than 30% bonds from sp<sup>2</sup>(C) whereas sp<sup>3</sup>(C) is approximately 0. More interesting trends are observed when the total bonding configurations are probed in Figures 5.23 to 5.25. The decrease in sp<sup>2</sup>(tot) still occurs in Figure 5.23 and this is indicative of the experimentally observed trend that the presence of hydrogen selectively etches graphitic bonds, see Section 2.2 and Figure 2.5) [3]. Figure 5.25 shows the sp<sup>3</sup>(tot) bonding relative the sum of sp<sup>2</sup>(tot) and sp<sup>3</sup>(tot) contributions. The trend shows evidence that sp<sup>3</sup> bonding begins to be promoted over sp<sup>2</sup> for a-C:H at very high hydrogen content. This matches very well with description of PLCH films which are low density films with hydrogen contents in excess of 40 at.% and high sp<sup>3</sup> contents in the range of 70% [27]. Although the sp<sup>3</sup> fraction does not nearly reach 70%, this can be explained through the conclusion presented prior that the ReaxFF significantly overestimates sp<sup>2</sup> contribution. Finally, Figures 5.26 and 5.27 show the use of the descriptor variable (see Section 5.2) to model variations in  $sp^2(C)$  and  $sp^3(C)$  bonding, respectively. The use of the descriptor was an attempt to translate the discrete values of hydrogen content investigated into more continuous datapoints by division of the system density. Although more continuous than results presented prior, one can still identify different groupings of systems based on the amount of hydrogen content in the a-C:H systems in Figures 5.26 and 5.27. For example, these groupings cluster with similar slopes where the first cluster after a-C in Figure 5.26 corresponds to a-C:H systems with 6.25 at% hydrogen content. At descriptor values above 15, the clustering begins to become less evident and a more continuous trend is observed in Figure 5.26. The trends in Figures 5.26 and 5.27 are similar to those in Figures 5.21 and 5.22 which suggest that the influence of hydrogen is too significant on the descriptor. Alternative descriptors might allow for new trends to be shown but the author is unsure how these might be employed.

For a-C systems, Tomas et al. and Liu et al. showed that other parametrizations of the ReaxFF force field also suffer from overestimating the sp<sup>2</sup> content [15, 59]. Better agreement to experiment for strictly MD approaches for a-C systems was obtained by Marks et al. and Sha et al. who used the environment-dependent interaction potential (EDIP) and modified Tersoff, respectively [66, 58]. Marks did not utilize liquid quenching procedures and instead simulated the energy dependence of incoming ions by utilizing MD protocols that model ion beams [66]. Sha et al. also showed that the modified Tersoff had excellent agreement to DFT and experimental DLC films with 30 at.% hydrogen content [58]. The main limitation of the work completed by Sha is that the system size is 64 atoms and simulation with the modified Tersoff utilized combined Monte Carlo and MD methods which were computationally expensive [58]. Overall, results from this investigation and the literature show that utilization of ReaxFF parametrizations do not model a-C nor a-C:H systems that are representative of experimental DLC since the sp<sup>2</sup> content is significantly overestimated.

#### 6.7 Density Functional Theory

Figures 5.28 and 5.29 show comparisons of the  $sp^2(C)$  and  $sp^3(C)$  bonding fraction as a function of density for the DFT and MD structures. Note that when figures show density for DFT and MD systems, the DFT densities are those obtained after structural relaxation of the simulation cell occurred which is shown by a new density range for the same simulations conducted in MD. Notably, Figure 5.28 shows that the DFT relaxation starts to decrease the densities of the systems for the low  $sp^2(C)$ structures. At higher densities,  $sp^2(C)$  begins to saturate for a-C:H at  $\sim 70\%$  and starts to decrease for a-C systems. This is showing 'corrective' behaviour to ReaxFF simulated systems where the preference for  $sp^2$  is being superseded by inclusion of the consideration of quantum mechanics, pushing these systems to more experimentally observable structures. This correction is more easily observed in Figure 5.29 where for a given density, the DFT relaxed a-C and a-C:H systems show an increase in  $sp^{3}(C)$  over the same systems simulated with MD. The exponential fit applied to Figure 5.29 DFT data in Equation 5.2.2 approximates a density of 3.14  $g \, cm^{-3}$  would be required for 100% sp<sup>3</sup> structure (diamond) whereas the fit applied to the MD data in Equation 5.2.1 estimates a density of 3.27  $g\,cm^{-3}$  for 100% sp<sup>3</sup>. Although both of these underestimate the density of diamond at 3.5  $g \, cm^{-3}$ , Equation 5.2.1 may be interpreted to provide the trajectory of sp<sup>3</sup> bonds as a function of density for the ReaxFF potential used in this investigation. Comparing results from Figure 5.30 shows the most agreement for sp<sup>3</sup>(tot) bonding fractions in a-C and a-C:H systems at densities  $\leq 2.0 \ g \ cm^{-3}$  [119, 71, 120]. Comparison against the majority of literature articles shows that the systems in this investigation are bias towards low sp<sup>3</sup> contents due to the influence of the starting structure from MD simulation with ReaxFF [119, 71, 19, 13, 120, 72, 76]. Under-counting of sp<sup>3</sup> bonds could be due to the cut-off distance chosen at 1.8 (see Section 4.3) whereas literature uses values of 1.85 to 1.9 but this does not impact the bonding fractions reported by more than 1% [32, 119, 71, 19, 13]. Although not excluded from following figures, it should be noted that some a-C:H systems show densities below 1.4  $g \ cm^{-3}$ . These systems should not be considered to be representative of DLC systems (see Section 3.2).

The trends in Figures 5.31 to 5.34 for DFT structures follow closely the trends for the MD structures and thus support the same conclusions made in Section 6.6. There is a pronounced increase in the sp<sup>3</sup> bonding in DFT structures compared to MD as discussed above. Figure 5.35 reinforces the conclusion that was made for MD structures with respect to high hydrogen content structures showing a pronounced increase in sp<sup>3</sup> while sp<sup>2</sup> decreases, mimicking the archetype of PLCH films.

