A Raman and scanning electron microscope analysis of magnetron sputtered thin-film carbon

by

Jonathan Laumer

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF APPLIED SCIENCE

in
THE COLLEGE OF GRADUATE STUDIES
(Electrical Engineering)

THE UNIVERSITY OF BRITISH COLUMBIA
(Okanagan)
December 2014
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Abstract

Thin-film carbon coatings possess properties, such as extreme hardness, smoothness, and a nice glossy finish, that make them desirable for a variety of industrial and military applications. This thesis examines the Raman spectra associated with thin-films of carbon that are prepared using magnetron sputtering. The goal is to achieve a high amount of strong bonds, i.e., sp$^3$ bonds, as in diamond, using this inexpensive and widely available deposition process. Raman spectroscopy is the chosen analytical method used for the purpose of this work, since it is non-destructive and widely available. Using Raman spectroscopy, an sp$^3$ content of up to 77% is determined. This suggests that it is possible to deposit thin-films of carbon that approach the properties of tetrahedral amorphous carbon, a material known for its excellent hardness and durability, using this inexpensive approach. A scanning electron microscope image of one of the thin-films of carbon is acquired and examined, conclusions regarding the transition between the underlaying titanium substrate and the thin-film of carbon being drawn. Further directions for possible research are mentioned.
# Table of Contents

Abstract ................................................................. ii

Table of Contents .................................................. iii

List of Tables ........................................................ vi

List of Figures ......................................................... vii

Acknowledgements ................................................... xi

Dedication .............................................................. xii

Chapter 1: Introduction .............................................. 1

Chapter 2: Background ................................................. 12

2.1 Thin-film carbon and its impact on society ............... 12
2.2 What is thin-film carbon ........................................ 14
2.3 Common deposition techniques ............................. 20
2.4 Applications of thin-film carbon ......................... 22
2.5 Raman spectroscopy in the characterization of thin-film carbon 24
2.6 Problems with the presence of oxygen and other contaminants 35
# TABLE OF CONTENTS

## Chapter 3: Experiment ............................ 37

3.1 Deposition of thin-film carbon .................. 37

3.2 Magnetron sputtering ............................ 38

3.2.1 Machine: Hummer XII ....................... 38

3.2.2 Chrome sputtering ............................ 42

3.2.3 Sample type and numbering .................. 43

3.2.4 Substrate preparation ......................... 43

3.2.5 RF cleaning ................................. 44

3.2.6 Recipe: a step-by-step guide ................ 45

3.2.7 Experiments ................................. 45

3.3 Raman Spectroscopy ............................. 48

3.3.1 Machine: LabRAM HR ....................... 48

3.3.2 Measurements ............................... 51

3.4 Scanning electron microscope .................. 55

3.4.1 Machine ................................. 55

3.4.2 Determination of the thickness .............. 55

3.4.3 Material analysis ........................... 57

## Chapter 4: Analysis ............................... 59

4.1 Experimental analysis of thin-film carbon .... 59

4.2 Description and overview of the examined samples 62

4.3 Raman analysis ................................. 64

4.3.1 Unprocessed Raman data .................... 64

4.3.2 Baseline correction ......................... 66

4.3.3 Peak fitting ............................... 68
TABLE OF CONTENTS

4.3.4 Background subtraction . . . . . . . . . . . . . . . . . . 72
4.4 Summary of the Raman results . . . . . . . . . . . . . . . 75
4.5 Raman interpretation . . . . . . . . . . . . . . . . . . . . . 96
4.6 Film thickness and material composition profile . . . . 98

Chapter 5: Conclusions . . . . . . . . . . . . . . . . . . . . . . 108

References . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 111

Appendix A: Step by step guide for the Hummer XII . . . . 117
# List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 1.1</td>
<td>A comparison of the properties of diamond and graphite.</td>
<td>5</td>
</tr>
<tr>
<td>Table 1.2</td>
<td>A comparison of the different forms of amorphous and crystalline carbon.</td>
<td>7</td>
</tr>
<tr>
<td>Table 3.1</td>
<td>An overview of the sputtering experiments corresponding to the different sample numbers.</td>
<td>47</td>
</tr>
<tr>
<td>Table 3.2</td>
<td>Pictures of the samples prepared and analyzed in this thesis.</td>
<td>49</td>
</tr>
<tr>
<td>Table 3.3</td>
<td>Overview of the Raman measurements and measurement settings.</td>
<td>54</td>
</tr>
<tr>
<td>Table 4.1</td>
<td>Overview of the samples with the deposition parameters and the Raman source identified.</td>
<td>63</td>
</tr>
<tr>
<td>Table 4.2</td>
<td>Overview of the Raman results corresponding to the different samples.</td>
<td>76</td>
</tr>
<tr>
<td>Table 4.3</td>
<td>Overview of the Raman results corresponding to the different samples.</td>
<td>87</td>
</tr>
<tr>
<td>Table 4.4</td>
<td>A comparison of common Raman interpretations found in the literature.</td>
<td>99</td>
</tr>
</tbody>
</table>
List of Figures

Figure 1.1  The atomic distribution within diamond. . . . . . . . 2
Figure 1.2  Atomic distribution within graphite and the nature
      of bondings. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 3
Figure 1.3  The relationship between the sp$^3$ content and the
      hardness . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 11
Figure 2.1  The hybridizations available to carbon atoms. . . . . 15
Figure 2.2  Thin-film deposition, PVD vs. CVD. . . . . . . . . . . 18
Figure 2.3  Ternary phase diagram for the different kinds of thin-
      film carbon. This figure is from Robertson et al. [9]. . 19
Figure 2.4  Scattering effects . . . . . . . . . . . . . . . . . . . . . . . 25
Figure 2.5  General schematic of a Raman spectroscopy system . 27
Figure 2.6  Raman scattering . . . . . . . . . . . . . . . . . . . . . . . 28
Figure 2.7  Different vibration modes . . . . . . . . . . . . . . . . . 32
Figure 2.8  The Raman interpretation of a thin-film carbon by
      Zhao et al. [10]. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 33
Figure 2.9  Raman interpretation of a thin-film carbon by Sung
      et al. [31]. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 34
Figure 2.10 Adhesion strength for different materials . . . . . . . 36
| Figure 3.1 | Sputtering machine Hummber XII. | 39 |
| Figure 3.2 | Terminology of the sputtering vacuum chamber. | 41 |
| Figure 3.3 | Water drop test for a titanium ring before and after argon plasma cleaning. | 46 |
| Figure 3.4 | Front side of the LabRAM HR Raman confocal microscope. | 50 |
| Figure 3.5 | Planar sample placement for Raman spectroscopy. | 52 |
| Figure 3.6 | Ring sample placement for Raman spectroscopy. | 53 |
| Figure 3.7 | The SEM machine at SEMLab/UBC Okanagan | 56 |
| Figure 3.8 | First thickness measurement of sample number 115-1. | 58 |
| Figure 4.1 | Unprocessed Raman spectrum of sample number 201-2. | 65 |
| Figure 4.2 | Unprocessed Raman spectrum of sample number 201-2 with the baseline. | 67 |
| Figure 4.3 | Baseline corrected Raman spectrum of sample number 201-2. | 69 |
| Figure 4.4 | Raman interpretation of sample number 201-2 with a Raman source of 442 nm. | 71 |
| Figure 4.5 | Baseline corrected Raman spectrum of sample number 207-1 without background compensation. | 73 |
| Figure 4.6 | Raman spectrum of plain glass and flat titanium. | 74 |
| Figure 4.7 | Raman interpretation of sample number 106-2. | 77 |
| Figure 4.8 | Raman interpretation of sample number 111-1. | 78 |
| Figure 4.9 | Raman interpretation of sample number 115-3. | 79 |
| Figure 4.10 | Raman interpretation of sample number 121-3. | 80 |
LIST OF FIGURES

Figure 4.11 Raman interpretation of sample number 123-3. . . . . 81
Figure 4.12 Raman interpretation of sample number 201-2 with a
Raman source of 633 nm. . . . . . . . . . . . . . . . . . . . . 82
Figure 4.13 Raman interpretation of sample number 204-2. . . . 83
Figure 4.14 Raman interpretation of sample number 207-1 with
background compensation. . . . . . . . . . . . . . . . . . 84
Figure 4.15 Raman interpretation of sample number 210-1. . . . 85
Figure 4.16 Raman interpretation of sample number 210-2. . . . 86
Figure 4.17 Comparison of Raman results with different argon gas
flow. . . . . . . . . . . . . . . . . . . . . . . . . . . . . 89
Figure 4.18 Comparison of Raman results with glass vs. titanium
ring substrate. . . . . . . . . . . . . . . . . . . . . . . 91
Figure 4.19 Comparison of Raman results with glass vs. flat tita-
nium substrate. . . . . . . . . . . . . . . . . . . . . . 92
Figure 4.20 Comparison of Raman results to test for reproducibility. 93
Figure 4.21 Comparison of Raman results with different Raman
source wavelengths. . . . . . . . . . . . . . . . . . . . 94
Figure 4.22 Comparison of Raman results with and without back-
ground compensation. . . . . . . . . . . . . . . . . . . 95
Figure 4.23 Comparison of Raman results with DC vs. RF power. 97
Figure 4.24 SEM picture of the thin-film carbon of sample number
115-1. . . . . . . . . . . . . . . . . . . . . . . . . . . . 101
Figure 4.25 Material line analysis of sample number 115-1. . . . 102
Figure 4.26 Thickness of sample number 115-1. . . . . . . . . . 104
LIST OF FIGURES

Figure 4.27 Material spectrum number 14 corresponding to sample number 115-1. 105
Figure 4.28 Material spectrum number 16 corresponding to sample number 115-1. 106
Figure A.1 Step-by-step guide for thin-film carbon deposition with the Hummer XII. 118
Acknowledgements

Special thanks goes to my supervisor, Dr. Stephen K. O’Leary. Without his guidance and help, this research would not have occurred. He is not only a great researcher, but also a great mentor, helping me along my academic path. I also would like to thank Dr. Guangrui Xia and her graduate students, Mr. Xiyue Li and Ms. Ye Zhu, both also being from The University of British Columbia Vancouver, for letting me use their Raman spectroscopy machine and any help relating those measurements. My gratitude also goes to Mr. David Arkinstall from the SEMLab at The University of British Columbia Okanagan for giving me the opportunity to do measurements with the scanning electron microscope. Thanks to the Charles E. Fipke Foundation of The University of British Columbia Okanagan, I was also able to acquire the use of the scanning electron microscope. Special thanks also goes to Mr. Ben Vos, the general manager of Arnell Workshop Inc. and Mr. Roy Arnell, for supporting me in the use of their magnetron sputtering machine, this being the machine used in these depositions.
Dedication

I would like to dedicate this thesis to my brother Simon. Since my very
earliest childhood, he has been a true friend.
Chapter 1

Introduction

Since the dawn of human civilization, diamonds have captured the popular imagination like no other material. Diamonds are exceptionally beautiful and possess material properties that surpass those associated with all other materials. The shiny look and bright appearance of diamonds makes them highly coveted for declarations of love, i.e., as in marriage, but also in the acquisition of might, i.e., as in the crown of a king. In addition to their clear and marvellous look, diamonds possess a hardness that is second to none. Unfortunately, these positive attributes of diamond have fuelled greed, and this has spawned human conflict. Indeed, wars have been fought over diamonds, and countries in possession of diamonds have found them to be a mixed blessing.

Given diamond’s hold on human curiosity, it has been the subject of a considerable amount of scientific scrutiny. Initial studies into the material properties of diamond have focused on the distribution of atoms within this material. These studies demonstrated that diamond is a pure form of carbon that is arranged in a tetrahedral crystalline structure, as shown in Figure 1.1 [1]. Alternatively, researchers also have found that carbon can crystallize in a trigonal form, known as graphite, this crystalline structure being depicted in Figure 1.2 [2]. The properties of graphite are quite distinct.
Figure 1.1: A representation of the distribution of atoms within diamond. The carbon atoms are represented with the spheres, while the bonds are depicted with the spokes. This figure is after Karamitaheri [1]. The electronic version of this figure is in color.
Chapter 1. Introduction

Figure 1.2: A representation of the distribution of atoms within graphite. The carbon atoms are represented with spheres, while the bonds are depicted with spokes. This figure is after Seo [2]. The electronic version of this figure is in color.
from those associated with diamond [2]; see Table 1.1 [3]. Diamond possesses strong tetrahedral bonds, i.e., $sp^3$ bonds, for all axes, while graphite bonds are weak along one axis, i.e., with $sp^2$ bonds, but also strong in the direction of the two other axes. This difference in the nature of the bonds accounts for the differences in its material properties.

In addition to these two crystalline forms of carbon, there are many other non-crystalline forms of carbon that are available, with properties that are quite distinct from those associated with diamond and graphite. Carbon comes in both polycrystalline and amorphous forms. Further enriching the situation, in some materials, the nature of the bonds is mixed, i.e., both $sp^2$ and $sp^3$ bonds are present. Carbon may also appear in powdered form, as soot, or in glassy form. A more recent addition to the constellation of carbon-based materials is thin-film carbon, deposited from the vapor phase, allowing for carbon coatings on a variety of substrates. Its introduction has substantially increased the breadth of the possible applications for carbon. As carbon can bond in so many different forms, it is referred to as being allotropic in character.

Of course, these properties of diamonds are also desirable for a wide array of industrial and military applications, where resistance to wear-and-tear is critical. The durability of tools and parts can be dramatically enhanced if diamonds are involved. As naturally occurring diamonds are rather rare and expensive, an interest in developing synthetic forms of diamond has thus developed. Research aimed at producing synthetic diamonds found its genesis in 1879 with the work of Hannay [4], in which hard crystals of carbon were formed through the heating of charcoal in a furnace. Today,
Table 1.1: A comparison of the properties of diamond with graphite. For graphite, the in-plane properties are mentioned first, the transverse properties second. This table is from Saada [3].

<table>
<thead>
<tr>
<th>Property</th>
<th>Graphite</th>
<th>Diamond</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant (300 K) [Å]</td>
<td>2.462, 6.708</td>
<td>3.567</td>
</tr>
<tr>
<td>Bond length (300 K) [Å]</td>
<td>1.421</td>
<td>1.545</td>
</tr>
<tr>
<td>Atomic density [cm$^{-3}$]</td>
<td>$1.14 \times 10^{23}$</td>
<td>$1.77 \times 10^{23}$</td>
</tr>
<tr>
<td>Thermal conductivity [W/cm·K]</td>
<td>30, 0.06</td>
<td>25</td>
</tr>
<tr>
<td>Debye temperature [K]</td>
<td>2500, 950</td>
<td>1860</td>
</tr>
<tr>
<td>Electron mobility [cm$^2$/V·sec]</td>
<td>$20 \times 10^{3}$, 100</td>
<td>1800</td>
</tr>
<tr>
<td>Hole mobility [cm$^2$/V·sec]</td>
<td>$15 \times 10^{3}$, 90</td>
<td>1500</td>
</tr>
<tr>
<td>Melting point [K]</td>
<td>4200</td>
<td>4500</td>
</tr>
<tr>
<td>Band gap [eV]</td>
<td>-0.04</td>
<td>5.47</td>
</tr>
</tbody>
</table>
synthetic diamonds are chiefly produced through the use of high pressures and high temperatures [5]. The resultant materials have been noted for their hardness and clarity. Other forms of synthetic diamonds, that are available in nano-crystalline form, may be produced through the use of explosives [6].

Synthetic diamonds, while in possession of many desirable material properties, are expensive to fabricate, albeit this expense is less than that required to purchase their naturally occurring counterparts. This has motivated researchers to consider the growth of thin-film carbon from the vapor phase. Thin-films of carbon, grown from the vapor phase, were first prepared using ion-beam deposition in 1971 by Aisenberg and Chabot, of the Space Science Division of the Whittaker Corporation in Waltham, Massachusetts [7]. Since that time, a variety of different deposition techniques, ranging from simple methods, such as sputtering, to more sophisticated approaches, such as plasma enhanced chemical vapor deposition (PECVD), have been employed in order to deposit thin-film carbon [8]. An overview of some of the basic forms of thin-film carbon, their basic properties, and their possible applications, are summarized in Table 1.2 [9].

Thin-films of carbon, prepared using the different available approaches, possess many different qualities, in terms of their adhesion to the underlying substrate, their smoothness, hardness, and color. Depending upon which application is being considered, the right deposition technique and deposition conditions must be selected. In this thesis, thin-films of carbon, with cosmetic jewelry applications in mind, will be fabricated and examined. The substrates primarily being considered are made of titanium, and are in the form of rings. Unfortunately, however, the ultimate question that is the
Chapter 1. Introduction

Table 1.2: A comparison of the different forms of amorphous and crystalline carbon. Diamond and graphite have a crystalline structure, and are considered as reference materials. Their properties are compared with some forms of thin-film carbon. This table is after Robertson et al. [9].

<table>
<thead>
<tr>
<th>Sample</th>
<th>sp³ (%)</th>
<th>H (%)</th>
<th>Density (g cm⁻¹)</th>
<th>Hardness (GPa)</th>
<th>Applications/Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond</td>
<td>100</td>
<td>0</td>
<td>3.515</td>
<td>100</td>
<td>cutting, jewelry</td>
</tr>
<tr>
<td>Graphite</td>
<td>0</td>
<td>0</td>
<td>2.267</td>
<td></td>
<td>batteries, lubricants</td>
</tr>
<tr>
<td>Evaporated C</td>
<td>0</td>
<td>0</td>
<td>1.9</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Sputtered C</td>
<td>5</td>
<td>0</td>
<td>2.2</td>
<td></td>
<td>thin-film coatings</td>
</tr>
<tr>
<td>ta-C</td>
<td>80-88</td>
<td>0</td>
<td>3.1</td>
<td>80</td>
<td>drilling and milling</td>
</tr>
<tr>
<td>a-C:H hard</td>
<td>40</td>
<td>30-40</td>
<td>1.6-2.2</td>
<td>10-20</td>
<td></td>
</tr>
<tr>
<td>a-C:H soft</td>
<td>60</td>
<td>40-50</td>
<td>1.2-1.6</td>
<td>less than 10</td>
<td></td>
</tr>
<tr>
<td>ta-C:H</td>
<td>70</td>
<td>30</td>
<td>2.4</td>
<td>50</td>
<td>low friction</td>
</tr>
</tbody>
</table>

7
Chapter 1. Introduction

focus of investigation is whether or not an inexpensive deposition technique, i.e., magnetron sputtering, is adequate for this particular application. Unfortunately, owing to limitations in the amount of time available, this thesis presents intermediary results that are required in order to address this overarching question. The ultimate resolution of this matter lies beyond the scope of this particular body of work and will have to be pursued in the future.

Even though the processes whereby thin-films of carbon may be deposited have been studied in detail, and the growing process of such films are now reasonably well understood, a systematic study on the influence of the substrate type and shape on the resultant thin-film carbon properties, and on how the deposition parameters also influence these properties, has yet to be performed. While there have been some studies performed on the effect of the substrate on the thin-film carbon properties, the focus of these studies was mostly on the impact of the substrate type and orientation. Zhao et al. [10], for example, examined the impact of depositing thin-film carbon on a variety of flat metal substrates. Bobzin et al. [11] deposited thin-film carbon using substrates tilted at an angle. Most studies have been performed on planar glass or silicon samples [12–15]. A critical comparison, in which the properties of thin-films of carbon deposited on flat substrates are contrasted with those associated with thin films of carbon deposited on curved substrates, has yet to be performed. This is a topic that will be studied within the context of this particular thesis.

Titanium rings, such as the ones serving as the substrate for the purposes of the application being considered in this analysis, combine both an
uncommon material and an unusual shape. For cosmetic jewelry applications, the challenges are different from those encountered in many other industrial or military applications. The primary focus of attention lies on the appearance and the comfort in wearing, combined with such considerations as long-lasting quality, as it is a luxury good. Unprocessed titanium substrates are in possession of a native oxide layer, and this makes adhesion a challenge, typically militating the use of an interlayer [16]. This work will be a first analysis of the influence of the substrate type, the substrate geometry, and the deposition parameters of magnetron sputtering on the $sp^3$ to $sp^2$ ratio of the thin-films of carbon, this ratio being a well accepted measure of thin-film carbon’s quality. This work gives insight into the dependence of the substrate type, shape, and the deposition parameters on the thin-film carbon properties. Understanding the exact influence of those parameters will allow for the proper growth of high quality thin-films of carbon. The properties of thin-film carbon, like its high strength and durability, due to extreme hardness, combined with its shiny and glossy look, make them a desired feature in cosmetic jewelry. Jewelry rings, with a black thin-film carbon coatings, are in high demand in our society. This scientific study has been accomplished in collaboration with a local company, Arnell Workshop Inc., with the eventual goal of determining the feasibility of growing high quality thin-films of carbon on titanium jewelry rings through the use of a magnetron sputtering machine.

This thesis aims to accomplish five distinct goals, that will eventually be used to certify the applicability of magnetron sputtering for the purposes of preparing thin-films of carbon for cosmetic jewelry applications. First,
Chapter 1. Introduction

the production of thin-films of carbon, using this technique, will be demonstrated; given the state of the magnetron sputtering system used prior to this work being performed, this was by no means guaranteed prior to this work being performed. Second, these films that arise from these depositions will be characterized using a Raman analysis, it being demonstrated that the resultant sp³ to sp² ratio is similar to that associated with other forms of thin-film carbon; the sp³ to sp² ratio is an often referred metric of thin-film carbon quality; see Figure 1.3.¹ Third, through the use of a variety of different deposition conditions, the deposition parameter space will be sampled, the resultant forms of thin-film carbon being examined through the use of Raman spectroscopy in order to evaluate the corresponding sp³ to sp² ratio [18]. Finally, a means of determining thin-film carbon profiles, through the use of a scanning electron microscope (SEM) analysis, will be developed. Pathways, wherein these intermediary results may ultimately be used in order to assess the adequacy of magnetron sputtering for cosmetic jewelry applications, will then be defined, albeit this work will have to be performed following the completion of this particular thesis.

This thesis is organized in the following manner. In Chapter 2, the background for this research is provided. Then, in Chapter 3, the experimental methodology employed is presented. The results obtained from these experiments are then analyzed in Chapter 4. Finally, conclusions are drawn and some suggestions for future investigation are provided.

¹This figure shows the dependence of the hardness on the sp³ bonding content, these results being from Neuville et al. [17]. Most parameters within thin-film carbon have been characterized in terms of the sp³ bonding content.
Figure 1.3: Relationship between the amount of diamond-like chemical bonds (sp³) in the thin-film carbon and the hardness. This figure is after Neuville et al. [17]. The electronic version of this figure is in color.
Chapter 2

Background

2.1 Thin-film carbon and its impact on society

Carbon’s unusual range of physical properties stems, in large measure, from the diversity of its constituent bonds. Typically, within carbon, sp\(^1\), sp\(^2\), and sp\(^3\) bonds are present. Carbon that is purely comprised of sp\(^2\) bonds in the trigonal crystalline structure, appears black, and is soft to the touch, this form of carbon being referred to as graphite. In contrast, carbon that is purely comprised of sp\(^3\) bonds and is in the tetrahedral crystalline structure, is transparent and exhibits a hardness unrivalled elsewhere in nature, this form of carbon being referred to as diamond. Forms of carbon that possess both sp\(^2\) and sp\(^3\) bonds exhibit material properties that are in between these two extreme cases; sp\(^1\) bonds do occur, but are typically available in much smaller quantities than the sp\(^2\) and sp\(^3\) bonds.

In general, thin-films of carbon possess both sp\(^2\) and sp\(^3\) bonds. It has been found that the ratio of sp\(^3\) bonds to sp\(^2\) bonds determines many of the properties of the resultant thin-films. A high sp\(^3\) bond content is found to provide these coatings with many diamond-like properties. Similarly, a high sp\(^2\) bond content is found to provide thin-film carbon with graphite-like characteristics. Thin-films of carbon are currently being deployed in a wide
2.1. Thin-film carbon and its impact on society

variety of industrial and military settings, including those in the automotive, milling, and drilling industries, in optics, and even in biomechanics [19–23]. For such applications, thin-films of carbon with an abundance of sp$^3$ bonds are preferable.

In this chapter, the background material required for this study is presented. Initially, the peculiar properties of thin-film carbon are accounted for in terms of the nature of the chemical bonds that are present within this material. Following an overview of the most common applications for thin-films of carbon, the societal importance of thin-film carbon is presented. Raman spectroscopy, a non-destructive tool that is to be used for the purposes of this analysis, is then discussed, its use in identifying the nature of the bonds that are present within thin-film carbon being clarified. Challenges, related to the presence of oxygen and contaminants on the surface of the substrate, thereby influencing the adhesion between the thin-film and the underlying substrate, are also presented.

This chapter is organized in the following manner. Section 2.2 explains what thin-film carbon is and discusses the nature of its chemical bonds. The most common deposition techniques, currently employed for the preparation of thin-film carbon, are then introduced in Section 2.3. Potential applications for thin-films of carbon are then presented in Section 2.4. Section 2.5 introduces the reader to the scientific background underlying Raman spectroscopy. Finally, in Section 2.6, the challenges associated with the presence of oxygen, and other contaminants, on underlying titanium substrates, is discussed.
2.2 What is thin-film carbon

Carbon is an element with an allotropic character. It can exist in the form of graphite, where only sp\textsuperscript{2} bonds are present, and in the form of diamond, where only sp\textsuperscript{3} bonds are present, or somewhere in between. It is noted that while graphite and diamond are both forms of carbon, they possess totally different physical properties. Materials with both types of bonds, i.e., sp\textsuperscript{2} and sp\textsuperscript{3} bonds, are found to have properties that are in between these extreme forms of carbon. It is natural to inquire as to what accounts for the differences in the observed properties. It may seem odd that the same element, carbon, can produce so many different types of matter, with such disparate physical properties.

The cause of carbon’s allotropic character lies in the diversity of the hybridization states that are available to it, i.e., sp\textsuperscript{1}, sp\textsuperscript{2} and sp\textsuperscript{3} hybridizations are available. Carbon based atomic orbitals, associated with thin-film carbon, can form new hybrid orbitals, thereby allowing for totally different types of chemical bonding, and therefore, different types of material properties. In diamond, the atomic bonding of the constitutive carbon atoms is entirely sp\textsuperscript{3} in character. Carbon has four valence electrons, and in the case of pure diamond, each of them is assigned to an sp\textsuperscript{3} orbital, $\sigma$ bonds being associated with each such orbital; see, for example, Figure 2.1 [9]. As the $\sigma$ bond is one of the strongest chemical bonds known in nature, it equips diamond with its unique hardness.

If the carbon atoms bond in the form of sp\textsuperscript{2} bonds, however, just three out of the four valence electrons form $\sigma$ bonds, the fourth valence electron
2.2. **What is thin-film carbon**

Figure 2.1: The hybridizations available to carbon atoms in the form of \( sp^1 \), \( sp^2 \), and \( sp^3 \) bonds. This figure is after Robertson *et al.* [9]. The electronic version of this figure is in color.
2.2. What is thin-film carbon

forming a $p\pi$ orbital with a normal orientation to the other $\sigma$ bonds; the bond associated with this $p\pi$ orbital is referred as a $\pi$ bond. $\pi$ bonds are weaker than $\sigma$ bonds, the bonding being weaker on the axis that includes this $p\pi$ orbital. Graphite, however, is comprised only of $sp^2$ bonds. In the $sp^1$ configuration, however, the carbon atom forms two $\pi$ bonds in the $y$ and $z$ axes. Just as in the $x$ axis, $\sigma$ bonds are formed with the two valence electrons. The ratio of the number of $sp^3$ bonds to the number of $sp^2$ bonds is a common parameter describing the bonding character of thin-films of carbon, and many of its material properties may be directly related to this ratio.

There are two commonly employed thin-film carbon deposition techniques that are widely used in order to fabricate thin-films of carbon: (1) chemical vapor deposition (CVD), and (2) physical vapor deposition (PVD). The most commonly used approach, the CVD process, is most commonly employed using the plasma enhanced form of this process, i.e., through the use of PECVD. In PECVD, a voltage is applied across an inert gas in order to create a plasma, thereby enabling the deposition of thin-film carbon. This process allows for the gas molecules within the plasma chamber to be cracked, the cracked gas molecules then depositing onto a heated substrate, thereby allowing for the growth of a thin-film of carbon. Given that it is a CVD process, the resultant thin-film coating is relatively uniform. In PVD techniques, however, such as sputtering, an inert gas is ionized in order to create a plasma. The source material, carbon for example, is then bombarded with these ions, and as a result, a stream of carbon atoms from this source are blasted into the vacuum. These carbon atoms will then deposit
2.2. What is thin-film carbon

onto the substrate, which has to be in a line-of-sight.

In PECVD, other gases are involved in the growth of the thin-film carbon. Therefore, in most forms of thin-film carbon, there is a fair amount of hydrogen incorporated into the film. Another characteristic of PVD processes is the shadowing effect that arises, that does not exist in CVD processes. Figure 2.2 [24] illustrates this shadowing effect. In sputtering, for example, the source material comes from one direction only, whereas in PECVD, the gaseous source material interacts everywhere on the growing thin-film surface. While PECVD and sputtering are the dominant deposition techniques used in research and industry in order to deposit thin-film carbon, other deposition techniques are also available for the preparation of this material. For example, ion beam, cathodic arc, and pulsed laser deposition process have also been used in order to deposit thin-film carbon. These techniques are described elsewhere in the literature [7, 9, 25].

Figure 2.3 [9] shows a ternary phase diagram by Robertson et al. [9], this diagram providing a good overview of the different forms of thin-films of carbon that have been produced. Amorphous carbon structures with a high sp\(^2\) content are presented in the lower left hand corner of this diagram and include materials such as soot, glassy, and evaporated carbon. Materials with a high sp\(^3\) content are referred to as ta-C, and placed in the upper corner of this ternary phase diagram. Various forms of thin-film carbon, with different amounts of hydrogen, can also be produced, as depicted in the lower right hand corner. Thin-film carbon, with a fair amount of hydrogen, are, for example, hydrocarbon polymers, polyacetylene (CH), and polyethylene (CH\(_2\)). Thin-film carbon, with a high sp\(^3\) content, is usually preferred due
2.2. What is thin-film carbon

Figure 2.2: Side view of a thin-film deposition in a groove. a) CVD processes are without a shadowing effect. b) PVD processes are with a shadowing effect. This figure is after Street [24]. The electronic version of this figure is in color.
2.2. What is thin-film carbon

Figure 2.3: Ternary phase diagram for the different kinds of thin-film carbon. The approximate locations for the samples considered in this work is indicated in this figure. This figure is after Robertson et al. [9]. The electronic version of this figure is in color.
to its diamond-like properties, such as durability and hardness. In addition, thin-films of carbon with a high sp\(^3\) content are chemically inert and fully biocompatible. Since the atomic distribution within most forms of thin-film carbon is amorphous in nature, the color of the resultant material appears black, but with a shiny and glossy look. Its lustrous appearance makes this coating very attractive for cosmetic jewelry application purposes.

In this thesis, a magnetron sputtering process is used in order to grow a particular form of thin-film carbon. Sputtered thin-film carbon is usually referred to as amorphous carbon (a-C), and most often possesses an amorphous distribution of atoms with no grain boundaries. If the sp\(^3\) content reaches a fairly high amount, i.e., in excess of 80\% of the overall bonds, then the carbon is referred to as ta-C. This material, i.e., ta-C, is considered to be one of the hardest materials, after pure diamond, and this property is believed to arise from its high content of sp\(^3\) bonds [9, 17].