The key result of the theoretical investigation is shown in Figure 5.36 where the bulk modulus is shown to correlate linearly with the DFT structure density. Utilization of an empirical approximation for hardness that is directly proportional to bulk modulus has been used (see Equation 2.4.5). The linear trend in Figure 5.36 given by Equation 5.2.3 and combined with Equation 2.4.5 allowed for an equation to be derived that related estimated hardness to the density of the amorphous carbon system investigated through Equation 5.2.4. Although these systems might not be representative of experimental systems because of the overestimation of  $sp^2$  bonding from the use of ReaxFF, the DFT systems show agreement to an increase in density corresponding to increased mechanical properties, a trend well known in theoretical and experimental studies of a-C and a-C:H [32, 27, 121, 19, 72, 2]. An additional equation may be derived that eliminates density between Equation 5.2.3 and Equation 5.2.2 and instead models the bulk modulus as a function of the  $sp^3(C)$  bonding fraction:

$$K[GPa] = 126[log_{10.6}\left(\frac{100}{6}\operatorname{sp}^{3}(C)[\%]\right) - 124$$
(6.7.1)

Unfortunately, Equation 6.7.1 incorrectly estimates that the diamond structure (100% sp<sup>3</sup>(C) bonds) should have a bulk modulus of 272 GPa instead of the experimental value of 443 GPa. Nevertheless, the method of derivation for Equation 6.7.1 may be useful to extend to existing literature results that show a closer relationship between experiment and theory for amorphous carbon systems. Figure 5.36 provides the important utility of being able to estimate the densities of the films experimentally investigated through connection between the hardness obtained in Section 5.1.4 and those plotted in Figure 5.36. For A(300) and B(300), Figure 5.36 shows a reasonable density might be ~2.0  $g \, cm^{-3}$  whereas A(450) or B(450) appear to lie at densities ~2.5  $g \, cm^{-3}$ . Note these assumptions do not account for matching the hydrogen content in the DFT structures and the experimental films. The results plotted in Figure 5.37 do not agree with literature where it has been shown that mechanical properties also show linear dependence on sp<sup>3</sup>(C) [27, 19, 2].

Figures 5.38 and 5.39 show the same trends in Figures 5.31 and 5.32 with the same clustering of points in groups as discussed for the use of the descriptor in MD simulations. Figure 5.40 shows that the descriptor is roughly inversely proportional to the bulk modulus for the DFT systems. Overall, the descriptor is not shown to greatly improve the continuity of the datapoints or elucidate a hidden trend with respect to describing the bonding fractions and bulk modulus as a function of normalized hydrogen content to density. Next steps, alternative methods, and further improvements are now discussed. The key result of showing bulk modulus variation with density should be compared from the DFT results to results obtained strictly with MD. This could be achieved if, for example, the particle count was increased to  $\gtrsim 10000$  and one system per parameter set in Table 3.4 was simulated instead of 100. Ab-initio MD could be used to show the differences for a-C and a-C:H systems prepared with liquid quench methods from first principles. Afterwards these structures could be relaxed similarly with DFT and compared against the MD-DFT approach. Implementation of AIMD is limited by the computational power required, but the prevalence of machine-learned potentials to speed up AIMD simulations with increasingly large system sizes and simulation time has been demonstrated to be especially useful for amorphous carbon systems [18, 32, 119, 17]. Simulating larger systems from first principles allows calculation of the vibrational density of states which can extend to calculate the Raman spectrum. More traditional DFT methods could also be employed to calculate the electronic structure of the systems simulated here which would be especially useful for comparison to trends with optical band gaps and  $sp^2$  content [70].

Altogether, the method attempted in this investigation to bridge MD and DFT was

somewhat effective. The bias introduced through preparation of amorphous systems with a MD force field that favours  $sp^2$  bonds was still prevalent in structures relaxed with DFT. The quantum mechanical descriptions of the systems in DFT induced corrective action during the relaxation and show  $sp^3$  promotion over  $sp^2$  as would be experimentally observed. Most importantly, the bulk moduli of the systems were shown to correlate linearly with system density and showed agreement between the mechanical properties of simulated systems to those experimentally characterized with nano-indentation.

# Chapter 7

# Conclusions

Hydrogenated amorphous carbon (a-C:H) thin films were deposited using a radiofrequency (RF) plasma enhanced chemical vapour deposition (PECVD) system provided by the industrial partner, Intlvac Thin Film. The bias voltage was varied as the key processing parameter for investigation of two sets of four films, where each set was deposited from a unique hydrocarbon precursor gas. Characterization of the films utilized Raman spectroscopy, elastic recoil detection analysis (ERDA), nanoindentation, scratch testing, and x-ray photo-electron spectroscopy (XPS). ERDA showed that the films investigated had hydrogen contents ranging from 25 to 30 at.% and that increasing bias voltage decreased hydrogen content. Nano-indentation revealed hardness ranging from 15 GPa to 24 GPa, where higher bias voltages corresponded to harder films. Scratch tests showed qualitative evidence that the adhesion between a-C:H and silicon is much stronger than adhesion of a-C:H to aluminum. XPS results that probed the sp<sup>2</sup> and sp<sup>3</sup> bonding in the films proved to be ineffective. This was attributed to the complexity of interactions between the significant amount

of hydrogen present and the disordered, amorphous structure of the a-C:H films. Results from Raman spectroscopy were cross correlated to ERDA for hydrogen content, and nano-indentation for hardness predictions. The predictions showed excellent agreement to quantitative results and reproduced the same trends as a function of bias voltage. The sp<sup>2</sup> bonding fractions as indicated by Raman did not change appreciably between the eight main films investigated. An outlook on these experimental results revealed two important points of discussion. First, although deposited from distinct hydrocarbon gases, the similarity in the hydrogen content, nano-indentation hardness, and bonding fractions between the two sets of films across the bias voltage range investigated signified that similar dissociation of molecular species may have occurred in the PECVD chamber and led to the presence of the same ions responsible for film growth. Second, the approximately static  $sp^2$  bonding fraction evolution estimated from Raman spectroscopy results as a function of bias voltage was not expected and somewhat contrasted results reported in literature where the  $sp^2$  content is shown to continually increase as a function of bias voltage. Since the hydrogen content decreased while the hardness increased as a function of increasing bias voltage, the structures of the films must have changed and it was proposed that instead of  $sp^2$  promotion, the carbon-hydrogen  $sp^3$  bonds present were converted into carbon-carbon sp<sup>3</sup> bonds. This provided a phenomenological mechanism that showed agreement to the decrease in hydrogen with increasing hardness and accounted for the unchanged  $sp^2$  content. Theoretical studies of a-C:H were completed utilizing frameworks of molecular dynamics (MD) and density functional theory (DFT). MD allowed preparation of amorphous carbon (a-C) and a-C:H structures which were investigated for determination of the effect of density and hydrogen content on the  $\rm{sp}^2$  and  $\rm{sp}^3$  bonding fractions. DFT was used to incorporate quantum mechanical interactions on a subset of systems obtained from MD simulations and allowed for the amorphous structures to be relaxed to a minimum energy state. Application of isotropic strain to the relaxed DFT structures permitted calculation of the bulk modulus which was then correlated to the hydrogen content, density, and bonding fractions. The isotropic solid assumption coupled with an empirical approximation that related indentation hardness and young's modulus was used to approximate the theoretical system's nano-indentation hardness. This calculation showed a subset of films investigated with theoretical methods overlapped with the experimental results for nano-indentation hardness values. These overlapping systems were related back to the DFT system density and allowed for the conjecture that the experimental film densities are between 2.0 and 2.6  $g \, cm^{-3}$ .

Experimental results showed proof that the fundamental material science connection between processing conditions and structure-property relationships were exemplified by a-C:H thin films deposited by RF-PECVD. Furthermore, a bridged approach that utilized MD and DFT simulations verified one aspect of experimental results and provided further information about the a-C:H systems that was not characterized experimentally. The work completed within this investigation should serve as an understanding for how a-C:H deposition processes may be tailored and allow for the precise engineering of thin films which exhibit desirable properties for a variety of applications.
### Bibliography

- L. Martinu, O. Zabeida, and J. Klemberg-Sapieha, "Plasma-enhanced chemical vapor deposition of functional coatings," in *Handbook of Deposition Technolo*gies for Films and Coatings. Elsevier Inc., 2010, ch. 9, pp. 392–465.
- [2] J. Robertson, "Diamond-like amorphous carbon," Mater Sci Eng , R, vol. 37, 2002.
- [3] L. Martinu, J. E. Klemberg-Sapieha, O. M. Küttel, A. Raveh, and M. R. Wertheimer, "Critical ion energy and ion flux in the growth of films by plasmaenhanced chemical-vapor deposition," *J Vac Sci Technol A*, vol. 12, no. 4, pp. 1360–1364, Jul. 1994.
- [4] P. Koidl, C. Wild, B. Dischler, J. Wagner, and M. Ramsteiner, "Plasma deposition, properties and structure of amorphous hydrogenated carbon films," *Mater Sci Forum*, vol. 52–53, pp. 41–70, Jan. 1991.
- [5] N. Ohtake, M. Hiratsuka, K. Kanda, H. Akasaka, M. Tsujioka, K. Hirakuri, A. Hirata, T. Ohana, H. Inaba, M. Kano, and H. Saitoh, "Properties and classification of diamond-like carbon films," *Materials*, vol. 14, no. 2, p. 315, Jan. 2021.

- [6] J. Sánchez-López and A. Fernández, "Doping and alloying effects on dlc coatings," in *Tribology of Diamond-Like Carbon Films:Fundamentals and Applications.* Springer, 2008, pp. 311–338.
- [7] I. Alaefour, S. Shahgaldi, J. Zhao, and X. Li, "Synthesis and ex-situ characterizations of diamond-like carbon coatings for metallic bipolar plates in pem fuel cells," *Int J Hydrogen Energ*, vol. 46, no. 19, pp. 11059–11070, Mar. 2021.
- [8] P. Yi, D. Zhang, D. Qiu, L. Peng, and X. Lai, "Carbon-based coatings for metallic bipolar plates used in proton exchange membrane fuel cells," Int J Hydrogen Energ, vol. 44, no. 13, pp. 6813–6843, Mar. 2019.
- [9] H. Dong, S. He, X. Wang, C. Zhang, and D. Sun, "Study on conductivity and corrosion resistance of n-doped and cr/n co-doped dlc films on bipolar plates for pemfc," *Diam Relat Mater*, vol. 110, p. 108156, Dec. 2020.
- [10] J.-I. Kim, J.-K. Kim, and Y.-J. Jang, "Stress relaxation through thermal gradient structure of tetrahedral amorphous carbon thin film deposited on ge-se-sbbased chalcogenide glass," *Diam Relat Mater*, vol. 100, p. 107547, Dec. 2019.
- [11] J. H. Lee, H. Kim, W. H. Lee, M. C. Kwon, and Y. G. Choi, "Surface modification of chalcogenide glass for diamond-like-carbon coating," *Appl Surf Sci*, vol. 478, pp. 802–805, Jun. 2019.
- [12] W. Kijaszek, A. Wiatrowski, M. Mazur, D. Wojcieszak, R. Paszkiewicz, and J. Kováč, "Study on properties of diamond-like carbon films deposited by rf icp pecvd method for micro- and optoelectronic applications," *Mater Sci Eng* , B, vol. 296, p. 116691, Oct. 2023.

- [13] N. A. Marks, N. C. Cooper, D. R. McKenzie, D. G. McCulloch, P. Bath, and S. P. Russo, "Comparison of density-functional, tight-binding, and empirical methods for the simulation of amorphous carbon," *Phys Rev B*, vol. 65, no. 7, p. 075411, Jan. 2002.
- [14] L. Li, M. Xu, W. Song, A. Ovcharenko, G. Zhang, and D. Jia, "The effect of empirical potential functions on modeling of amorphous carbon using molecular dynamics method," *Appl Surf Sci*, vol. 286, pp. 287–297, Dec. 2013.
- [15] C. de Tomas, I. Suarez-Martinez, and N. A. Marks, "Graphitization of amorphous carbons: A comparative study of interatomic potentials," *Carbon*, vol. 109, pp. 681–693, Nov. 2016.
- [16] T. Laurila, S. Sainio, and M. A. Caro, "Hybrid carbon based nanomaterials for electrochemical detection of biomolecules," *Prog Mater Sci*, vol. 88, pp. 499–594, Jul. 2017.
- [17] V. L. Deringer, M. A. Caro, R. Jana, A. Aarva, S. R. Elliott, T. Laurila, G. Csányi, and L. Pastewka, "Computational surface chemistry of tetrahedral amorphous carbon by combining machine learning and density functional theory," *Chem Mater*, vol. 30, no. 21, pp. 7438–7445, Sep. 2018.
- [18] M. A. Caro, V. L. Deringer, J. Koskinen, T. Laurila, and G. Csányi, "Growth mechanism and origin of high sp3 content in tetrahedral amorphous carbon," *Phys Rev Lett*, vol. 120, no. 16, p. 166101, Apr. 2018.
- [19] R. Jana, D. Savio, V. L. Deringer, and L. Pastewka, "Structural and elastic

properties of amorphous carbon from simulated quenching at low rates," *Model Simul Mater Sc*, vol. 27, no. 8, p. 085009, Oct. 2019.

- [20] H. Park, D. Woo, J. M. Lee, S. J. Park, S. Lee, H. J. Kim, E. Yoon, and G.-D. Lee, "First principles investigation on energetics, structure, and mechanical properties of amorphous carbon films doped with b, n, and cl," *Sci Rep*, vol. 9, no. 1, Dec. 2019.
- [21] A. W. Zia, S. A. Hussain, and M. M. F. A. Baig, "Optimizing diamond-like carbon coatings - from experimental era to artificial intelligence," *Ceram Int*, vol. 48, no. 24, pp. 36 000–36 011, Dec. 2022.
- [22] K. Vikram, K. Kalita, and R. K. Ghadai, "Multi-attribute optimization of diamond-like carbon thin films," in *AIP Conference Proceedings*. AIP Publishing, 11 2020.
- [23] C. Sauer, B. Rothammer, N. Pottin, M. Bartz, B. Schleich, and S. Wartzack, "Design of amorphous carbon coatings using gaussian processes and advanced data visualization," *Lubricants*, vol. 10, no. 2, p. 22, Feb. 2022.
- [24] L. Pauling, "The nature of the chemical bond. application of results obtained from the quantum mechanics and from a theory of paramagnetic susceptibility to the structure of molecules," *JACS*, vol. 53, no. 4, pp. 1367–1400, Apr. 1931.
- [25] S. Nasir, M. Hussein, Z. Zainal, and N. Yusof, "Carbon-based nanomaterials/allotropes: A glimpse of their synthesis, properties and some applications," *Materials*, vol. 11, no. 2, p. 295, Feb. 2018.