### 2.3 Common deposition techniques

Sputtering is a commonly available PVD technique, used for a variety of industrial application owing to its adaptability, the possibility to sputter many different materials, and the option to easily scale up the deposition system [9]. An overview of the terminology of the vacuum chamber, regarding this deposition technique, is given in Section 3.2.1. Sputtering is a PVD process. For the case of thin-film carbon deposition, the source material is a solid block of graphite that is bombarded by ionized inert gases. The loosened graphite material then deposits onto the substrate. The deposition
2.3. Common deposition techniques

occurs in a line-of-sight, and the resultant deposition is not necessarily uni-
form in thickness. In contrast, in CVD, the source material is introduced as
a gas, and it reacts with the substrate surface at an elevated temperature,
i.e., around 1000°C. With sputtering, on the other hand, the process takes
place almost at room temperature, which allows for film depositions on plas-
tic substrates, this being a considerable advantage for certain applications.
For the special case of magnetron sputtering, the electrons in the plasma
are trapped close to the target through the use of magnets, which are placed
behind the sputtering source so as to increase the formation of argon ions,
and hence, the bombardment rate of the target. The sputtering process is
relatively easy to control through the application of power and through the
amount of gas introduced into the deposition chamber [9].

PECVD is another very common deposition technique. In this approach,
a plasma assists the deposition process, thereby allowing for the use of a
lower processing temperature; for the case of thin-film carbon depositions,
temperatures as low as 700 K can be maintained. The difference with sput-
ttering is that the source material may be introduced in a gas instead of as a
solid block. A challenge with gas-based deposition systems is that the depo-
sition chambers themselves, employed for such depositions, possess a mem-
ory corresponding to past depositions, i.e., trace elements, from previous
depositions, incorporate themselves into present depositions, thereby chang-
ing the properties of the resultant thin-films. The advantage of PECVD is
its ability to deposit relatively uniform thin-film layers, not just in a line-
of-sight manner. Unfortunately, in order to get a uniform thin-film carbon
layer, the gas is not pure carbon, but part of a larger gaseous hydrocarbon,
2.4 Applications of thin-film carbon

As described previously, thin-films of carbon, with a high sp\(^3\) content, possess exceptional qualities, such as high durability, hardness, and biocompatibility. The smooth coating that results from such depositions also possess a very low coefficient of friction and, therefore, thin-films of carbon are often used for coating tools and machine parts in order to increase their lifetime. Aside from their mechanical advantages, thin-film carbon coatings can also be used for decorative purposes. The nice shiny black coating associated with such films has a very attractive look and feel. This is what makes them particularly appealing for the cosmetic jewelry industry. This thesis investigates the influence of substrate geometry, i.e., flat titanium as opposed to titanium rings, on the resultant thin-film carbon properties. Cosmetic jewelry rings benefit from all of the properties of a thin-film carbon coating, and therefore, it is crucial to achieve the same quality of films deposited on rings as on flat substrates.

High performance applications in the automotive industry are inconceivable without the use of thin-film coatings. With such coatings, the piston pins can withstand much more pressure over longer periods of time. Thus, faster and stronger cars can be produced using this technology. The Dodge 2015 Challenger SRT is a good example of an automotive application for 

such as methane (CH\(_4\)). Thus, thin-films of carbon, grown with a PECVD system, possess a fair amount of hydrogen, and this undoubtedly influences the properties of the resultant thin-films.
2.4. Applications of thin-film carbon

diamond-like-carbon coatings. Such coatings have played a decisive role in achieving the gains in performance that have been attained in this new model when contrasted with that associated with previous models.

Another industry that has benefitted from the increased hardness and durability associated with thin-film carbon is the milling and drilling industries [19]. Besides a significant increase in the hardness of cutting tools, and therefore, a corresponding enhancement in their durability, cutting tools coated with a thin-film carbon layer have been found to reduce the surface roughness of the cut material [20]. This realization has substantially contributed to the success of these industries.

Carbon can be considered to be the basis of life, as it exists abundantly on Earth and bonds readily with other elements, such as oxygen, hydrogen, and nitrogen, to form long and complex molecules. Carbon is therefore compatible with living tissues. Since thin-films of carbon are biocompatible, they may also be used for implants, such as hip joint replacements. Moving parts in the body require a smooth and almost frictionless surface without any residual metallic wear debris. Allen et al. [23] investigated the biocompatibility of thin-film carbon coated parts, both in vitro and in vivo. These tests have demonstrated that thin-films of carbon can coexist with living tissues or organisms without causing harm. Thus, in terms of biomedical engineering applications, thin-film carbon has a virtually unlimited potential.

Thin-films of carbon are also commonly applied in optics. The sensitivity of long-period fibre gratings to variations in the external refractive index, for example, can be improved through the use of a thin-film of carbon [21].
The advantage of thin-film carbon over other types of thin-films in optical applications, is the enhanced resistance to mechanical impact and corrosion. For front looking infrared cameras, which are also used in military applications, a thin-film carbon coating on the lens assembly has found to reduce the Narcissus effect, which is a reflection of the detector onto itself from the front lens [22].

2.5 Raman spectroscopy in the characterization of thin-film carbon

The Raman effect was first discovered by Chandrasekhara Venkata Raman (1888 - 1970), who was born in southern India. On a sea voyage, going back home to India from England, he was able to experimentally demonstrate that the blue color of the sea is not due to a reflection from the blue sky. To do this, Raman showed, through the use of a diffraction grating, that the maximum spectral intensity for the sea and the sky occur at different wavelengths, and therefore, another explanation for the blue color of the sea must exist. He later discovered a frequency shift in the scattered light. This change in the frequency, and therefore, in the wavelength of the incident light due to inelastic scattering by water molecules, is the actual cause for the blue color of the sea. The color of the sky, however, is due to Rayleigh scattering, which is an elastic scattering process. Since the Rayleigh scattering intensity is proportional to $1/\lambda^4$, blue light gets Rayleigh scattered the most owing to its short wavelength in the visible spectrum. The different scattering processes are summarized in Figure 2.4 [18].

24
2.5. *Raman spectroscopy in the characterization of thin-film carbon*

Figure 2.4: Light scattering can be either elastic (Rayleigh scattering) or inelastic (Stokes or anti-Stokes Raman scattering). This figure is after Barton *et al.* [18]. The electronic version of this figure is in color.
A Raman spectroscopy system consists of four basic components: (1) a Raman source, or excitation source with an incident laser beam, (2) some optical elements in order to focus this laser beam onto the sample, (3) a collection of optical elements and filters, and finally, (4) a detector, i.e., spectrograph, and a camera in order to collect the scattered light. Figure 2.5 provides a schematic overview of a Raman spectroscopy system. In order to separate Raman scattering from Rayleigh scattering, a dichroic beamsplitter, i.e., a band-pass filter, is used. Notch filters confine the laser within the Raman spectrum, and reduce, in this way, the strong Rayleigh scattering of light.

In thin-film carbon, the light associated with a laser beam gets scattered differently for the different hybridization states. The change in frequency/wavelength is usually denoted as the Raman shift ($\Delta k$ in cm$^{-1}$), which is the difference between the reciprocal of the excitation wavelength, $\lambda_0$, from the reciprocal of the scattered wavelength, $\lambda_1$, i.e.,

$$\Delta k (\text{cm}^{-1}) = \left( \frac{1}{\lambda_0 (\text{nm})} - \frac{1}{\lambda_1 (\text{nm})} \right) \times \left( \frac{10^7 \text{ nm}}{\text{cm}} \right).$$

(2.1)

The change in frequency is caused either by the emission or the absorption of energy, which results in a lower and higher vibrational mode of the molecules, respectively; see Figure 2.4. The energy emission or absorption, $\Delta E$, is related to the frequency shift, $\Delta \omega$, according to

$$\Delta E_{\text{Raman}} = h \cdot \Delta \omega_{\text{Raman}}.$$

(2.2)

In the case of a phonon emission, the frequency shift (downshift) is termed a Stokes shift. Instead, the absorption of a phonon causes an upshift of the frequency, and is denoted as an anti-Stokes shift; see Figure 2.6 [26]. The

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2.5. *Raman spectroscopy in the characterization of thin-film carbon*

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2.5. *Raman spectroscopy in the characterization of thin-film carbon*

Figure 2.5: General schematic overview of a Raman spectroscopy system. This figure is after Barton *et al.* [18]. The electronic version of this figure is in color.
2.5. **Raman spectroscopy in the characterization of thin-film carbon**

Figure 2.6: Raman scattering: + sign for phonon emission (Stokes process) / - sign for phonon absorption (anti-Stokes process). This figure is after Kittel [26]. The electronic version of this figure is in color.
2.5. *Raman spectroscopy in the characterization of thin-film carbon*

intensity of the scattering is much smaller for the anti-Stokes shift, as the population of molecules with a higher initial energy ground state is much lower due to the Boltzmann distribution, i.e.,

\[ N \propto \exp\left( -\frac{E}{k_B T} \right). \]  

(2.3)

Today, Raman spectroscopy is the most commonly used method to determine the chemical nature of thin-films of carbon, and the Stokes shift is the primary focus of analysis [10, 12, 15, 26–31]. The major advantage of Raman spectroscopy is its non-destructive character, and the wide availability of such equipment.

For the specific case of thin-film carbon, Raman spectra, between 800 to 2000 cm\(^{-1}\), are the most commonly considered; beyond this range, the Raman spectra associated with thin-film carbon is typically flat and featureless. The Raman spectrum associated with a sample of thin-film carbon tends to exhibit two distinct peaks, one being around 1350 cm\(^{-1}\), the other being around 1580 cm\(^{-1}\). These two peaks are referred as the D and G peaks, respectively. The G peak, where G denotes graphite, is believed to be related to the sp\(^2\) stretch vibrations of benzene rings, or other such molecular chains [15, 32]. The D peak, where D denotes disordered, is associated with the presence of sp\(^3\) bonding. The scattering related to the presence of sp\(^2\) bonds causes a frequency shift, or a Raman shift, centered around 1580 cm\(^{-1}\), and the scattering related to the presence of sp\(^3\) bonds causes a Raman shift, centered around 1350 cm\(^{-1}\). These two peaks in the Raman spectra are often used in order to provide an indication as to the sp\(^3\) to sp\(^2\) bonding ratio. A controversy exists in the literature as to whether it is the
2.5. *Raman spectroscopy in the characterization of thin-film carbon*

ratio of the peaks or the integrated intensities of the Raman spectrum that determines the sp$^3$ to sp$^2$ bonding ratio. For the purposes of this particular analysis, the ratio of the integrated intensities is employed, this being the more common approach.

Schwan *et al.* [15] suggest that the D peak in the Raman spectrum is due to disordered structures of carbon, or also the ring stretch vibration of benzene rings. A Raman peak around 1180 cm$^{-1}$ is suggested to be due to sp$^3$-rich phases, although no peak around 1180 cm$^{-1}$ Raman shift is found for the raw measured experimental data found in this work.

Several other peaks in the Raman spectra are observed besides the D-and G-peaks. Some of the key peaks, found in the literature, are summarized by Schwan *et al.* [15]:

- 1140 cm$^{-1}$: nanocrystalline diamond
- 1170 cm$^{-1}$: hexagonal diamond
- 1180 cm$^{-1}$: nanocrystalline diamond or hexagonal diamond or sp$^3$ rich phases
- 1237 cm$^{-1}$ and 1306 cm$^{-1}$: hexagonal diamond
- 1305 cm$^{-1}$: hexagonal diamond
- 1332 cm$^{-1}$: cubic diamond
- 1350 cm$^{-1}$: D-Peak, microcrystalline graphite, alternating ring stretch vibration in benzene rings
- 1490 cm$^{-1}$: semicircle ring stretch vibration of benzene rings
- 1580 cm$^{-1}$: G-Peak, sp$^2$ stretch vibration in benzene rings or sp$^2$ stretch vibration of olefinic/conjugated chains
2.5. Raman spectroscopy in the characterization of thin-film carbon

Some of these different vibrational modes are visually depicted in Figure 2.7 [15].

The most common laser source excitation wavelengths used in the literature are 632.8 nm by Wu et al. [25], 325 and 532 nm by Cekada et al. [33], 633 nm by Khun et al. [27] and Maharizi et al. [14], 532 nm by Wojciechowski et al. [13] and Zhao et al. [10], and 514.5 nm by Buijnsters et al. [34]. In this work, the excitation wavelengths 442 and 633 nm are used. 325 nm was not an option as there is not enough scattering intensity obtained for such an excitation. The noise is found to be much greater for the case of 633 nm laser excitation. Therefore, 442 nm is the chosen wavelength for most of the Raman analyzes presented in this thesis.

A representative Raman spectrum, from the work of Zhao et al. [10], corresponding to a thin-film of carbon, is shown in Figure 2.8 [10]. The sp\(^3\) to sp\(^2\) bonding ratio was stated to be 0.76, and this corresponds to the ratio of the integrated intensities of two Gaussian curves that fit this Raman spectrum in a least-squares sense. In Section 4.5, a result similar to this is verified and discussed, along with other results from the literature. While Zhao et al. [10] has a very congruent Gaussian fit with the experimentally obtained Raman spectrum, Sung et al. [31] was not able to fit the Gaussian peaks as nicely; see Figure 2.9 [31], for example. It is clear that there is a significant deviation between the fitted curve and the original data. Nevertheless, both used the same approach in interpreting the experimental results, and assessed the sp\(^3\) to sp\(^2\) bonding ratio using the integrated

\(^2\)This is because the optical absorption coefficient at this wavelength is so pronounced that a very small amount of material is probed for this wavelength.
2.5. Raman spectroscopy in the characterization of thin-film carbon

Figure 2.7: (a) 1588 cm$^{-1}$: stretch vibrations in benzene, (b) 1486 cm$^{-1}$: semicircle stretch vibrations in benzene, and (c) 1311 cm$^{-1}$: alternating ring stretch vibrations in benzene. This figure is after Schwan et al. (1996) [15]. The electronic version of this figure is in color.
2.5. Raman spectroscopy in the characterization of thin-film carbon

The spectra of Raman cannot determine the absolute amount of sp<sup>3</sup> and sp<sup>2</sup> fraction, but the relative quantity can be deduced. The spectra of our films were analyzed by Origin 75 using Gauss fit, and the D peak and G peak are found at 1380 cm<sup>-1</sup> and 1560 cm<sup>-1</sup> respectively, which is shown in figure 3. The ratio of \( \frac{I_D}{I_G} \) is ranging from 0.68 to 0.94 for particles and the main values are focused between 0.7 and 0.8 when the data was collected from a more smooth area. This suggests that the structure of DLC film structure have no relations to substrates as expected.

Figure 2.8: The Raman spectrum determined by Zhao et al. [10]. The two Gaussian peaks, selected for this peak fitting process, are depicted, as is their sum. The resultant integrated intensities suggest that \( \frac{I_D}{I_G} = 0.76 \) [10], where \( I_D \) and \( I_G \) denote the integrated intensities associated with the D- and G-peaks, respectively. The electronic version of this figure is in color.
Figure 2.9: The Raman spectrum of a thin-film carbon sample, referred as Sample A in the original article, by Sung et al. [31].
2.6 Problems with the presence of oxygen and other contaminants

Even if the thin-film carbon is hard, presumably due to a high sp$^3$ content, there is no guarantee that it will adhere to the underlying substrate. Adhesion is critical to the effectiveness of the resultant layer of thin-film carbon. Good adhesion can only be achieved with a very clean and oxide-free substrate surface. In order to achieve proper adhesion, there are several conditions that one must typically satisfy prior to deposition. First, before deposition, the substrate surface has to be free from any dirt and dust. Second, the substrate surface must be cleaned from organic contamination and metal oxidation, as oxygen can significantly reduce the strength of the interatomic bonding, thereby reducing the ability of the resultant thin-film to adhere with the underlying substrates; see Figure 2.10 [17], for example. The surface of the substrate can be cleaned through the use of soapy water and acetone in an ultrasonic cleaning for pre-treatment. In order to remove the oxygen layer, the substrate must be cleaned in a vacuum chamber through the use of a plasma. This is further discussed in Section 3.2.5.
2.6. Problems with the presence of oxygen and other contaminants

Figure 2.10: Adhesion strength for different substrates and coating materials. This figure is after Neuville et al. [17]. The electronic version of this figure is in color.
Chapter 3

Experiment

3.1 Deposition of thin-film carbon

Thin-film carbon is presently being employed for a variety of industrial and military settings. It has also allowed for the development of many new and innovative products, such as high performance drills and other tools, and even pistons for a car. A number of deposition techniques that may be employed for the fabrication of thin-film carbon are available. Each method presents its unique advantage and produces a different kind of thin-film carbon. The selection as to which form of thin-film carbon should be employed depends critically on the particular application at hand. A long-term goal of this research thrust would be the determination of a price-performance curve for thin-film carbon, in which the trade-off between price and quality is quantitatively established. Given the time limitations encountered during the writing of this thesis, this determination will be beyond the scope of this thesis. This thesis may be viewed as taking the first step towards the realization of this long-term goal.