- [26] A. Ferrari and J. Robertson, "Interpretation of raman spectra of disordered and amorphous carbon," *Phys Rev B*, 11 1999.
- [27] C. Casiraghi, A. C. Ferrari, and J. Robertson, "Raman spectroscopy of hydrogenated amorphous carbons," *Phys Rev B*, vol. 72, no. 8, p. 085401, Aug. 2005.
- [28] J. Robertson, "Amorphous carbon," Adv Phys, vol. 35, no. 4, pp. 317–374, Jan. 1986.
- [29] A. Merlen, J. Buijnsters, and C. Pardanaud, "A guide to and review of the use of multiwavelength raman spectroscopy for characterizing defective aromatic carbon solids: from graphene to amorphous carbons," *Coatings*, vol. 7, no. 10, p. 153, Sep. 2017.
- [30] M. A. Tamor and W. C. Vassell, "Raman "fingerprinting" of amorphous carbon films," J Appl Phys, vol. 76, no. 6, pp. 3823–3830, Sep. 1994.
- [31] Y. Lifshitz, ', S. Kasi, and J. Rabalais, "Subplantation model for film growth from hyperthermal species," *Phys Rev B*, 1990.
- [32] M. A. Caro, G. Csányi, T. Laurila, and V. L. Deringer, "Machine learning driven simulated deposition of carbon films: From low-density to diamondlike amorphous carbon," *Phys Rev B*, vol. 102, no. 17, p. 174201, Nov. 2020.
- [33] K. Carduner, M. Rokosz, W. Tamor, and Vassell, "Solid state nmr study of carbon bonding in amorphous hydrogenated carbon films," *Appl Magn Reson*, 1991.

- [34] P. Reinke, W. Jacob, and W. Möller, "Influence of the ion energy on the growth and structure of thin hydrocarbon films," *J Appl Phys*, vol. 74, no. 2, pp. 1354– 1361, Jul. 1993.
- [35] D. P. Manage, "Structural and optical characterization of hydrogenated amorphous carbon thin films," Ph.D. dissertation, University of Toronto, 1998.
- [36] M. A. Lieberman and A. J. Lichtenberg, Principles of Plasma Discharges and Materials Processing. Wiley Interscience, 2005.
- [37] J. W. Zou, K. Schmidt, K. Reichelt, and B. Dischler, "The properties of a-c:h films deposited by plasma decomposition of c2h2," *J Appl Phys*, vol. 67, no. 1, pp. 487–494, Jan. 1990.
- [38] T. Schwarz-Selinger, A. von Keudell, and W. Jacob, "Plasma chemical vapor deposition of hydrocarbon films: The influence of hydrocarbon source gas on the film properties," *J Appl Phys*, vol. 86, no. 7, pp. 3988–3996, Oct. 1999.
- [39] Y. Lu, S. Wang, G. Huang, L. Xi, G. Qin, M. Zhu, and H. Chu, "Fabrication and applications of the optical diamond-like carbon films: a review," *J Mater Sci*, vol. 57, no. 6, pp. 3971–3992, Jan. 2022.
- [40] K. Carduner, M. Rokosz, W. Tamor, and Vassell, "Solid state nmr study of carbon bonding in amorphous hydrogenated carbon films," *Appl Magn Reson*, 1991.
- [41] C. Donnet, J. Fontaine, F. Lefèbvre, A. Grill, V. Patel, and C. Jahnes, "Solid state c13 and h1 nuclear magnetic resonance investigations of hydrogenated amorphous carbon," *J Appl Phys*, vol. 85, no. 6, pp. 3264–3270, Mar. 1999.

- [42] A. Grill and V. Patel, "Characterization of diamondlike carbon by infrared spectroscopy?" Appl Phys Lett, vol. 60, no. 17, pp. 2089–2091, Apr. 1992.
- [43] T. Dey, "Microplastic pollutant detection by surface enhanced raman spectroscopy (sers): a mini-review," Nanotechnology for Environmental Engineering, vol. 8, no. 1, pp. 41–48, Feb. 2022.
- [44] S. R. Elliot, *Physics of amorphous materials*. Longman, 1984.
- [45] B. Marchon, J. Gui, K. Grannen, G. C. Rauch, J. W. Ager, S. R. P. Silva, and R. John, "Photoluminescence and raman spectroscopy in hydrogenated carbon films," *IEEE Trans Magn*, vol. 33, no. 5, 1997.
- [46] L. Zhang, X. Wei, Y. Lin, and F. Wang, "A ternary phase diagram for amorphous carbon," *Carbon*, vol. 94, pp. 202–213, Nov. 2015.
- [47] L. Lajaunie, C. Pardanaud, C. Martin, P. Puech, C. Hu, M. Biggs, and R. Arenal, "Advanced spectroscopic analyses on a:c-h materials," *Carbon*, 2017.
- [48] M. Veres, S. Tóth, and M. Koós, "New aspects of raman scattering in carbonbased amorphous materials," *Diam Relat Mater*, vol. 17, no. 7–10, pp. 1692– 1696, Jul. 2008.
- [49] S. Möller, Accelerator Technology: Applications in Science, Medicine, and Industry. Springer International Publishing, 2020.
- [50] H. Fager, "Growth and characterization of amorphous multicomponent nitride thin films," Ph.D. dissertation, Linkoping University, May 2014.

- [51] B. D. Beake and T. W. Liskiewicz, Applied Nanoindentation in Advanced Materials. Wiley, Aug. 2017, ch. Nanomechanical Characterization of Carbon Films, pp. 19–68.
- [52] ASTM, Standard Test Method for Adhesion Strength and Mechanical Failure Modes of Ceramic Coatings by Quantitative Single Point Scratch Testing, American Society for Testing and Materials International Std. C1624-22, 2022.
- [53] D. F. B. Smit, Understanding Molecular Simulation From Algorithms to Applications, 3rd ed., A. Gariguez, Ed. Academic Press, 2023.
- [54] J. Thijssen, *Computational Physics*, 2nd ed. Cambridge University Press, 2007.
- [55] R. Jones, "Density functional theory: Its origins, rise to prominence, and future," *Rev Mod Phys*, vol. 87, no. 3, pp. 897–923, Aug. 2015.
- [56] B. J. Alder and T. E. Wainwright, "Studies in molecular dynamics. i. general method," J Chem Phys, vol. 31, no. 2, pp. 459–466, Aug. 1959.
- [57] E. Hairer, C. Lubich, and G. Wanner, "Geometric numerical integration illustrated by the störmer-verlet method," Acta Numerica 2011, Vol 20, vol. 12, pp. 399–450, May 2003.
- [58] Z. Sha, P. Branicio, Q. Pei, V. Sorkin, and Y. Zhang, "A modified tersoff potential for pure and hydrogenated diamond-like carbon," *Computational Materials Science*, vol. 67, pp. 146–150, Feb. 2013.

- [59] Q. Liu, L. Li, Y.-R. Jeng, G. Zhang, C. Shuai, and X. Zhu, "Effect of interatomic potentials on modeling the nanostructure of amorphous carbon by liquid quenching method," *Comput Mater Sci*, vol. 184, p. 109939, Nov. 2020.
- [60] M. Mrovec, M. Moseler, C. Elsasser, and P. Gumbsch, "Atomistic modeling of hydrocarbon systems using analytic bond-order potentials," *Prog Mater Sci*, vol. 52, no. 2–3, pp. 230–254, Feb. 2007.
- [61] V. Rosato, M. Celino, and L. Colombo, "On the effect of quench rate on the structure of amorphous carbon," *Comput Mater Sci*, 1998.
- [62] J. T. Titantah, D. Lamoen, E. Neyts, and A. Bogaerts, "The effect of hydrogen on the electronic and bonding properties of amorphous carbon," J Phys Condens Matter, vol. 18, no. 48, pp. 10803–10815, Nov. 2006.
- [63] Y.-N. Chen, T.-B. Ma, P.-Z. Zhu, D.-C. Yue, Y.-Z. Hu, Z. Chen, and H. Wang, "Growth mechanism of hydrogenated amorphous carbon films: Molecular dynamics simulations," *Surface and Coatings Technology*, vol. 258, pp. 901–907, Nov. 2014.
- [64] N. Wang and K. Komvopoulos, "The effect of deposition energy of energetic atoms on the growth and structure of ultrathin amorphous carbon films studied by molecular dynamics simulations," *J Phys D*, vol. 47, no. 24, p. 245303, May 2014.
- [65] N. Kametani, M. Nakamura, K. Yashiro, and T. Takaki, "Investigating residual stress evolution in the deposition process of diamond-like carbon film through molecular dynamics," *Comput Mater Sci*, vol. 209, p. 111420, Jun. 2022.

- [66] N. Marks, J. Bell, G. Pearce, D. Mckenzie, and M. Bilek, "Atomistic simulation of energy and temperature effects in the deposition and implantation of amorphous carbon thin films," *Diam Relat Mater*, 2003.
- [67] P. A. M. Dirac, "Note on exchange phenomena in the thomas atom," Math Proc Cambridge Philos Soc, vol. 26, no. 3, pp. 376–385, Jul. 1930.
- [68] P. H. W. Kohn, "Inhomogeneous electron gas," Phys Rev B, vol. 136, 1964.
- [69] W. Kohn and L. Sham, "Self-consistent equations including exchange and correlation effects\*," *Phys Rev A*, vol. 140, 1965.
- [70] M. A. Caro, R. Zoubkoff, O. Lopez-Acevedo, and T. Laurila, "Atomic and electronic structure of tetrahedral amorphous carbon surfaces from density functional theory: Properties and simulation strategies," *Carbon*, vol. 77, pp. 1168–1182, Oct. 2014.
- [71] J. Han, W. Gao, J. Zhu, S. Meng, and W. Zheng, "Density-functional theory study of the microstructure, electronic structure, and optical properties of amorphous carbon," *Phys Rev B*, vol. 75, no. 15, p. 155418, Apr. 2007.
- [72] H. Park, D. Woo, J. M. Lee, S. J. Park, S. Lee, H. J. Kim, E. Yoon, and G.-D. Lee, "The influence of hydrogen concentration in amorphous carbon films on mechanical properties and fluorine penetration: a density functional theory and ab initio molecular dynamics study," *RSC Advances*, vol. 10, no. 12, pp. 6822–6830, 2 2020.
- [73] M. Komelj, "Ab initio investigation of magnetism in cr-doped diamond-like carbon," *physica status solidi* (b), vol. 248, no. 10, pp. 2266–2268, Apr. 2011.

- [74] A. F. Bower, Applied Mechanics of Solids. CRC Press, 2009.
- [75] P. Bruno, G. Cicala, A. Losacco, and P. Decuzzi, "Mechanical properties of pecvd hydrogenated amorphous carbon coatings via nanoindentation and nanoscratching techniques," *Surf Coat Technol*, vol. 180–181, pp. 259–264, Mar. 2004.
- [76] M. Weiler, R. Kleber, S. Sattel, K. Jung, H. Ehrhardt, G. Jungnickel, S. Deutschmann, U. Stephan, P. Blaudeck, and T. Frauenheim, "Structure of amorphous hydrogenated carbon: experiment and computer simulation," *Diam Relat Mater*, no. cannot, 1994.
- [77] T. Frauenheim, P. Blaudeck, U. Stephan, and G. Jungnickel, "Atomic structure and physical properties of amorphous carbon and its hydrogenated analogs," *Phys Rev B*, no. Germany, 1993.
- [78] Y. Z. Mathioudakis, "Diamond like carbon," Intlvac Thin Film Inc., Tech. Rep., 2021.
- [79] ISO, Metallic materials Instrumented indentation test for hardness and materials parameters - Part 4: Test method for metallic and non-metallic coatings, International Organization for Standardization Std. 14577-4, 2016.
- [80] W. Oliver and G. Pharr, "An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments," *J Mater Res*, vol. 7, no. 6, pp. 1564–1583, Jun. 1992.
- [81] J. Lascovich and S. Scaglione, "Comparison among xaes, pels and xps techniques for evaluation of sp2 percentage in a-c:h," *Appl Surf Sci*, 1994.

- [82] M. Mayer, "Simnra user's guide," Max-Planck-Institut f
  ür Plasmaphysik, Tech. Rep., 1997.
- [83] A. P. Thompson, H. M. Aktulga, R. Berger, D. S. Bolintineanu, W. M. Brown,
  P. S. Crozier, P. J. in 't Veld, A. Kohlmeyer, S. G. Moore, T. D. Nguyen,
  R. Shan, M. J. Stevens, J. Tranchida, C. Trott, and S. J. Plimpton, "Lammps
   a flexible simulation tool for particle-based materials modeling at the atomic,
  meso, and continuum scales," *Comput Phys Commun*, vol. 271, p. 108171, Feb. 2022.
- [84] G. Kresse and J. Furthmüller, "Efficient iterative schemes forab initiototalenergy calculations using a plane-wave basis set," *Phys Rev B*, vol. 54, no. 16, pp. 11169–11186, Oct. 1996.
- [85] A. H. L. et al, "The atomic simulation environment a python library for working with atoms," J Phys Condens Matter, 2017.
- [86] C. H. K. M. S. van der Walt; et al., "Array programming with numpy," Nature, vol. 585, pp. 357–362, 2020.
- [87] P. V. R. G. T. O. et al., "Scipy 1.0: fundamental algorithms for scientific computing in python," *Nat Methods*, vol. 17, pp. 261–272, 2020.
- [88] A. Stukowski, "Visualization and analysis of atomistic simulation data with ovito-the open visualization tool," *Model Simul Mater Sc*, vol. 18, 2009.
- [89] J. D. Hunter, "Matplotlib: A 2d graphics environment," Comput Sci Eng, vol. 9, no. 3, pp. 90–95, 2007.