In this work, magnetron sputtering is used to create amorphous thin-films of carbon. Even though amorphous carbon is not the hardest material available, its hardness can be readily increased through increases in the sp$^3$
3.2. Magnetron sputtering

Bond content, to become ta-C, at the expense of a slow growth rate [9, 12]. In this thesis, the feasibility of producing thin-films of carbon with a high amount of sp³ bonds with the magnetron sputtering system that is available will be assessed. The answer to this question provides the first step towards the resolution of the ultimate question that this body of research work aims to address, i.e., whether or not magnetron sputtering is adequate for the cosmetic jewelry applications in mind.

After an introduction to the magnetron sputtering machine used in this study, a description of the sample numbering and preparation means is provided. The pre-cleaning process with argon plasma is also explained and documented. Finally, the specifications of the Raman and the SEM machines, respectively, used for analyzing the samples, is given.

This chapter is organized in the following manner. Section 3.2 describes the sputtering machine used for preparing the thin-film carbon samples along with a description about the sample preparation, numbering, and cleaning as well as the deposition processes. The Raman measurements, performed on the thin-film carbon samples, are then described in Section 3.3. Finally, the SEM machine, and the approach to measure the thickness and the material composition of the thin-films of carbon, are explained in Section 3.4.

3.2 Magnetron sputtering

3.2.1 Machine: Hummer XII

The deposition system used for this research is a magnetron sputtering machine manufactured by Anatech LTD. The particular machine, that is
Figure 3.1: The sputtering machine, the Hummer XII by Anatech Ltd, used in this work for thin-film carbon depositions. The electronic version of this figure is in color.
3.2. Magnetron sputtering

employed for the purposes of this study, is depicted in Figure 3.1. This machine was manufactured about 10 years ago. All control knobs are analog and manually controlled. There is no closed-loop control system, and visual inspection during operation is required. The chamber has no load lock available in order to allow one to insert a sample without breaking the vacuum. The top lid has to be opened in order to place the samples in the chamber, and the chamber is exposed to oxygen and contaminants during every use; the same difficulties were noted by Dr. Jonathan E. Lee in his Ph. D. Thesis for the same kind of sputtering machine [35]. Due to the lack of any closed-loop control and inaccuracies in the analog control knobs, i.e., it has a 10 kΩ potentiometer with ±10% tolerance, it is not possible to keep all process parameters the same for each run. For most runs, an argon gas flow of 12.5 sccm is chosen, except for sample numbers 106-2, 207-1, 210-1 and 210-2. To achieve a deposition pressure of 1 mTorr, the argon gas flow is set at 3.5 standard cubic centimetre per minute (sccm) for experiment 207-1 and 4.7 sccm for experiment 106-2.

The deposition parameters that are manually controllable in this set of experiments are the following: (1) the choice of using DC power excitation (at 400 W) or RF power excitation (at 200 W), (2) the gas flow rate, and (3) the deposition times. The throttling valve is not used during these depositions. The temperature can be controlled, but the heater is not used in this setup, since, for thin-film carbon sputtering, usually the temperature is kept low [12]. Figure 3.2 shows the setup of the vacuum chamber, with its components.
Figure 3.2: Terminology of the sputtering vacuum chamber. The electronic version of this figure is in color.
3.2. Magnetron sputtering

3.2.2 Chrome sputtering

The magnetron sputtering machine, i.e., the Hummer XII, is also used for chrome sputtering. Even though this sputtering machine offers the advantage of multiple material depositions, there is always some inevitable cross-contamination that occurs from one deposition to the next. The chrome sputtering is performed with a very similar recipe to the thin-film carbon depositions, i.e., chrome sputtering is accomplished with a DC power of 400 W and an argon gas flow of 12.5 sccm for about 11 minutes. The chrome material deposits not only on the substrate, but also on the walls of the vacuum chamber. This thin-film layer of chrome entraps a lot of oxygen and other contaminant gases. The more the machine is used, the more contaminated it becomes. It is found that it is best to grind, or wipe away, the resultant thin-film of chrome from the wall of the vacuum chamber after every use. In order to save time, however, for the purposes of those experiments, the chamber is cleaned after every 50 depositions. Tests, aimed at contrasting the thin-film carbon that is produced following many depositions without cleaning with those produced immediately following a cleaning, have been performed. No significant change in the quality of the obtained films is observed. It is believed that the main problem that detracts from the thin-film quality, in terms of its adhesion at least, is the oxygen layer on the titanium substrate, which is much larger than the entrapped amount of oxygen in the contaminated wall.
3.2. Magnetron sputtering

3.2.3 Sample type and numbering

Different types and shapes of substrates are employed for the purposes of this research. These include consideration of the following:

− Corning® EAGLE XG™ AMLCD glass substrates
− titanium substrates
− chrome substrates
− flat substrates
− ring substrates with a diameter of about 1 inch

Each deposition run has a unique number assigned to it to describe the substrate, the experimental number, and the sample number considered. The first number indicates if the substrate is a titanium ring (number 1) or flat (number 2). The second and third numbers are the experimental numbers in chronological order. The last number, following the dash, describes which chamber run the sample is prepared in, there being several samples prepared for each such run. A full list of all of the samples, their type and numbers, is provided in Chapter 4 in Section 4.2.

3.2.4 Substrate preparation

Prior to deposition, the titanium samples are mechanically polished with a buffing machine. It is found that a shiny and smooth surface increases the glossy look of the resultant thin-film carbon layer, and that this is important for cosmetic jewelry applications. Then, the substrates are cleaned in an ultrasonic bath in hot water with some all purpose cleaner (TSP) for about 20 minutes in order to remove any dirt accumulated from the polishing
process. Finally, the substrates are cleaned in another ultrasonic bath with pure acetone in order to eliminate any residual organic contaminants. In order to allow the substrates to dry in a streak-free manner, they are swung on a cord to dry equally in the air. The rings are never touched by human hands during the entire cleaning process.

3.2.5 RF cleaning

Part of substrate preparation is the proper cleaning of the surface. As was described in the previous subsection, the substrates are cleaned with soapy water and through the use of acetone in an ultrasonic bath. After putting the substrates in the vacuum chamber, in order to reduce as much oxygen as possible, a vacuum pressure of about $1.3 \times 10^{-4}$ Torr is created. Still, there is an oxygen and contamination layer on the substrate that cannot be removed with the cleaning bath.

To clean the substrates from contamination and oxygen on a molecular level, an argon based plasma cleaning process is used. The vacuum chamber is filled with argon gas at a fairly high argon gas flow, i.e., 75 sccm, and ionized through the application of an RF power of 200 W at 13.56 MHz. The substrate surface gets bombarded with argon ions, and this removes the foreign molecules that cause contamination, and thus, no chemical reaction, or oxidation, takes place during this process. Argon RF plasma cleaning removes many types of contamination, such as fluorine, organic contamination, and metal oxides [36]. By bombarding the substrate with argon ions, the surface gets roughened, and the bonding or adhesion is improved. A water drop test is performed in order to verify the successful titanium
ring substrate cleaning with this process. For this purpose, a water drop is dropped on an uncleaned titanium ring. With an unprocessed ring, the water drop splits into several little drops that stick onto the surface. After an RF cleaning for 85 minutes, however, the water drop will slide perfectly down the ring surface, and does not stick to the surface as with the uncleaned ring. The comparison between this water drop test is illustrated in Figure 3.3.

### 3.2.6 Recipe: a step-by-step guide

The overall sputtering process may be divided into four basic steps: (1) a startup phase, (2) an RF argon plasma cleaning process, (3) sputtering, and (4) the shut-down sequence. After cleaning the substrate, the samples are placed into the chamber, and the power and gas supplies are switched on for the machine. After pumping down to a vacuum of about $1.3 \times 10^{-4}$ Torr, the RF argon plasma cleaning process can be started. After cleaning the substrate surface, the substrate has to be cooled down before the sputtering procedure can take place. After executing the proper shut-down sequence, the chamber can be vented and the coating process is finished. This recipe is explained, in detail, in Appendix 5 in a chart for a step-by-step guide.

### 3.2.7 Experiments

Ten different sputtering experiments are performed in order to partially probe the deposition parameter space in terms of different argon gas flows, power selections, sputtering times, and substrate types and geometries employed. Table 3.1 provides an overview of all the performed experiments.
3.2. Magnetron sputtering

Figure 3.3: Water drop test for a titanium ring before and after argon plasma cleaning. Left: The uncleaned ring, with water drops sticking onto the surface. Right: An RF argon plasma cleaned ring, with water drops sliding down the cleaned surface without residual stuck water drops. The right image is blurry owing to the absence of a proper focal point and photographic equipment limitation. The electronic version of this figure is in color.
3.2. Magnetron sputtering

Table 3.1: An overview of the sputtering experiments corresponding to the different sample numbers. Deposition parameters for each sample, with the setup and deposition time information indicated. Reference sample number 201-2 is shaded.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Substrate</th>
<th>RF / DC</th>
<th>Power</th>
<th>Gun-substrate distance</th>
<th>RF Cleaning time</th>
<th>Pre-sputtering time</th>
<th>Sputtering time</th>
<th>Argon</th>
</tr>
</thead>
<tbody>
<tr>
<td>106-2</td>
<td>Ti ring</td>
<td>RF</td>
<td>200 W</td>
<td>60 mm</td>
<td>87 min</td>
<td>5 min</td>
<td>175 min</td>
<td>4.7 sccm</td>
</tr>
<tr>
<td>111-1</td>
<td>Cr on Ti ring</td>
<td>DC</td>
<td>400 W</td>
<td>60 mm</td>
<td>61 min</td>
<td>3 min</td>
<td>360 min</td>
<td>12.5 sccm</td>
</tr>
<tr>
<td>115-1</td>
<td>Ti ring</td>
<td>RF</td>
<td>200 W</td>
<td>60 mm</td>
<td>30 min</td>
<td>5 min</td>
<td>120 min</td>
<td>12.5 sccm</td>
</tr>
<tr>
<td>115-3</td>
<td>Ti ring</td>
<td>RF</td>
<td>200 W</td>
<td>60 mm</td>
<td>30 min</td>
<td>5 min</td>
<td>120 min</td>
<td>12.5 sccm</td>
</tr>
<tr>
<td>121-3</td>
<td>Ti ring</td>
<td>RF</td>
<td>200 W</td>
<td>60 mm</td>
<td>40 min</td>
<td>5 min</td>
<td>118 min</td>
<td>12.5 sccm</td>
</tr>
<tr>
<td>123-3</td>
<td>Ti ring</td>
<td>RF</td>
<td>200 W</td>
<td>60 mm</td>
<td>40 min</td>
<td>5 min</td>
<td>120 min</td>
<td>12.5 sccm</td>
</tr>
<tr>
<td>201-2</td>
<td>Glass</td>
<td>DC</td>
<td>400 W</td>
<td>60 mm</td>
<td>20 min</td>
<td>3 min</td>
<td>60 min</td>
<td>12.5 sccm</td>
</tr>
<tr>
<td>204-2</td>
<td>Glass</td>
<td>RF</td>
<td>200 W</td>
<td>60 mm</td>
<td>20 min</td>
<td>3 min</td>
<td>60 min</td>
<td>12.5 sccm</td>
</tr>
<tr>
<td>207-1</td>
<td>Glass</td>
<td>RF</td>
<td>200 W</td>
<td>60 mm</td>
<td>20 min</td>
<td>3 min</td>
<td>60 min</td>
<td>3.5 sccm</td>
</tr>
<tr>
<td>210-1</td>
<td>Glass</td>
<td>RF</td>
<td>200 W</td>
<td>60 mm</td>
<td>20 min</td>
<td>3 min</td>
<td>60 min</td>
<td>25 sccm</td>
</tr>
<tr>
<td>210-2</td>
<td>Flat Ti</td>
<td>RF</td>
<td>200 W</td>
<td>60 mm</td>
<td>20 min</td>
<td>3 min</td>
<td>60 min</td>
<td>25 sccm</td>
</tr>
</tbody>
</table>
Sample number 115-1 and 115-3 are produced in the same sputtering run. The thickness of the thin-film carbon is determined for sample number 115-1 and the Raman spectrum is obtained for all other samples; the thin-film thickness corresponding to only one thin-film is determined owing to time limitations. Table 3.2 shows all of the sputtering samples that are prepared and analyzed for the purposes of this thesis.

### 3.3 Raman Spectroscopy

#### 3.3.1 Machine: LabRAM HR

The machine used for this Raman analysis is a LabRAM HR Raman confocal microscope by Horiba Scientific, a picture of which is shown in Figure 3.4. The source laser is an HeCd laser with a 442 nm wavelength and 2400 gratings. For all Raman measurements, an objective lens, with a 100 × magnification and a numerical aperture (NA) of 0.9 is used. For sample 115-3, the lens is changed to 50 × magnification in order to obtain a better Raman result. The laser spot size is about 0.8 µm for this setup for a Raman source of 442 nm. The original laser power is 2 mW/µm² and no power filter is used for the measurements. Therefore, the total applied power on a spot of about 2 µm² is around 4 mW. The spectral resolution is 0.05 cm⁻¹ over the Raman shift range, i.e., between 800 and 2000 cm⁻¹. Two scans for each spectrum are performed, so as to reduce the corresponding signal-to-noise ratio. This machine also supports the source wavelengths of 325 and 632.817 nm. The later will be referred to as 633 nm for the purposes of this work, as no signal is obtained for the 325 nm case.
3.3. Raman Spectroscopy

Table 3.2: Eleven samples are prepared and analyzed in this work. Six titanium ring substrates, four flat glass substrates, and one flat piece of titanium substrate are considered. Sample number 201-2 is the reference sample. The electronic version of these figures is in color.

<table>
<thead>
<tr>
<th>Sample number 106-2</th>
<th>Sample number 111-1</th>
<th>Sample number 115-1</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Image" /></td>
<td><img src="image2" alt="Image" /></td>
<td><img src="image3" alt="Image" /></td>
</tr>
<tr>
<td>Sample number 115-3</td>
<td>Sample number 121-3</td>
<td>Sample number 123-3</td>
</tr>
<tr>
<td><img src="image4" alt="Image" /></td>
<td><img src="image5" alt="Image" /></td>
<td><img src="image6" alt="Image" /></td>
</tr>
<tr>
<td>Sample number 201-2</td>
<td>Sample number 204-2</td>
<td>Sample number 207-1</td>
</tr>
<tr>
<td>(Reference)</td>
<td><img src="image7" alt="Image" /></td>
<td><img src="image8" alt="Image" /></td>
</tr>
<tr>
<td>Sample number 210-1</td>
<td>Sample number 210-2</td>
<td></td>
</tr>
<tr>
<td><img src="image9" alt="Image" /></td>
<td><img src="image10" alt="Image" /></td>
<td></td>
</tr>
</tbody>
</table>
3.3. Raman Spectroscopy

Figure 3.4: Front side of the LabRAM HR Raman confocal microscope by Horiba Scienfic. The electronic version of this figure is in color.
3.3. Raman Spectroscopy

3.3.2 Measurements

All ten sputtering samples are analyzed using Raman spectroscopy. All the Raman measurements are performed with the following settings:

− no power filter
− a 100 µm hole
− a 100 × magnification lens with a NA³ = 0.9
− 20 seconds of acquisition time
− 442 nm laser source excitation (except for sample 201-2, also 633 nm)
− a spot size of 0.8 µm at 442 nm
− power intensity: 2 µm²
− 2400 gratings for 442 nm
− spectral resolution of 0.05 cm⁻¹ over a Raman shift range from 800 to 2000 cm⁻¹
− two scans per spectrum, so as to reduce the signal-to-noise ratio

The samples are placed on microscope glass, as shown in Figure 3.5 for the reference sample (sample number 201-2), i.e., a thin-film of carbon deposited on glass using magnetron sputtering at a DC power of 400 W for 60 minutes, with a 12.5 sccm argon gas flow. The titanium rings are hung on a pen under the lens so as to focus the laser on top of the curved area, as depicted in Figure 3.6. Table 3.3 summarizes all of the Raman measurements that are performed in this work with the specific Raman settings.