- [90] V. Ramasubramani, B. D. Dice, E. S. Harper, M. P. Spellings, J. A. Anderson, and S. C. Glotzer, "freud: A software suite for high throughput analysis of particle simulation data," *Comput Phys Commun*, vol. 254, 2020.
- [91] M. N. R. O. A. N. et al., "lmfit/lmfit-py: 1.3.1," 2024.
- [92] M. Kanski, D. Maciazek, Z. Postawa, C. M. Ashraf, A. C. T. van Duin, and B. J. Garrison, "Development of a charge-implicit reaxff potential for hydrocarbon systems," *The Journal of Physical Chemistry Letters*, vol. 9, no. 2, pp. 359–363, Jan. 2018.
- [93] J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized gradient approximation made simple," *Phys Rev Lett*, vol. 77, no. 18, pp. 3865–3868, Oct. 1996.
- [94] F. Birch, "Finite elastic strain of cubic crystals," *Phys Rev*, vol. 71, no. 11, pp. 809–824, Jun. 1947.
- [95] E. C. T. Ba, M. R. Dumont, P. S. Martins, B. da Silva Pinheiro, M. P. M. da Cruz, and J. W. Barbosa, "Deconvolution process approach in raman spectra of dlc coating to determine the sp3 hybridization content using the id/ig ratio in relation to the quantification determined by x-ray photoelectron spectroscopy," *Diam Relat Mater*, vol. 122, p. 108818, Feb. 2022.
- [96] T. R. Gengenbach, G. H. Major, M. R. Linford, and C. D. Easton, "Practical guides for x-ray photoelectron spectroscopy (xps): Interpreting the carbon 1s spectrum," *Journal of Vacuum Science Technology A*, vol. 39, no. 1, Jan. 2021.
- [97] N. Fairley, V. Fernandez, M. Richard-Plouet, C. Guillot-Deudon, J. Walton,E. Smith, D. Flahaut, M. Greiner, M. Biesinger, S. Tougaard, D. Morgan,

and J. Baltrusaitis, "Systematic and collaborative approach to problem solving using x-ray photoelectron spectroscopy," *Appl Surf Sci Adv*, vol. 5, p. 100112, Sep. 2021.

- [98] G. H. Major, T. G. Avval, D. I. Patel, D. Shah, T. Roychowdhury, A. J. Barlow,
  P. J. Pigram, M. Greiner, V. Fernandez, A. Herrera-Gomez, and M. R. Linford,
  "A discussion of approaches for fitting asymmetric signals in x-ray photoelectron spectroscopy (xps), noting the importance of voigt-like peak shapes," Surf Interface Anal, vol. 53, no. 8, pp. 689–707, May 2021.
- [99] G. H. Major, N. Fairley, P. M. A. Sherwood, M. R. Linford, J. Terry, V. Fernandez, and K. Artyushkova, "Practical guide for curve fitting in x-ray photoelectron spectroscopy," J Vac Sci Technol A, vol. 38, no. 6, Oct. 2020.
- [100] G. Greczynski and L. Hultman, "X-ray photoelectron spectroscopy: Towards reliable binding energy referencing," *Prog Mater Sci*, vol. 107, p. 100591, Jan. 2020.
- [101] M. H. Engelhard, D. R. Baer, A. Herrera-Gomez, and P. M. A. Sherwood, "Introductory guide to backgrounds in xps spectra and their impact on determining peak intensities," J Vac Sci Technol A, vol. 38, no. 6, Sep. 2020.
- [102] J. Lascovich, R. Giorgi, and S. Scaglione, "Evaluation of the sp2/sp3 ratio in amorphous carbon structure by xps and xaes," *Appl Surf Sci*, vol. 47, no. 1, pp. 17–21, Jan. 1991.
- [103] S. Jackson, "Determining hybridization differences for amorphous carbon from the xps c 1s envelope," *Appl Surf Sci*, vol. 90, no. 2, pp. 195–203, Oct. 1995.

- [104] I. Montero, L. Galán, A. Laurent, J. Perrière, and J. Spousta, "X-ray photoelectron spectroscopy and x-ray-excited auger electron spectroscopy studies of the initial deposition of hydrogenated amorphous carbon," *Thin Solid Films*, vol. 228, no. 1–2, pp. 72–75, May 1993.
- [105] B. Lesiak, L. Kövér, J. Tóth, J. Zemek, P. Jiricek, A. Kromka, and N. Rangam, "C sp2/sp3 hybridisations in carbon nanomaterials – xps and (x)aes study," *Appl Surf Sci*, vol. 452, pp. 223–231, Sep. 2018.
- [106] D. J. Morgan, "Comments on the xps analysis of carbon materials," C, vol. 7, no. 3, p. 51, Jul. 2021.
- [107] Y. Mizokawa, T. Miyasato, S. Nakamura, K. M. Geib, and C. W. Wilmsen, "Comparison of the ckll first-derivative auger spectra from xps and aes using diamond, graphite, sic and diamond-like-carbon films," *Surf Sci*, vol. 182, no. 3, pp. 431–438, Apr. 1987.
- [108] L. Calliari, "Aes and core level photoemission in the study of a-c and a-c:h," *Diam Relat Mater*, vol. 14, no. 8, pp. 1232–1240, Aug. 2005.
- [109] S. Tanuma, C. J. Powell, and D. R. Penn, "Calculations of electron inelastic mean free paths. ix. data for 41 elemental solids over the 50 ev to 30 kev range," *Surf Interface Anal*, vol. 43, no. 3, pp. 689–713, 2011.
- [110] B. Lenz, H. Hasselbruch, H. Großmann, and A. Mehner, "Application of cnn networks for an automatic determination of critical loads in scratch tests on a-c:h:w coatings," *Surf Coat Technol*, vol. 393, p. 125764, Jul. 2020.

- [111] X. B. Yan, T. Xu, S. R. Yang, H. W. Liu, and Q. J. Xue, "Characterization of hydrogenated diamond-like carbon films electrochemically deposited on a silicon substrate," *J Phys D: Appl Phys*, vol. 37, no. 17, pp. 2416–2424, Aug. 2004.
- [112] S. Meskinis, A. Vasiliauskas, M. Andrulevicius, D. Peckus, S. Tamulevicius, and K. Viskontas, "Diamond like carbon films containing si: Structure and nonlinear optical properties," *Materials*, vol. 13, no. 4, p. 1003, Feb. 2020.
- [113] A. J. Haq, P. Munroe, M. Hoffman, P. Martin, and A. Bendavid, "Berkovich indentation of diamondlike carbon coatings on silicon substrates," *J Mater Res*, vol. 23, no. 7, pp. 1862–1869, Jul. 2008.
- [114] S.-m. Baek, T. Shirafuji, N. Saito, and O. Takai, "Adhesion property of sioxdoped diamond-like carbon films deposited on polycarbonate by inductively coupled plasma chemical vapor deposition," *Thin Solid Films*, vol. 519, no. 20, pp. 6678–6682, Aug. 2011.
- [115] W. Dai, L. Wu, and Q. Wang, "Structure and property of diamond-like carbon coating with si and o co-doping deposited by reactive magnetron sputtering," *Journal of Composites Science*, vol. 7, no. 5, p. 180, May 2023.
- [116] R. J. Jaccodine, "Surface energy of germanium and silicon," J Electrochem Soc, vol. 110, no. 6, p. 524, 1963.
- [117] H. L. Skriver and N. M. Rosengaard, "Surface energy and work function of elemental metals," *Phys Rev B*, vol. 46, no. 11, pp. 7157–7168, Sep. 1992.

- [118] C. Pardanaud, C. Martin, P. Roubin, G. Giacometti, C. Hopf, T. Schwarz-Selinger, and W. Jacob, "Raman spectroscopy investigation of the h content of heated hard amorphous carbon layers," *Diam Relat Mater*, vol. 34, pp. 100– 104, Apr. 2013.
- [119] V. L. Deringer and G. Csányi, "Machine learning based interatomic potential for amorphous carbon," *Phys Rev B*, vol. 95, no. 9, p. 094203, Mar. 2017.
- [120] D. G. McCulloch, D. R. McKenzie, and C. M. Goringe, "Ab initiosimulations of the structure of amorphous carbon," *Phys Rev B*, vol. 61, no. 3, pp. 2349–2355, Jan. 2000.
- [121] A. C. Ferrari and J. Robertson, "Raman spectroscopy of amorphous, nanostructured, diamond-like carbon, and nanodiamond," *Philosophical Transac*tions of the Royal Society of London. Series A: Mathematical, Physical and Engineering Sciences, vol. 362, no. 1824, pp. 2477–2512, Sep. 2004.
- [122] S. G. Srinivasan, A. C. T. van Duin, and P. Ganesh, "Development of a reaxff potential for carbon condensed phases and its application to the thermal fragmentation of a large fullerene," *J Phys Chem A*, vol. 119, no. 4, pp. 571–580, Jan. 2015.
- [123] K. Chenoweth, A. C. T. van Duin, and W. A. Goddard, "Reaxff reactive force field for molecular dynamics simulations of hydrocarbon oxidation," J Phys Chem A, vol. 112, no. 5, pp. 1040–1053, Jan. 2008.
- [124] K. Li, H. Zhang, G. Li, J. Zhang, M. Bouhadja, Z. Liu, A. A. Skelton, and M. Barati, "Reaxff molecular dynamics simulation for the graphitization of

amorphous carbon: A parametric study," *J Chem Theory Comput*, vol. 14, no. 5, pp. 2322–2331, Apr. 2018.

- [125] G. I. Csonka, J. P. Perdew, A. Ruzsinszky, P. H. T. Philipsen, S. Lebègue, J. Paier, O. A. Vydrov, and J. G. Ángyán, "Assessing the performance of recent density functionals for bulk solids," *Phys Rev B*, vol. 79, no. 15, p. 155107, Apr. 2009.
- [126] S. Chinkanjanarot, "Density of amorphous carbon by using density functional theory," Master's thesis, Michigan Technological University, 2014.

#### Appendix A

## Benchmarking and Protocols for MD Simulations

Benchmarking was used to determine if the simulation protocols employed during this investigation were reliable. This was achieved by comparison of system size, comparison against other ReaxFF parametrizations, and replication of literature results.

Since MD is typically used for systems of thousands to upwards of billions of particles, it was important to ensure that the small system size of 128 particles used in this investigation replicated similar results from larger systems. This was tested by simulating systems pure a-C systems with 1024 atoms and 128 atoms, following the same liquid quench method as described in Section 3.2.1. The densities chosen for comparison were 2.0, 2.3, and 2.6  $g \, cm^{-3}$ . One hundred seeds were simulated for each system size and density, and the results for  $sp^2$  and  $sp^3$  bonding fractions are presented in Table A.1. The results show that simulation of 128 particle systems closely resembles 1024 particle systems and thus the use of the small system size was justified.

System Size	$\begin{array}{c} \mathbf{Density} \\ [gcm^{-3}] \end{array}$	$\mathbf{sp}^3 \ [\%]$	${ m sp}^2 \ [\%]$
1024	2.00	4.34	74.29
	2.30	8.24	81.13
	2.60	17.00	79.51
128	2.00	4.16	74.02
	2.30	7.93	81.42
	2.60	16.25	80.12

Table A.1: Bonding fractions calculated from average of 100 seeds for a-C systems simulated with MD for different system sizes of 1024 and 128 carbon atoms.

The behaviour of the ci-ReaxFF parametrization used in this investigation was compared to the two most popular versions of ReaxFF for simulation of a-C systems, a 2015 version from Srinivasan et al. and the 2008 version from Chenoweth et al. [122, 123]. Although the 2015 version was parametrized for use in condensed carbon systems, which is unique among ReaxFF parametrizations, this version was not able to be obtained to model the inclusion of hydrogen interactions and therefore could not be used in this investigation to model a-C:H systems. For comparison, Figure A.1 shows comparison of the RDFs generated for an a-C system with density of 2.2  $g \, cm^{-3}$ . Overall, the RDFs show good agreement between location of first and second nearest neighbours. The ci-ReaxFF has the narrowest first neighbour peak and does not show as many oscillations after the first peak which are shown in the 2008 and 2015 versions.



**Figure A.1:** Example of RDF produced for a-C system with density of 2.2  $g cm^{-3}$  for comparison between three different parametrizations of ReaxFF. RDFs correspond to an average of the last frames in each seed simulation for a given ReaxFF parametrization.

The liquid quench procedure for the generation of the ReaxFF 2008 and 2015 systems followed the study completed by Li et al. [124]. This allowed comparison between results presented in literature to the liquid quench method utilized in this investigation for ci-ReaxFF. The ci-ReaxFF systems followed the methods outlined in Section 3.2.1. The 2008 and 2015 systems followed the method from Li et al. where 2000 particles were held at 6000 K for 5 ps, then quenched to 300 K in 1 ps, and equilibrated at 300 K for 4 ps. The timestep (0.1 fs) and temperature damping coefficient (10 fs) used were both the same as investigated for ci-ReaxFF systems. A total of 20 seeds were simulated for each system. Figures A.2 and A.3 show the evolution of sp<sup>2</sup> and sp<sup>3</sup> bonding fractions evolving as a function of simulation time, whereas Figure A.4 shows the average nearest neighbour value. The results from the 2008 and 2015 systems match the results presented in Li et al. [124]. The ci-ReaxFF systems evolve much more slowly to the final bonding fractions as indicative of the quench rate being a factor of 5.7 times lower than those for the 2008 and 2015 systems. Across Figures A.2 to A.4, the ci-ReaxFF more closely mimics the 2015 parametrization. This was unexpected but pleasant to observe since the ci-ReaxFF parametrization was not made explicitly for generation of solid carbon structures but the 2015 version was [122, 92]. This cemented the choice of ci-ReaxFF potential for use in this investigation.



**Figure A.2:** sp<sup>2</sup> bonding fraction evolution for a-C system with density of 2.2  $g \, cm^{-3}$  for comparison between three different parametrizations of ReaxFF.



**Figure A.3:** sp<sup>3</sup> bonding fraction evolution for a-C system with density of 2.2  $g \, cm^{-3}$  for comparison between three different parametrizations of ReaxFF.



Figure A.4: Average nearest neighbour evolution for a-C system with density of 2.2  $g \, cm^{-3}$  for comparison between three different parametrizations of ReaxFF.