³The numerical aperture (NA) defines over what range the lens can accept or emit light. The numerical aperture is dimensionless.
3.3. Raman Spectroscopy

Figure 3.5: Planar sample placement for Raman spectroscopy. The reference sample, i.e., sample number 201-2, a thin-film of carbon deposited on glass using magnetron sputtering at a DC power of 400 W for 60 minutes, with a 12.5 sccm argon gas flow, is depicted in this image. The electronic version of this figure is in color.
Figure 3.6: Sample placement for Raman spectroscopy. A plain titanium ring is shown as an example. The electronic version of this figure is in color.
3.3. Raman Spectroscopy

Table 3.3: Overview of the Raman measurements and measurement settings. All Raman measurements, performed in this work, with the corresponding measurement settings. Reference sample number 201-2 is shaded. (* without background compensation, ** with background compensation; see Section 4.3.4).

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Raman source</th>
<th>Lens magnification</th>
<th>Acq. time</th>
<th>Power filter</th>
</tr>
</thead>
<tbody>
<tr>
<td>106-2</td>
<td>442 nm</td>
<td>100×</td>
<td>20 sec</td>
<td>none</td>
</tr>
<tr>
<td>111-1</td>
<td>442 nm</td>
<td>100×</td>
<td>20 sec</td>
<td>none</td>
</tr>
<tr>
<td>115-3</td>
<td>442 nm</td>
<td>50×</td>
<td>20 sec</td>
<td>none</td>
</tr>
<tr>
<td>121-3</td>
<td>442 nm</td>
<td>100×</td>
<td>20 sec</td>
<td>none</td>
</tr>
<tr>
<td>123-3</td>
<td>442 nm</td>
<td>100×</td>
<td>20 sec</td>
<td>none</td>
</tr>
<tr>
<td>201-2</td>
<td>442 nm</td>
<td>100×</td>
<td>20 sec</td>
<td>none</td>
</tr>
<tr>
<td>201-2</td>
<td>633 nm</td>
<td>100×</td>
<td>20 sec</td>
<td>none</td>
</tr>
<tr>
<td>204-2</td>
<td>442 nm</td>
<td>100×</td>
<td>20 sec</td>
<td>none</td>
</tr>
<tr>
<td>207-1*</td>
<td>442 nm</td>
<td>100×</td>
<td>20 sec</td>
<td>none</td>
</tr>
<tr>
<td>207-1**</td>
<td>442 nm</td>
<td>100×</td>
<td>20 sec</td>
<td>none</td>
</tr>
<tr>
<td>210-1</td>
<td>442 nm</td>
<td>100×</td>
<td>20 sec</td>
<td>none</td>
</tr>
<tr>
<td>210-2</td>
<td>442 nm</td>
<td>100×</td>
<td>20 sec</td>
<td>none</td>
</tr>
</tbody>
</table>
3.4 Scanning electron microscope

3.4.1 Machine

The SEM machine, used in this work, was manufactured by Tescan USA Inc.; it is a Mira3 XMU Field Emission SEM. This microscope is as depicted in Figure 3.7. This machine is part of the SEMLab at The University of British Columbia, and it allows for high resolution imaging from a sample surface of up to several hundred thousand times magnification. The surface is probed with an electron beam, and a greyscale image is thus produced. The SEM has an 80 mm$^2$ EDS X-ray detector from Oxford Instruments in order to detect X-ray emissions due to ionized electrons falling back into the inner shells. Each X-ray photon emission has an energy, or wavelength, that is characteristic of the element it is emitted from. The software associated with this machine then matches the energy spectrum against known elemental standards in order to determine the relative amounts of material. In this way, a material compositional analysis can be performed, as described in Sections 3.4.3 and 3.4.

3.4.2 Determination of the thickness

In order to determine the thickness of the thin-film carbon films, for sample number 115-1, i.e., a thin-film of carbon deposited on a titanium ring using magnetron sputtering at an RF power of 200 W for 120 minutes, with a 12.5 sccm argon gas flow, the SEM is used. The approach used in this work is the first trial of this technique, and just sample number 115-1 is analyzed in this manner. To find the transition from the underlying
Figure 3.7: The SEM machine from the SEMLab at The University of British Columbia. The electronic version of this figure is in color.
3.4. Scanning electron microscope

titanium substrate to the thin-film, a side of the titanium ring sample is polished in order to obtain a nice transition from the titanium substrate to the thin-film carbon. The titanium ring substrate has a curved surface, and the electron microscope detector is looking at the thin-film carbon from a non-planar point of view. Thin-film carbon has a much brighter appearance than the underlying titanium substrate, as seen in Figure 3.8. Since the point of view is from an angle, the bright thin-film carbon in Figure 3.8 is not the actual thickness, but rather a look on the surface. To find the actual thickness, i.e., the transition from substrate to the thin-film, the sample has to be tilted, and the picture zoomed in towards the thin-film of carbon. A zoomed in picture of the thin-film carbon on the titanium ring sample is shown in Figure 4.24.

3.4.3 Material analysis

As described in the previous section, it is a challenge to find the transition from the titanium substrate of sample number 115-1 to the thin-film carbon. In order to determine the right visual interpretation of the image, a material compositional analysis is performed so as to distinguish the titanium substrate from the thin-film carbon. Several spectra are taken. Spectrum number 13 and 14 analyzed the titanium substrate and spectrum number 15 and 16 of the thin-film carbon. Spectra 14 and 16 are shown and discussed in Section 4.6. A line material analysis is also performed between spectra 13 or 14 and 15 or 16, respectively, in order to acquire the material compositional transition from titanium to carbon. All the corresponding material analysis results are discussed, in detail, in Section 4.6.
3.4. Scanning electron microscope

Figure 3.8: SEM: The first thickness measurement of sample number 115-1, i.e., a thin-film of carbon deposited on a titanium ring using magnetron sputtering at an RF power of 200 W for 120 minutes, with a 12.5 sccm argon gas flow. The thin-film carbon is much brighter than the underlying titanium substrate. This view is from an angular point of view. Image obtained with the assistance of Mr. D. Arkinstall. The electronic version of this figure is in color.
Chapter 4

Analysis

4.1 Experimental analysis of thin-film carbon

Forms of thin-films of carbon are currently being used for a wide variety of industrial and military applications [8, 9, 17]. Differences in the deposition technique and deposition conditions used have been found to have an enormous impact on the properties of the resultant forms of thin-film carbon. Based on the demands of the application at hand, the right deposition technique and conditions must be sought. If extreme hardness is required, a hydrogen-free form of thin-film carbon should be employed [9], this typically not being achievable through the use of a CVD process [25]. On the other hand, CVD processes offer uniformity in terms of thin-film deposition [24], and this is a great advantage for applications where wear-and-tear resistance is required, non-uniformity in the thin-film thickness and composition having potentially disastrous consequences in terms of performance.

In this thesis, magnetron sputtering is employed in order to deposit thin-film carbon. This is because this technique is inexpensive to use and requires the use of commonly available experimental equipment. As of the present moment, whether or not this form of thin-film carbon offers adequate quality for the particular application under consideration, i.e., cosmetic jewelry,
remains unknown. In this chapter, results corresponding to these thin-film carbon samples, are presented. The ultimate purpose of this experimental work is to critically assess the suitability of these films for cosmetic jewelry applications. Unfortunately, owing to limitations in the amount of time available, the results presented in this thesis represent only the first step taken in the process required in order to address this question. The quality of the resultant films will be determined through an evaluation of the $sp^3$ bond fraction, this usually being taken as a proxy measure for the durability and hardness of such films. As an exhaustive probing of the deposition parameter space lies beyond the scope of the present analysis, the approach adopted will be to contrast the thin-film carbon samples on a sample-by-sample basis, all conditions being the same except for one; in a sense, the conditions considered represent a sampling of the deposition parameter space. A systematic study, in which the deposition parameter space is probed in its totality, will be the goal of future work related to this project, but is beyond the scope of this particular thesis.

Initially, an overview of all of the experimental samples that are considered in this analysis is provided, a brief description of the deposition conditions employed and the experimental procedures used being tabulated. Then, for one particular sample, which is henceforth referred to as the reference sample, the means whereby unprocessed Raman spectroscopy results, i.e., raw experimental Raman results, are prepared for subsequent analysis, through a process of baseline correction, is detailed; this processing is used for all Raman spectra considered in this analysis, the intermediary steps only being explicitly shown for the reference sample case. Following
4.1. Experimental analysis of thin-film carbon

baseline correction, the experimental spectra are then decomposed into two distinct peaks, the G-peak, being related to the presence of sp² bonds, and the D-peak, being related to the presence of sp³ bonds. Two Gaussian peaks are employed for this peak fitting purpose, and the sum of these peaks is least-squares fit to the overall processed Raman spectra, i.e., the peak parameters are selected in such a manner that the difference between the sum of the two peaks and the baseline corrected Raman spectra has the least-squares error value⁴. After explaining this procedure of data processing, all of the resultant results are presented and contrasted with each other. A particular interpretation for the Raman spectra associated with these experimental results is then discussed, varying opinions, from the scientific literature, also being presented. Finally, a preliminary analysis of one of the thin-film carbon samples, using the SEM machine, is then presented, and the meaning of the results is discussed.

This chapter is organized in the following manner. In Section 4.2, the samples considered in this analysis are tabulated, the experimental conditions employed being specified. Then, in Section 4.3, the procedure of Raman analysis is then presented. A summary of the Raman results obtained is then featured in Section 4.4. Further interpretation of the Raman results is presented in Section 4.5. Finally, in Section 4.6, the scanning electron microscopy results, obtained for one of the thin-film carbon samples considered in this analysis, are presented.

⁴For the special case of very thin-films, i.e., sputtering with a low argon gas flow, a process of background compensation is also used.
4.2 Description and overview of the examined samples

Eleven Raman measurements on ten different samples of thin-film carbon are performed for the purposes of this analysis. Table 4.1 provides an overview of all of the samples considered in this analysis, the deposition conditions, the substrates employed, and the Raman source wavelength being tabulated for each such Raman measurement. For all of the samples considered, the Raman source beam is projected onto the middle of the sample, i.e., away from its edges. All samples are probed using a Raman source of 442 nm, except for sample number 201-2, which is measured using a Raman source of 633 nm in order to ascertain what effect the selection of the Raman excitation wavelength produces. It should be noted that sample number 201-2 is the reference sample, this sample being produced through magnetron sputtering at a DC power of 400 W for 60 minutes with an argon gas flow of 12.5 sccm on glass. Variations in the nature of the sputtering, i.e., the duration of the sputtering, the nature of the plasma excitation, i.e., whether DC or RF, and the argon gas flow rates, are considered. Variations in the type of substrate employed are also considered. For the case of RF excitation, an RF power of 200 W is considered. The sputtering time is varied from 60 minutes up to 360 minutes. An argon gas flow of 3.5 sccm is almost the minimal value required for successful sputtering. The argon gas flow is increased up to double of the reference flows, i.e., 25 scm for sample 210-1 and 210-2. Different substrates are considered in order to provide a feel for the influence of the substrate on the resultant film properties.
4.2. Description and overview of the examined samples

Table 4.1: Overview of the samples with the deposition parameters and the Raman source identified. Ten different experimental samples were examined with Raman spectroscopy. Sample 201-2, the reference (shaded) sample, is analyzed with two different Raman laser source excitation wavelengths, 442 and 633 nm.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Substrate</th>
<th>RF / DC</th>
<th>Power</th>
<th>Sputter time</th>
<th>Argon</th>
<th>Raman source</th>
</tr>
</thead>
<tbody>
<tr>
<td>106-2</td>
<td>Ti ring</td>
<td>RF</td>
<td>200 W</td>
<td>175 min</td>
<td>4.7 sccm</td>
<td>442 nm</td>
</tr>
<tr>
<td>111-1</td>
<td>Cr on Ti ring</td>
<td>DC</td>
<td>400 W</td>
<td>360 min</td>
<td>12.5 sccm</td>
<td>442 nm</td>
</tr>
<tr>
<td>115-3</td>
<td>Ti ring</td>
<td>RF</td>
<td>200 W</td>
<td>120 min</td>
<td>12.5 sccm</td>
<td>442 nm</td>
</tr>
<tr>
<td>121-3</td>
<td>Ti ring</td>
<td>RF</td>
<td>200 W</td>
<td>118 min</td>
<td>12.5 sccm</td>
<td>442 nm</td>
</tr>
<tr>
<td>123-3</td>
<td>Ti ring</td>
<td>RF</td>
<td>200 W</td>
<td>120 min</td>
<td>12.5 sccm</td>
<td>442 nm</td>
</tr>
<tr>
<td>201-2</td>
<td>Glass</td>
<td>DC</td>
<td>400 W</td>
<td>60 min</td>
<td>12.5 sccm</td>
<td>442 nm</td>
</tr>
<tr>
<td>201-2</td>
<td>Glass</td>
<td>DC</td>
<td>400 W</td>
<td>60 min</td>
<td>12.5 sccm</td>
<td>633 nm</td>
</tr>
<tr>
<td>204-2</td>
<td>Glass</td>
<td>RF</td>
<td>200 W</td>
<td>60 min</td>
<td>12.5 sccm</td>
<td>442 nm</td>
</tr>
<tr>
<td>207-1</td>
<td>Glass</td>
<td>RF</td>
<td>200 W</td>
<td>60 min</td>
<td>3.5 sccm</td>
<td>442 nm</td>
</tr>
<tr>
<td>210-1</td>
<td>Glass</td>
<td>RF</td>
<td>200 W</td>
<td>60 min</td>
<td>25 sccm</td>
<td>442 nm</td>
</tr>
<tr>
<td>210-2</td>
<td>Flat Ti</td>
<td>RF</td>
<td>200 W</td>
<td>60 min</td>
<td>25 sccm</td>
<td>442 nm</td>
</tr>
</tbody>
</table>
4.3 Raman analysis

The following sample-by-sample comparisons are made:

- DC power of 400 W (sample number 201-2) vs. RF power of 200 W (sample number 204-2)
- glass substrate (sample number 207-1) vs. titanium ring substrate (sample number 106-2)
- glass substrate (sample number 210-1) vs. flat titanium substrate (sample number 210-2)
- low argon gas flow (sample number 210-1) vs. high argon gas flow (sample number 207-1)
- test for reproducibility (sample numbers 115-3, 121-3, and 123-3)
- Raman source laser excitation wavelengths of 442 vs. 633 nm (sample number 201-2)
- thin-film carbon, prepared with exceptional low argon gas flow (sample number 207-1): background compensation vs. no background compensation

4.3 Raman analysis

4.3.1 Unprocessed Raman data

The unprocessed Raman spectrum, corresponding to the reference sample (sample number 201-2), i.e., a thin-film of carbon deposited using magnetron sputtering at a DC power of 400 W for 60 minutes, with a 12.5 sccm argon gas flow, is depicted in Figure 4.1. This spectra is determined using a 442 nm Raman source, and the spot size is about 10 µm; this spot is cast upon the center at the sample, i.e., away from the edges. The spectrum
Figure 4.1: The unprocessed Raman spectrum of the reference sample (sample number 201-2), i.e., a thin-film of carbon deposited on glass using magnetron sputtering at a DC power of 400 W for 60 minutes, with a 12.5 sccm argon gas flow. This spectrum is depicted between 800 and 2000 cm$^{-1}$. 
between 800 and 2000 cm\(^{-1}\) is plotted, as this is the region in which peaks, relevant to this particular analysis, are found. Distinctive peaks are noted at both \(~1350\) and \(~1580\) cm\(^{-1}\) in this figure. These peaks, D and G, respectively, are believed to be representative of the presence of sp\(^3\) and sp\(^2\) carbon bonds, respectively, as was suggested by Zhao et al. [10].

4.3.2 Baseline correction

Experimental measurements are susceptible to noise. For the case of Raman spectroscopy, the noise present will lead to the presence of a baseline in the spectrum, that must be compensated for prior to any spectral analysis. This compensation process, otherwise known as baseline correction, is a common practice amongst researchers in this field. The process of baseline correction is explained in the following paragraph.

Baseline correction is typically achieved by subtracting a baseline from the unprocessed data, this baseline arising as a consequence of these “noisy” processes. In Figure 4.2, the baseline is depicted for the Raman spectrum corresponding to the reference sample (sample number 201-2), i.e., a thin-film of carbon deposited on glass using sputtering at a DC power of 400 W for 60 minutes with a 12.5 sccm argon flow, this being the same sample as that considered in Figure 4.1. The baseline corresponding to this particular data set is chosen to span from 1000 to 1800 cm\(^{-1}\), and is drawn by connecting the data points corresponding to these limits; this range for the baseline correction was suggested by Zhao et al. [10]. Other researchers use different means of determining this baseline, but the essence remains the same as that depicted in Figure 4.2, these other techniques being further discussed in the
Figure 4.2: The unprocessed Raman spectrum of the reference sample (sample number 201-2), i.e., a thin-film of carbon deposited on glass using magnetron sputtering at a DC power of 400 W for 60 minutes, with a 12.5 sccm argon gas flow, depicted in Figure 4.1, with a baseline, connecting the data points corresponding to 1000 and 1800 cm$^{-1}$, being shown with the dashed line. The electronic version of this figure is in color.
4.3. Raman analysis

literature. The data is baseline corrected by removing this baseline from the unprocessed spectrum. For the case of the reference sample (sample number 201-2), the resultant baseline corrected data is depicted in Figure 4.3.

4.3.3 Peak fitting

There is a general consensus in the field that the amount of sp\(^2\) and sp\(^3\) bonds within a given sample of thin-film carbon is proportional to the integrated intensity of the corresponding peaks. That is, the ratio of the integrated intensity of the \(\sim 1350\) cm\(^{-1}\) peak (D-peak) and the \(\sim 1580\) cm\(^{-1}\) peak (G peak) provides a measure of the sp\(^3\) to sp\(^2\) bonding ratio within the thin-film of carbon. Accordingly, peak fitting is critical to the subsequent analysis. If one accepts that the presence of sp\(^2\) bonds leads to the existence of a peak at \(\sim 1580\) cm\(^{-1}\) and that the presence of sp\(^3\) bonds leads to the existence of a peak at \(\sim 1350\) cm\(^{-1}\), it is usually assumed that the overall baseline corrected spectrum is the sum of these two peaks. Thus, the task becomes identifying the peak parameters that best fit the resultant baseline corrected data.

For the purposes of this analysis, each peak is assumed to be in the form of a Gaussian function, i.e., each peak is assumed to be of the form

\[
A \exp \left[ -\frac{(x - m)^2}{\sigma^2} \right],
\]

where \(A\) denotes the peak amplitude, \(m\) represents the peak location, and \(\sigma\) provides a measure of the peak breadth. The total fit of the Raman spectrum is therefore a fit to

\[
A_G \exp \left[ -\frac{(x - m_G)^2}{\sigma_G^2} \right] + A_D \exp \left[ -\frac{(x - m_D)^2}{\sigma_D^2} \right],
\]
Figure 4.3: The baseline corrected Raman spectrum of the reference sample (sample number 201-2), i.e., a thin-film of carbon deposited on glass using magnetron sputtering at a DC power of 400 W for 60 minutes, with a 12.5 sccm argon gas flow, between 1000 and 1800 cm$^{-1}$. 
where \( A_G \) and \( A_D \) denote the peak amplitudes of the G- and D-peaks, respectively, \( m_G \) and \( m_D \) represent their peak locations, and \( \sigma_G \) and \( \sigma_D \) represent their breadth. Assuming that the baseline corrected data corresponds to the sum of two appropriately selected Gaussian peaks, as in Eq. (4.2), the approach employed is to select the model parameters, i.e., \( A_G \), \( A_D \), \( m_G \), \( m_D \), \( \sigma_G \), and \( \sigma_D \), so that the difference between this sum of two peaks and the baseline corrected experimental data is minimized; this analysis is performed within the framework of a least-squares error analysis. For the reference sample, i.e., sample number 201-2, for the baseline corrected Raman experimental data, depicted in Figure 4.3, the two peaks that arise from this peak decomposition process, and the sum of the two peaks, are all depicted in Figure 4.4. The integrated peaks, for this particular fit, suggest that the \( sp^3 \) to \( sp^2 \) bonding ratio is \( 3.21 \pm 0.07 \) for this sample of thin-film carbon. This is close to that typically found in high-quality thin-film carbon [12].

It should be noted that, as has been hinted earlier, some researchers instead assert that it is the peak magnitude that should be looked at, rather than the peak integrations; see, for example, Tai et al. [29]. Given that the majority of researchers employ the integrated intensity, this will be the procedure employed for the purposes of this particular analysis, where

\[
I_D = \int_{1000 \text{ cm}^{-1}}^{1800 \text{ cm}^{-1}} A_D \exp \left[ -\frac{(x - m_D)^2}{\sigma_D^2} \right],
\]

(4.3)

for the D-peak, and

\[
I_G = \int_{1000 \text{ cm}^{-1}}^{1800 \text{ cm}^{-1}} A_G \exp \left[ -\frac{(x - m_G)^2}{\sigma_G^2} \right],
\]

(4.4)

for the G-Peak. This issue is further discussed in Section 4.5.
4.3. Raman analysis

Figure 4.4: The peak fitting corresponding to the baseline corrected Raman spectrum of the reference sample (sample number 201-2), i.e., a thin-film of carbon deposited on glass using magnetron sputtering at a DC power of 400 W for 60 minutes, with a 12.5 sccm argon gas flow, between 1000 and 1800 cm$^{-1}$. The two Gaussian peaks selected for this peak fitting process are depicted, as is the sum. The resultant integrated intensities suggest that $I_D / I_G = 3.21 \pm 0.07$. The fitting parameters are found to be $A_D = 2042$ and $A_G = 2174$, $m_D = 1388$ cm$^{-1}$ and $m_G = 1588$ cm$^{-1}$, $\sigma_D = 197$ cm$^{-1}$ and $\sigma_D = 57.4$ cm$^{-1}$. The root mean square error is 69.74. The electronic version of this figure is in color.
4.3. Raman analysis

4.3.4 Background subtraction

One of the samples considered in this analysis, sample number 207-1, i.e., a thin-film of carbon deposited on glass using magnetron sputtering at an RF power of 200 W for 60 minutes, with a 3.5 sccm argon gas flow, appears to be very thin due to the low argon gas flow that is employed for this particular deposition. As this sample is thinner, the number of interactions with the Raman source will be reduced. Thus, while most Raman spectra considered in this thesis reach a maximum of thousands of counts per Raman shift interval, as is seen in Figure 4.1, the Raman spectrum corresponding to sample number 207-1 only reaches a maximum of a couple of hundreds counts per Raman shift interval, as may be seen in Figure 4.5.

As this sample is very thin, interactions with the underlying substrate and background are much more likely to influence the resultant Raman spectrum. These interactions should be compensated for. To do this, the Raman spectrum corresponding to a pure glass substrate is measured; see Figure 4.6. The Raman spectrum of sample 207-1, without background compensation, is given in Figure 4.5. The ratio of the integrated intensity of the two Gaussian peaks is very different if the background is taken into consideration, i.e., \( I_D / I_G = 3.35 \pm 0.13 \). With background compensation, the true ratio of sp\(^3\) to sp\(^2\) is determined as \( I_D / I_G = 2.24 \pm 0.05 \). The least-squares error of the Gaussian fit is lower after background compensation; see Figure 4.14.
Figure 4.5: The baseline corrected Raman spectrum without background compensation of sample number 207-1, i.e., a thin-film of carbon deposited on glass using magnetron sputtering at an RF power of 200 W for 60 minutes, with a 3.5 sccm argon gas flow. The two Gaussian peaks selected for this peak fitting process are depicted, as is the sum. The resultant integrated intensities suggest that $I_D/I_G = 3.35 \pm 0.13$. The fitting parameters are found to be $A_D = 203.2$ and $A_G = 206$, $m_D = 1407 \text{ cm}^{-1}$ and $m_G = 1585 \text{ cm}^{-1}$, $\sigma_D = 197.3 \text{ cm}^{-1}$ and $\sigma_D = 57.81 \text{ cm}^{-1}$. The root mean square error is 11.80. The electronic version of this figure is in color.
4.3. Raman analysis

Figure 4.6: The Raman spectrum of a piece of plain glass and flat titanium.

The electronic version of this figure is in color.
4.4 Summary of the Raman results

The other thin-film carbon samples considered in this analysis, tabulated in Table 4.2, have also had their Raman spectra measured. The results of this peak fitting, on the baseline corrected Raman spectra, are depicted in Figures 4.7, 4.8, 4.9, 4.10, 4.11, 4.12, 4.13, 4.14, 4.15, and 4.16 for sample numbers 106-2, 111-1, 115-3, 121-3, 123-3, 201-2 with a Raman source of 633 nm, 204-2, 207-1, 210-1, 210-2, respectively. Table 4.2 gives an overview of all of the experimental samples considered in this work and the corresponding Raman results for the $sp^3$ to $sp^2$ bonding ratio, i.e., $I_D/I_G$. It is noted that all samples have $sp^3$ to $sp^2$ bonding ratios that are close to that of high-quality thin-film carbon [12]. The error is based on a Matlab® result within a 95% confidence interval. Matlab® uses the method of least-squares when peak fitting data. The error is basically a range of possible results within 95% of the best fit. For a specification of the thin-film carbon quality, in terms of hardness and durability, often the $sp^3$ content is employed. In Table 4.3, the Raman results, in terms of the $sp^3$ to $sp^2$ ratio, $I_D/I_G$, is given along with the corresponding $sp^3$ content, i.e., $I_D/(I_D + I_G)$. The $sp^3$ content shows minimal variation, i.e., the differences between these values are quite slight. Since in the literature Raman results are mostly expressed in terms of the $sp^3$ to $sp^2$ ratio, i.e., $I_D/I_G$, this work will also present this bonding ratio as the final result, rather than just the $sp^3$ content. Also, in Table 4.3, the fitting parameters, $A_D$ and $A_G$, $m_D$ and $m_G$, $\sigma_D$ and $\sigma_G$, according Eq. (4.2) from Section 4.3.3, are given.
4.4. Summary of the Raman results

Table 4.2: Experimental parameters for each sample with the Raman results obtained for the sp\(^3\) to sp\(^2\) bonding ratio, i.e., \(I_D/I_G\). Reference sample number 201-2 is shaded. (* without background compensation, ** with background compensation; see Section 4.3.4).

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Substrate</th>
<th>RF / DC</th>
<th>Power</th>
<th>Sputter time</th>
<th>Argon</th>
<th>Raman source</th>
<th>(I_D/I_G)</th>
<th>Figure / Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>106-2</td>
<td>Ti ring</td>
<td>RF</td>
<td>200 W</td>
<td>175 min</td>
<td>4.7 sccm</td>
<td>442 nm</td>
<td>3.30 ± 0.07</td>
<td>4.7 / 77</td>
</tr>
<tr>
<td>111-1</td>
<td>Cr on Ti ring</td>
<td>DC</td>
<td>400 W</td>
<td>360 min</td>
<td>12.5 sccm</td>
<td>442 nm</td>
<td>2.77 ± 0.06</td>
<td>4.8 / 78</td>
</tr>
<tr>
<td>115-3</td>
<td>Ti ring</td>
<td>RF</td>
<td>200 W</td>
<td>120 min</td>
<td>12.5 sccm</td>
<td>442 nm</td>
<td>3.20 ± 0.06</td>
<td>4.9 / 79</td>
</tr>
<tr>
<td>121-3</td>
<td>Ti ring</td>
<td>RF</td>
<td>200 W</td>
<td>118 min</td>
<td>12.5 sccm</td>
<td>442 nm</td>
<td>3.39 ± 0.06</td>
<td>4.10 / 80</td>
</tr>
<tr>
<td>123-3</td>
<td>Ti ring</td>
<td>RF</td>
<td>200 W</td>
<td>120 min</td>
<td>12.5 sccm</td>
<td>442 nm</td>
<td>3.20 ± 0.07</td>
<td>4.11 / 81</td>
</tr>
<tr>
<td>201-2</td>
<td>Glass</td>
<td>DC</td>
<td>400 W</td>
<td>60 min</td>
<td>12.5 sccm</td>
<td>442 nm</td>
<td>3.21 ± 0.07</td>
<td>4.4 / 71</td>
</tr>
<tr>
<td>201-2</td>
<td>Glass</td>
<td>DC</td>
<td>400 W</td>
<td>60 min</td>
<td>12.5 sccm</td>
<td>633 nm</td>
<td>3.18 ± 0.10</td>
<td>4.12 / 82</td>
</tr>
<tr>
<td>204-2</td>
<td>Glass</td>
<td>RF</td>
<td>200 W</td>
<td>60 min</td>
<td>12.5 sccm</td>
<td>442 nm</td>
<td>2.91 ± 0.06</td>
<td>4.13 / 83</td>
</tr>
<tr>
<td>207-1*</td>
<td>Glass</td>
<td>RF</td>
<td>200 W</td>
<td>60 min</td>
<td>3.5 sccm</td>
<td>442 nm</td>
<td>3.35 ± 0.13</td>
<td>4.5 / 73</td>
</tr>
<tr>
<td>207-1**</td>
<td>Glass</td>
<td>RF</td>
<td>200 W</td>
<td>60 min</td>
<td>3.5 sccm</td>
<td>442 nm</td>
<td>2.24 ± 0.05</td>
<td>4.14 / 84</td>
</tr>
<tr>
<td>210-1</td>
<td>Glass</td>
<td>RF</td>
<td>200 W</td>
<td>60 min</td>
<td>25 sccm</td>
<td>442 nm</td>
<td>3.01 ± 0.06</td>
<td>4.15 / 85</td>
</tr>
<tr>
<td>210-2</td>
<td>Flat Ti</td>
<td>RF</td>
<td>200 W</td>
<td>60 min</td>
<td>25 sccm</td>
<td>442 nm</td>
<td>2.88 ± 0.05</td>
<td>4.16 / 86</td>
</tr>
</tbody>
</table>
4.4. Summary of the Raman results

Figure 4.7: The baseline corrected Raman spectrum of sample number 106-2, i.e., a thin-film of carbon deposited on a titanium ring using magnetron sputtering at an RF power of 200 W for 175 minutes, with a 4.7 sccm argon gas flow. The two Gaussian peaks selected for this peak fitting process are depicted, as is the sum. The resultant integrated intensities suggest that $I_D/I_G = 3.30 \pm 0.07$. The fitting parameters are found to be $A_D = 1992$ and $A_G = 1936$, $m_D = 1389 \text{ cm}^{-1}$ and $m_G = 1588 \text{ cm}^{-1}$, $\sigma_D = 199 \text{ cm}^{-1}$ and $\sigma_D = 61.78 \text{ cm}^{-1}$. The root mean square error is 57.80. The electronic version of this figure is in color.
4.4. Summary of the Raman results

Figure 4.8: The baseline corrected Raman spectrum of sample number 111-1, i.e., a thin-film of carbon deposited on a chrome layer on a titanium ring using magnetron sputtering at a DC power of 400 W for 360 minutes, with a 12.5 sccm argon gas flow. The two Gaussian peaks selected for this peak fitting process are depicted, as is the sum. The resultant integrated intensities suggest that $I_D/I_G = 2.77 \pm 0.06$. The fitting parameters are found to be $A_D = 2506$ and $A_G = 3228$, $m_D = 1372 \text{ cm}^{-1}$ and $m_G = 1589 \text{ cm}^{-1}$, $\sigma_D = 190.9 \text{ cm}^{-1}$ and $\sigma_D = 53.38 \text{ cm}^{-1}$. The root mean square error is 102.01. The electronic version of this figure is in color.
4.4. Summary of the Raman results