Figure A.5 shows the protocol used for input scripts for LAMMPS files. Note that this input script generated one seed, thus bash scripting was used to generate 100 seeds for each simulation parameter set in Table 3.4. These scripts are not provided. An important consideration from the example script was that the charge equilibration capability of the ReaxFF potential is turned off, following suggestion by de Tomas et al. [15].

a-C:H system	with 2.6 density, 16 hydrogen atoms.
#Initia	lization
units	real
dimension	3
boundary	ррр
atom_style	charge
#Geor	netry
region	simboxreg block 0 9.93928 0 9.93928 0 9.93928 units box
create_box	2 simboxreg
create_atoms	1 random 112 235462 NULL overlap 1.0 units box
create_atoms	2 random 16 235462 NULL overlap 1.0 units box
mass	1 12.011
mass	2 1.008
timestep	0.1
pair_style	hybrid/overlay reax/c lmp_control.txt checkqeq no table linear 11000
pair_coeff	* * reax/c ffield.ci-reax2018.txt C H
pair_coeff	1 1 table ffield.ci-reax2018_inputfile2.txt CC_cireaxFF
pair_coeff	1 2 table ffield.ci-reax2018_inputfile2.txt CH_cireaxFF
pair_coeff	2 2 table ffield.ci-reax2018_inputfile2.txt HH_cireaxFF
#Quer	nching
thermo	1000
dump	mydump all custom 1000
dump_aC_20	18_112C_16H_2p6_1000k_per_ps_seed235462.xyz x y z ix iy iz id type
timestep	0.1
fix	mynvt all nvt temp 6000.0 6000.0 10.0
run	50000
unfix	mynvt
fix	mynvt all nvt temp 6000.0 300.0 10.0
run	57000
unfix	mynvt
fix	mynyt all nyt temp 300.0 300.0 10.0
run	50000
unfix	mynvt

Figure A.5: LAMMPS script protocol used in this investigation. Example shows generation of 128 particle system (112 carbon, 16 hydrogen) with a starting density of 2.6  $g \, cm^{-3}$ .

### Appendix B

# Benchmarking and Protocols for DFT Simulations

Benchmarking was used to determine the effect of the choice of exchange correlation functional, energy convergence threshold, and reciprocal space grid points (KPOINTS) on bulk modulus for a structure of a-C with density of 2.6  $g \, cm^{-3}$  that was obtained from the MD protocols used in this investigation. This was completed by first testing the difference between the PBE, PBED3 (van der Waals dispersion energy correction term included), and PBEsol (revised PBE functional for solids) exchange functionals for different values of the energy convergence threshold. The choice of functionals was motivated after work by Csonka et al. that showed PBE modelled the bulk modulus of diamond better than PBEsol [125]. The PBED3 functional was included after Park et al. investigated a-C:H systems similar to this investigation [72]. Energy convergence thresholds from -0.02 to -0.001 eV/Å were chosen based off literature that simulated a-C using DFT [126, 72]. Figure B.1 shows that both PBE and PBED3 perform similar to each other while PBEsol shows bulk moduli around 10% higher than PBE or PBED3. The overestimation of bulk modulus for PBEsol is consistent with results from Csonka et al. for diamond [125]. For this reason and since PBED3 simulations took more computational power and provided very similar results to PBE, PBE was chosen as the exchange correlation to be used in this investigation.



**Figure B.1:** Comparison of PBE, PBED3, and PBEsol exchange correlation functionals utilized in VASP for benchmarking bulk modulus. The system was a pure a-C system with density 2.6  $g \, cm^{-3}$  that was obtained from the MD protocols. A 3x3x3 KPOINTS grid was used for each datapoint.

Figure B.2 shows that the use of gamma point only reciprocal space grid (1x1x1) does not agree with results for bulk modulus when compared to 3x3x3 and 5x5x5 reciprocal space grids. Since the bulk modulus changed by less than 1 GPa between 3x3x3 and 5x5x5 grids, the choice of 3x3x3 was justified for this investigation.



**Figure B.2:** Comparison of different KPOINTS mesh values corresponding to number of reciprocal space points included for simulation of pure a-C system with density 2.6  $g \, cm^{-3}$  with PBE functional and convergence threshold of -0.02 eV/Å.

Figure B.3 shows the protocol used for input scripts for VASP files. POSCAR files used were provided from the last frame of simulations of MD simulations. Bash scripts were used to ensure systems that did not converge after 1200 NSW steps were restarted from the final configuration (CONTCAR to POSCAR) until convergence was obtained for all systems. These scripts are not provided. The ISIF4 settings were used during the modification of the simulation volumes by  $\pm 1$  to  $\pm 5\%$ to derive energy-volume relationships which were used to obtain the bulk moduli of the systems. Note that the choice of 20 steps for NSW was arbitrary and the systems did not relax within this number of steps. The three MD systems chosen to be relaxed with DFT (out of 100 MD structures) was based on identification of structures that had sp<sup>3</sup> bonding fractions closest to the mean value for a given parameter set. This was an attempt to choose structures that might relax similarly with DFT. This was an oversimplification and often each structure took significantly different amounts of time to relax. Figure B.3 shows that the convergence setting was changed to -0.001 eV/Å because it was found that after a few systems of a-C:H were simulated with -0.02 eV/Å, the energy-volume relationship used to obtain the bulk modulus was not parabolic and led to inconsistent bulk modulus values. Changing to an EDIFFG setting of -0.001 eV/Å solved this problem. It should be mentioned that the total CPU usage used to complete this thesis investigation was approximately 130 CPU core years.

INCAR (ISIF3)	INCAR (ISIF4)	KPOINTS
ISTART=0	ISTART=0	Automatic Monkhorst Mesh
ICHARG=2	ICHARG=2	0
PREC=Accurate	PREC=Accurate	Monkhorst-Pack
ENCUT=520	ENCUT=520	333
EDIFF=1E-8	EDIFF=1E-8	
EDIFFG=-0.001	EDIFFG=-0.001	
NBANDS=322	NBANDS=322	
#real space projection operators	#real space projection operators	
#and plane wave data	#and plane wave data	
LREAL=Auto	LREAL=Auto	
LPLANE=.TRUE.	LPLANE=.TRUE.	
NCORE=16	NCORE=16	
LSCALU=.FALSE.	LSCALU=.FALSE.	
NSIM=4	NSIM=4	
LCHARG=.FALSE.	LCHARG=.FALSE.	
LWAVE=.FALSE.	LWAVE=.FALSE.	
#ionic minimization	#ionic minimization	
NSW=1200	NSW=20	
IBRION=2	IBRION=2	
ISIF=3	ISIF=4	

**Figure B.3:** DFT input files for VASP used in this investigation. Example shows ISIF3, ISIF4, and KPOINTS settings. Note that for systems exceeding 24 hydrogen atoms, the NSW of 1200 steps was often not enough to reach the energy convergence threshold, thus a bash script was used to test if systems had converged. If systems were not converged, the same ISIF3 settings were used and the POSCAR was replaced with the CONTCAR file until convergence was reached.

#functional

GGA=PE

ISMEAR=0

SIGMA=0

#functional

GGA=PE

ISMEAR=0

SIGMA=0