Figure 4.9: The baseline corrected Raman spectrum of sample number 115-3, i.e., a thin-film of carbon deposited on a titanium ring using magnetron sputtering at an RF power of 200 W for 120 minutes, with a 12.5 sccm argon gas flow. The two Gaussian peaks selected for this peak fitting process are depicted, as is the sum. The resultant integrated intensities suggest that $I_D/I_G = 3.20 \pm 0.06$. The fitting parameters are found to be $A_D = 2507$ and $A_G = 2952$, $m_D = 1395 \text{ cm}^{-1}$ and $m_G = 1590 \text{ cm}^{-1}$, $\sigma_D = 218.6 \text{ cm}^{-1}$ and $\sigma_D = 57.42 \text{ cm}^{-1}$. The root mean square error is 89.78. The electronic version of this figure is in color.
4.4. Summary of the Raman results

Figure 4.10: The baseline corrected Raman spectrum of sample number 121-3, i.e., a thin-film of carbon deposited on a titanium ring using magnetron sputtering at an RF power of 200 W for 118 minutes, with a 12.5 sccm argon gas flow. The two Gaussian peaks selected for this peak fitting process are depicted, as is the sum. The resultant integrated intensities suggest that $I_D/I_G = 3.39 \pm 0.06$. The fitting parameters are found to be $A_D = 751.9$ and $A_G = 761.7$, $m_D = 1400 \text{ cm}^{-1}$ and $m_G = 1583 \text{ cm}^{-1}$, $\sigma_D = 218.1 \text{ cm}^{-1}$ and $\sigma_D = 62.86 \text{ cm}^{-1}$. The root mean square error is 21.18. The electronic version of this figure is in color.
4.4. Summary of the Raman results

Figure 4.11: The baseline corrected Raman spectrum of sample number 123-3, i.e., a thin-film of carbon deposited on a titanium ring using magnetron sputtering at an RF power of 200 W for 120 minutes, with a 12.5 sccm argon gas flow. The two Gaussian peaks selected for this peak fitting process are depicted, as is the sum. The resultant integrated intensities suggest that $I_D/I_G = 3.20 \pm 0.07$. The fitting parameters are found to be $A_D = 1128$ and $A_G = 1201$, $m_D = 1394$ cm$^{-1}$ and $m_G = 1590$ cm$^{-1}$, $\sigma_D = 202.2$ cm$^{-1}$ and $\sigma_D = 58.94$ cm$^{-1}$. The root mean square error is 39.78. The electronic version of this figure is in color.
4.4. Summary of the Raman results

Figure 4.12: The baseline corrected Raman spectrum (with 633 nm excitation wavelength) of the reference sample (sample number 201-2), i.e., a thin-film of carbon deposited on glass using magnetron sputtering at a DC power of 400 W for 60 minutes, with a 12.5 sccm argon gas flow. The two Gaussian peaks selected for this peak fitting process are depicted, as is the sum. The resultant integrated intensities suggest that $I_D/I_G = 3.18 \pm 0.10$. The fitting parameters are found to be $A_D = 913.2$ and $A_G = 702.6$, $m_D = 1339$ cm$^{-1}$ and $m_G = 1582$ cm$^{-1}$, $\sigma_D = 170.8$ cm$^{-1}$ and $\sigma_D = 69.63$ cm$^{-1}$. The root mean square error is 58.70. The electronic version of this figure is in color.
4.4. Summary of the Raman results

Figure 4.13: The baseline corrected Raman spectrum of sample number 204-2, i.e., a thin-film of carbon deposited on glass using magnetron sputtering at an RF power of 200 W for 60 minutes, with a 12.5 sccm argon gas flow. The two Gaussian peaks selected for this peak fitting process are depicted, as is the sum. The resultant integrated intensities suggest that $I_D/I_G = 2.91 \pm 0.06$. The fitting parameters are found to be $A_D = 1842$ and $A_G = 2172$, $m_D = 1389 \text{ cm}^{-1}$ and $m_G = 1594 \text{ cm}^{-1}$, $\sigma_D = 193.6 \text{ cm}^{-1}$ and $\sigma_D = 56.15 \text{ cm}^{-1}$. The root mean square error is 63.26. The electronic version of this figure is in color.
4.4. Summary of the Raman results

Figure 4.14: The baseline corrected Raman spectrum (with background compensation) of sample number 207-1, i.e., a thin-film of carbon deposited on glass using magnetron sputtering at an RF power of 200 W for 60 minutes, with a 3.5 sccm argon gas flow. The two Gaussian peaks selected for this peak fitting process are depicted, as is the sum. The resultant integrated intensities suggest that $I_D/I_G = 2.24 \pm 0.05$. The fitting parameters are found to be $A_D = 290.6$ and $A_G = 288.5$, $m_D = 1356 \text{ cm}^{-1}$ and $m_G = 1583 \text{ cm}^{-1}$, $\sigma_D = 178.4 \text{ cm}^{-1}$ and $\sigma_D = 80.2 \text{ cm}^{-1}$. The root mean square error is 9.75. The electronic version of this figure is in color.
Figure 4.15: The baseline corrected Raman spectrum of sample number 210-1, i.e., a thin-film of carbon deposited on glass using magnetron sputtering at an RF power of 200 W for 60 minutes, with a 25 sccm argon gas flow. The two Gaussian peaks selected for this peak fitting process are depicted, as is the sum. The resultant integrated intensities suggest that $I_D/I_G = 3.01 \pm 0.06$. The fitting parameters are found to be $A_D = 1844$ and $A_G = 2092$, $m_D = 1385$ cm$^{-1}$ and $m_G = 1594$ cm$^{-1}$, $\sigma_D = 194.2$ cm$^{-1}$ and $\sigma_D = 56.6$ cm$^{-1}$. The root mean square error is 59.68. The electronic version of this figure is in color.
4.4. Summary of the Raman results

Figure 4.16: The baseline corrected Raman spectrum of sample number 210-2, i.e., a thin-film of carbon deposited on a flat piece of titanium using magnetron sputtering at an RF power of 200 W for 60 minutes, with a 25 sccm argon gas flow. The two Gaussian peaks selected for this peak fitting process are depicted, as is the sum. The resultant integrated intensities suggest that $I_D/I_G = 2.88 \pm 0.05$. The fitting parameters are found to be $A_D = 3209$ and $A_G = 3802$, $m_D = 1391$ cm$^{-1}$ and $m_G = 1591$ cm$^{-1}$, $\sigma_D = 197.8$ cm$^{-1}$ and $\sigma_D = 57.62$ cm$^{-1}$. The root mean square error is 94.75. The electronic version of this figure is in color.
### 4.4. Summary of the Raman results

Table 4.3: Comparison of the Raman results obtained for the sp\(^3\) to sp\(^2\) bonding ratio, i.e., \(I_D/I_G\) vs sp\(^3\) content. Reference sample number 201-2 is shaded. (* without background compensation, ** with background compensation; see Section 4.3.4).

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Raman source</th>
<th>(I_D/I_G)</th>
<th>sp(^3) content</th>
<th>(A_D)</th>
<th>(m_D)</th>
<th>(\sigma_D)</th>
<th>(A_G)</th>
<th>(m_G)</th>
<th>(\sigma_G)</th>
<th>Root mean square error</th>
<th>Figure / Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>106-2</td>
<td>442 nm</td>
<td>3.30 ± 0.07</td>
<td>0.77 ± 0.004</td>
<td>1992</td>
<td>1389</td>
<td>199</td>
<td>1936</td>
<td>56.18</td>
<td>61.78</td>
<td>5.78 ± 0.07</td>
<td>4.7 / 77</td>
</tr>
<tr>
<td>111-1</td>
<td>442 nm</td>
<td>2.77 ± 0.06</td>
<td>0.73 ± 0.004</td>
<td>2506</td>
<td>1372</td>
<td>190.9</td>
<td>3228</td>
<td>53.38</td>
<td>102.01</td>
<td>4.8 ± 0.06</td>
<td>4.8 / 78</td>
</tr>
<tr>
<td>115-3</td>
<td>442 nm</td>
<td>3.20 ± 0.06</td>
<td>0.76 ± 0.004</td>
<td>2507</td>
<td>1395</td>
<td>218.6</td>
<td>2952</td>
<td>57.42</td>
<td>88.78</td>
<td>5.0 ± 0.06</td>
<td>4.9 / 79</td>
</tr>
<tr>
<td>121-3</td>
<td>442 nm</td>
<td>3.39 ± 0.06</td>
<td>0.77 ± 0.003</td>
<td>751.9</td>
<td>1400</td>
<td>218.1</td>
<td>761.7</td>
<td>62.86</td>
<td>21.18</td>
<td>4.10 ± 0.06</td>
<td>4.10 / 80</td>
</tr>
<tr>
<td>123-3</td>
<td>442 nm</td>
<td>3.20 ± 0.07</td>
<td>0.76 ± 0.004</td>
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<td>1394</td>
<td>202.2</td>
<td>1201</td>
<td>58.94</td>
<td>39.78</td>
<td>4.11 ± 0.06</td>
<td>4.11 / 81</td>
</tr>
<tr>
<td>201-2</td>
<td>442 nm</td>
<td>3.21 ± 0.07</td>
<td>0.76 ± 0.004</td>
<td>2042</td>
<td>1388</td>
<td>197</td>
<td>2174</td>
<td>57.4</td>
<td>69.74</td>
<td>4.4 ± 0.07</td>
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</tr>
<tr>
<td>201-2</td>
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<td>3.18 ± 0.10</td>
<td>0.76 ± 0.006</td>
<td>911.2</td>
<td>1339</td>
<td>170.8</td>
<td>702.6</td>
<td>65.63</td>
<td>58.70</td>
<td>4.12 ± 0.08</td>
<td>4.12 / 82</td>
</tr>
<tr>
<td>204-2</td>
<td>442 nm</td>
<td>2.91 ± 0.06</td>
<td>0.74 ± 0.004</td>
<td>1842</td>
<td>1389</td>
<td>193.6</td>
<td>2172</td>
<td>56.15</td>
<td>63.26</td>
<td>4.13 ± 0.06</td>
<td>4.13 / 83</td>
</tr>
<tr>
<td>207-1*</td>
<td>442 nm</td>
<td>3.35 ± 0.13</td>
<td>0.77 ± 0.007</td>
<td>203.2</td>
<td>1407</td>
<td>197.3</td>
<td>206</td>
<td>55.71</td>
<td>11.80</td>
<td>4.5 ± 0.05</td>
<td>4.5 / 73</td>
</tr>
<tr>
<td>207-1**</td>
<td>442 nm</td>
<td>2.24 ± 0.05</td>
<td>0.69 ± 0.005</td>
<td>290.6</td>
<td>1356</td>
<td>178.4</td>
<td>288.5</td>
<td>50.2</td>
<td>9.75</td>
<td>4.14 ± 0.06</td>
<td>4.14 / 84</td>
</tr>
<tr>
<td>210-1</td>
<td>442 nm</td>
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<td>0.75 ± 0.004</td>
<td>1844</td>
<td>1385</td>
<td>194.2</td>
<td>2692</td>
<td>56.6</td>
<td>59.68</td>
<td>4.15 ± 0.06</td>
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</tr>
<tr>
<td>210-2</td>
<td>442 nm</td>
<td>2.88 ± 0.05</td>
<td>0.74 ± 0.003</td>
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<td>1391</td>
<td>197.8</td>
<td>3802</td>
<td>57.62</td>
<td>94.75</td>
<td>4.16 ± 0.06</td>
<td>4.16 / 86</td>
</tr>
</tbody>
</table>

87
4.4. Summary of the Raman results

The root mean-square error is defined as

\[
RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^{n} w_i (\hat{y}_i - y_i)^2},
\]  

(4.5)

where \( n \) is the number of data points, required to calculate the error minus the number of fitted coefficients, \( \hat{y}_i \) is the \( i \)th fitted data point, and \( y_i \) is the \( i \)th true measurement data point. In the following figures, i.e., Figures 4.17, 4.18, 4.19, 4.20, 4.21, 4.22, and 4.23, the Raman results are compared with each other. The aim is to compare samples with just one parameter changed in the deposition parameters selected. Due to time limitations, it is not possible to fully probe the deposition parameter space. Nevertheless, a preliminary comparison, with significant differences in the Raman results observed, can be presented. The sp\(^3\) to sp\(^2\) bonding ratio is notably higher for higher argon gas flows. With a gas flow of 25 sccm, the sp\(^3\) to sp\(^2\) bonding ratio is 3.01 ±0.06 compared with a ratio of 2.24 ±0.05 with a low gas flow of 3.5 sccm, as is seen in Figure 4.17. Schwan et al. [12] achieved a high sp\(^3\) content, up to 87 %, in thin-film carbon, using magnetron sputtering. The present work aims to replicate this same process and result. Therefore, a deposition pressure of 1 mTorr is targeted. Due to inaccuracies in the sputtering system used in this particular work, the argon gas flow had to be adjusted in order to achieve the desired deposition pressure. For experiment number 207-1, i.e., a thin-film of carbon deposited on glass using magnetron sputtering at an RF power of 200 W for 60 minutes, the argon gas flow was 3.5 sccm and the sp\(^3\) to sp\(^2\) bonding ratio is 2.24 ±0.05. For experiment number 106-2, i.e., a thin-film of carbon deposited on a titanium ring using magnetron sputtering at an RF power of 200 W for 175 minutes, the argon...
Figure 4.17: Raman analysis comparison of sample number 210-1 on the left and 207-1 (with background compensation) on the right. For both samples: glass substrate, RF power of 200 W, 60 min sputtering, Raman source 442 nm. The electronic version of this figure is in color.
4.4. Summary of the Raman results

gas flow was 4.7 sccm in order to achieve a deposition pressure of 1 mTorr and the corresponding sp$^3$ to sp$^2$ bonding ratio is found to be 3.30 ±0.07. Figure 4.18 shows a comparison of those two experiments. At this point, it is not possible to state if the substrate type or the deposition time is the cause for the differences in the nature of the chemical bonding.

Very similar sp$^3$ to sp$^2$ bonding ratios are found for planar glass and planar titanium substrate (sp$^3$ to sp$^2$ bonding ratio of 3.01 ±0.06 vs. 2.88 ±0.05, respectively), but with a higher argon gas flow, as depicted in Figure 4.19. The implications are that differences in the type of the substrate have a small influence on the nature of the chemical bonding, but rather on the deposition time. A more systematic study should be employed in order to determine exactly the impact of the substrate geometry or the deposition time.

To verify the reproducibility of the employed sputtering deposition system, three independent runs are employed; see Figure 4.20. It seems like the second experiment has a higher sp$^3$ to sp$^2$ bonding ratio with just 2 minutes difference in the deposition time. This difference in the sp$^3$ to sp$^2$ bonding ratio is most probably due to variations in the system and not due to the 2 minutes difference in the deposition time.

In Figure 4.21, the variation of the sp$^3$ to sp$^2$ bonding ratio with respect to the Raman source is given. There is much more noise related to a Raman source of 633 nm. However, the Raman result is very similar if a Raman source of 442 nm is used.

A proper consideration of the background for samples, prepared with unusually low argon gas flows, is very critical. As shown in Figure 4.22, the
4.4. Summary of the Raman results

Figure 4.18: Raman analysis comparison of sample number 207-1 (glass substrate, 60 min sputtering, 3.5 sccm argon gas flow, with background compensation) on the left and 106-2 (titanium ring substrate, 175 min sputtering, 4.7 sccm argon gas flow) on the right (similar gas flows produced the same vacuum pressure of about 1 mTorr). For both samples: RF power of 200 W and Raman source 442 nm. The electronic version of this figure is in color.
4.4. Summary of the Raman results

Figure 4.19: Raman analysis comparison of sample number 210-1 on the left and 210-2 on the right: For both samples: RF power of 200 W, 60 min sputtering, 25 sccm argon gas flow, Raman source 442 nm. The electronic version of this figure is in color.
Figure 4.20: Raman analysis comparison of sample number 115-3 on the left, 121-3 in the middle and 123-3 on the right. For all samples: titanium ring substrate, RF power of 200 W, 12.5 sccm argon gas flow, Raman source 442 nm, about 120 min sputtering. The electronic version of this figure is in color.
Figure 4.21: Raman analysis comparison of the reference sample 201-2 on the left and also 201-2 on the right. For these samples: glass substrate, DC power of 400 W, 60 min sputtering, 12.5 sccm argon gas flow. The electronic version of this figure is in color.
4.4. Summary of the Raman results

Figure 4.22: Raman analysis comparison of sample number 207-1 on the left and also 207-1 on the right. For these samples: glass substrate, RF power of 200 W, Raman source 442 nm, 60 min sputtering, 3.5 sccm argon gas flow. The electronic version of this figure is in color.
4.5 Raman interpretation

difference in the obtained Raman results is significant. It seems like the type of power applied, i.e., RF of 200 W or DC of 400 W, does not effect the sp$^3$ to sp$^2$ ratio, as depicted in Figure 4.23.

Based on the spot tests, performed in this thesis, four basic trends are observed; (1) it seems like RF power of 200 W with a medium amount of gas flow of 12.5 sccm and a long deposition time of 120 minutes produces a high sp$^3$ to sp$^2$ bond ratio of 3.2 as experienced with sample numbers 115-3, 121-3 and 123-3. (2) If the gas flow is not too high the adhesion is better on glass substrates and the thin-film carbon does not easily rub off the substrate surface and (3) low gas flows of 3.5 sccm on glass and 4.7 sccm on titanium rings, respectively, produces very low adhesion, i.e., the thin-film carbon can easily be rubbed off. Finally (4), DC power seems to produce a form of thin-film carbon with a deeper black color, probably due to the higher power of 400 W that produces a thicker film.

4.5 Raman interpretation

Means of interpreting the spectrum associated with a sample of thin-film carbon has been the subject of controversy over the years, with a variety of different approaches being suggested [10, 29, 31, 37–39]. Raman spectroscopy relates to the interaction of the source light with the vibrational modes, for the material under consideration. In essence, the source light excites these vibrational modes, and the energy is lost due to the emission of phonons, i.e., the quanta of vibration, is what is measured, this corresponding to the observed shifts in the Raman spectrum. Accordingly, as
Figure 4.23: Raman analysis comparison of the reference sample 201-2 on the left and 204-2 on the right. For both samples: glass substrate, 60 min sputtering, 12.5 sccm argon gas flow, Raman source 442 nm. The electronic version of this figure is in color.
the vibrational character of a material may be expressed in terms of the nature of the chemical bonds that are present. From a chemist’s perspective, the Raman results may be accounted for in terms of the chemical bonds that are present. While this may lead to an oversimplification in the analysis, and while the finer details associated with the Raman spectrum are beyond the scope of this elementary point of view, it provides a very intuitive perspective of the source of the peaks that are observed in the Raman spectrum. The most common approach is to fit the Raman data with two Gaussian curves and create the ratio of the integrated peak intensities for a measure of the sp\(^3\) to sp\(^2\) ratio. Another way to interpret the Raman data, employed by some in the literature [29, 38], is to determine the ratio of the intensity peak values. Table 4.4 lists some literature references with their published sp\(^3\) to sp\(^2\) ratio and stated approach for the Raman data interpretation, along with an estimate of the peak ratio and integrated intensity ratios, i.e., area ratio, respectively, based on their published figures. This compilation shows that most researchers use the ratio of the integrated peak intensities and therefore, this approach is used in this work as well.

4.6 Film thickness and material composition profile

In order to determine the thickness of a magnetron sputtered sample of thin-film carbon, a SEM is employed. While other approaches may be employed, the SEM offers an ideal opportunity to study the obtained films on a micron scale. Furthermore, it may be used in circumstances where
4.6. Film thickness and material composition profile

Table 4.4: A comparison of common Raman interpretations found in the literature. Six different Raman studies on thin-film carbon and a verification of their resultant ratio of sp$^3$ to sp$^2$ bonds. The peak ratio and integrated intensity, i.e., area, ratio was estimated from the presented figures and compared with the claimed sp$^3$ to sp$^2$ ratio. The last column draws a conclusion how the Raman spectra might have been interpreted.

<table>
<thead>
<tr>
<th>Author / Year</th>
<th>$I_D/I_G$ Peak</th>
<th>$I_D/I_G$ Area</th>
<th>$I_D/I_G$ Claim</th>
<th>Peak / Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zhao et al. [10] / 2008</td>
<td>0.468</td>
<td>0.776</td>
<td>0.76</td>
<td>Area</td>
</tr>
<tr>
<td>Tai et al. [29] / 2006</td>
<td>0.556</td>
<td>0.851</td>
<td>1.72</td>
<td>Peak</td>
</tr>
<tr>
<td>Ma et al. [37] / 2002</td>
<td>0.732</td>
<td>1.32</td>
<td>1.3</td>
<td>Area</td>
</tr>
<tr>
<td>Sung et al. [31] / 1997</td>
<td>Sample 1: 1.28</td>
<td>Sample 1: 4.85</td>
<td>Sample 1: 2.9</td>
<td>Area</td>
</tr>
<tr>
<td></td>
<td>Sample 2: 0.54</td>
<td>Sample 2: 2.16</td>
<td>Sample 2: 1.7</td>
<td></td>
</tr>
<tr>
<td>Sheeja et al. [38] / 2001</td>
<td>1.68</td>
<td>3.89</td>
<td>1.76</td>
<td>Peak</td>
</tr>
<tr>
<td>Zhang et al. [39] / 2000</td>
<td>Sample 1: 0.581</td>
<td>Sample 1: 1.81</td>
<td>Sample 1: 1.8</td>
<td>Area</td>
</tr>
<tr>
<td></td>
<td>Sample 2: 0.722</td>
<td>Sample 2: 2.19</td>
<td>Sample 2: 2.1</td>
<td></td>
</tr>
</tbody>
</table>
traditional means of determining film thicknesses are frustrated by practical constraints; determining the film thickness on, for example, rings. In addition, the use of the SEM for this purpose, while admittedly overblown, offers other tangential pieces of information that allow one to glean further insights into the nature of these films. In order to demonstrate the use of an SEM for determining the thickness of the thin-film carbon on a substrate, the sample number 115-1, i.e., a thin-film of carbon deposited on a titanium ring using magnetron sputtering at an RF power of 200 W for 120 minutes, with a 12.5 sccm argon gas flow, is considered. The primary challenge is to determine where the transition from substrate (titanium ring) to the thin-film carbon occurs. It is critical to analyze the thin-film perpendicular to its surface, as rings possess cylindrical geometry, that pose challenges for planar focusing. Figure 4.24 provides a representative view of this sample of thin-film carbon on a titanium ring from a certain angle. The material line capabilities of the SEM machine available at The University of British Columbia allow one to distinguish the thin-film from the substrate. In Figure 4.25, a zoomed-in version of the line, depicted in Figure 4.24, is shown. The material content across this line is given in the sub-figure immediately below. From this information, it is clear that the dark section in the image corresponds to the thickness of the thin-film carbon, because the content of carbon increases linearly due to the angular point of view. Another approach is to determine the thickness of the thin-film carbon based on this material line analysis. The carbon content increases from around 5.5 up to around 9.5 µm. Since this view is from an angle, the thickness appears to be bigger than in actual reality. Therefore, 4 µm must be too much, as
4.6. Film thickness and material composition profile

Figure 4.24: An SEM picture of sample number 115-1, i.e., a thin-film of carbon deposited on a titanium ring using magnetron sputtering at an RF power of 200 W for 120 minutes, with a 12.5 sccm argon gas flow. Original and colored picture (colors are artificial). Image obtained with the assistance of Mr. D. Arkinstall. The electronic version of this figure is in color.
4.6. Film thickness and material composition profile

Figure 4.25: Material line analysis of sample number 115-1, i.e., a thin-film of carbon deposited on a titanium ring using magnetron sputtering at an RF power of 200 W for 120 minutes, with a 12.5 sccm argon gas flow. Image obtained with the assistance of Mr. D. Arkinstall. The electronic version of this figure is in color.


4.6. Film thickness and material composition profile

shown with a visual inspection in Figure 4.26. Furthermore, the transition is fringed due to insufficient polishing. For future measurements, this has to be improved. Nevertheless, the order of magnitude for the thickness is consistent.

The thickness can be more accurately identified by tilting the sample until the surface is in line with the viewer. Based on the resolution of the microscope image picture, the thickness of the thin-film carbon can be measured; see Figure 4.26. For sample number 115-1, the thickness is to be about 1.7 \( \mu \text{m} \).

Another feature of the SEM machine is the possibility of measuring the content of the material. A high energy electron ionizes electrons from the inner shell of the material, and when they transition back to their normal state, an X-ray is emitted. The SEM has an X-ray detector, and is therefore able to determine the number of X-rays and their energy. The program matches those energy peaks with known elemental standards. The amount that is being presented normalized to 100% of the total measured X-rays. Therefore, the x-axis of the spectra images is in keV (each material emits a different energy). Figure 4.27 shows the material analysis spectrum 14; see Figure 4.24 on sample number 115-1, i.e., a thin-film of carbon deposited on a titanium ring using magnetron sputtering at an RF power of 200 W for 120 minutes, with a 12.5 sccm argon gas flow. The titanium content is 64.5 wt% and shows clearly that this part of the sample is the substrate itself, i.e., the titanium ring. Spectrum 16 in Figure 4.28 shows a titanium content of just 8.6 wt%, and a carbon content of 73.8 wt% and confirms the existence of thin-film carbon. There is also a fair amount of oxygen evident
4.6. Film thickness and material composition profile

Figure 4.26: SEM: Thickness of sample number 115-1, i.e., a thin-film of carbon deposited on a titanium ring using magnetron sputtering at an RF power of 200 W for 120 minutes, with a 12.5 sccm argon gas flow. Image obtained with the assistance of Mr. D. Arkinstall. The electronic version of this figure is in color.
4.6. Film thickness and material composition profile

Figure 4.27: Material spectrum 14 corresponding to thin-film carbon sputtering sample number 115-1, i.e., a thin-film of carbon deposited on a titanium ring using magnetron sputtering at an RF power of 200 W for 120 minutes, with a 12.5 sccm argon gas flow. (Spectrum 14 in Figure 4.24).
Figure 4.28: Material spectrum 16 corresponding to thin-film carbon sputtering sample number 115-1, i.e., a thin-film of carbon deposited on a titanium ring using magnetron sputtering at an RF power of 200 W for 120 minutes, with a 12.5 sccm argon gas flow. (Spectrum 16 in Figure 4.24).
4.6. Film thickness and material composition profile

in both spectra. As presented in Chapter 2, in Section 2.6, the presence of oxygen can effect the adhesion immensely. Since the thin-film carbon associated with most of the samples does not adhere very well, and is pretty easy to buff or polish off, the conclusion can be made that contamination and the oxygen layer will probably prevent good adhesion properties.

With this X-ray detector, it is not possible to detect the amount of hydrogen, because hydrogen has just one valence electron. The amount of hydrogen in the thin-film carbon, produced in this thesis, is assumed to be low, since the samples were prepared with magnetron sputtering, and no hydrogen based gases were employed.
Chapter 5

Conclusions

Magnetron sputtering provides an inexpensive means of depositing thin-films of carbon using widely available equipment. In this thesis, experiments were performed on thin-films of carbon prepared using magnetron sputtering. The resultant thin-films were then examined using Raman and SEM analyzes. Four distinct goals were accomplished as a result of this body of work. First, the production of thin-film carbon, using this technique, was demonstrated, the resultant sp\(^3\) to sp\(^2\) bonding ratio being comparable to that observed in other forms of high-quality ta-C [12]. Second, the thin-films were characterized using Raman spectroscopy, the sp\(^3\) to sp\(^2\) bonding ratios corresponding to these thin-films being determined using the experimental obtained spectra corresponding to these thin-films. Third, through the use of a variety of deposition conditions, the deposition parameter space was sampled, the resultant forms of thin-film carbon being examined through the use of Raman spectroscopy in order to evaluate the corresponding sp\(^3\) to sp\(^2\) ratio. Further, a means of determining the thin-film carbon profiles, through the use of an SEM analysis, was developed.

The sp\(^3\) content, achieved in the deposited thin-films of carbon, was found to reach up to 77%. Therefore, the thin-films of carbon produced in this work can be almost considered a form of ta-C, which requires an
sp\textsuperscript{3} content minimum of 80\% [9]; ta-C is viewed as being the best quality type of thin-film carbon. Unfortunately, a fair amount of oxygen, between 11 to 15\%, is found within these samples of thin-film carbon. As oxygen detracts from good adhesion, it is expected that the adhesion of these films is limited, although this has yet to be put to the experimental test. A high argon gas flow of 25 sccm is found to produce thin-films of carbon with a significantly higher ratio of sp\textsuperscript{3} to sp\textsuperscript{2} bonding ratio, i.e., 3.01 ±0.06, than with a low argon gas flow of 3.5 sccm, where the sp\textsuperscript{3} to sp\textsuperscript{2} bonding ratio is found to be 2.24 ±0.05. With a low gas flow of around 3.5 sccm or 4.7 sccm (a process pressure of 1 mTorr was employed), the sp\textsuperscript{3} to sp\textsuperscript{2} bonding ratio is different from glass substrate to titanium ring substrate for different deposition times, namely 2.24 ±0.05 for 60 minutes and 3.30 ±0.07 for 175 minutes, respectively. Further experiments are required in order to investigate if the type of substrate, or the duration of the deposition, is the reason for the differences in the sp\textsuperscript{3} to sp\textsuperscript{2} bonding ratio. Not much difference in the sp\textsuperscript{3} to sp\textsuperscript{2} bonding ratio was detected between planar glass and planar titanium substrate for high argon gas flows of 25 sccm. The Raman source, of either 442 or 633 nm, seems not to have a significant impact on the sp\textsuperscript{3} to sp\textsuperscript{2} ratio, even though the noise related to a Raman source of 633 nm is much bigger; the sp\textsuperscript{3} to sp\textsuperscript{2} bonding ratio of 3.21 ±0.07 vs. 3.18 ±0.10. It was also discovered, that the background of samples, prepared with a low argon gas flow, has to be considered in the Raman data analysis. Without background subtraction, the sp\textsuperscript{3} to sp\textsuperscript{2} bonding ratio is 3.35 ±0.13, whereas with background subtraction it is 2.24 ±0.05.

There are a number of important matters that could be further studied
related to this topic. First, the analysis presented herein focused on contrasting samples prepared through a variety of different means with each other. A systematic probing of the deposition parameter space was not performed, owing to time limitations. This is a critical deficiency of this work. How the selection of substrate influences the properties of the obtained films, i.e., be it the material employed (glass or titanium) or the shape of the substrate (ring or planar), should also be examined in a more systematic manner. Finally, how the sample of thin-film carbon that have been fabricated for the purposes of this particular analysis contrast with those associated with other research groups, would also be worth of further investigation. These important topics, that build up on the results presented in this thesis, will be addressed at a later point. Ultimately, these future studies will allow one to answer as to whether or not magnetron sputtering is adequate for cosmetic jewelry applications. This thesis represents the first step in this deeper research problem.
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References


Appendix A: Step by step guide for the Hummer XII

Figure A.1 provides a step-by-step guide for the operation of the Hummer XII, in terms of thin-film carbon depositions.
Appendix A: Step by step guide for DLC magnetron sputtering with the Hummer XII

**Shut down**
- Turn off power supply
- Turn off turbo pump
- After 1.5 min, turn off roughing pump
- Turn off nitrogen and argon gas
- Venting of the chamber

**RF cleaning**
- Set argon gas flow to 75 sccm
- Turn on RF power (200W, 13.56 MHz)
- Open Turbo pump
- Cool down to about 40°C
- Pump down to about 1 x 10^-6 mbar

**Startup**
- Fit rings onto spindle
- Turn on nitrogen and argon gas
- Plug-in power cables
- Turn on cooling water
- Turn on roughing pump
- Turn on turbo pump at 1 x 10^-6 mbar
- Set argon gas flow to 12.5 sccm
- Pre-sputtering for about 2 min
- Open gun shutter
- Sputtering process
- Turn off power supply
- Turn off turbo pump
- After 15 min, turn off roughing pump
- Turn off nitrogen and argon gas
- Venting of the chamber

**Sputtering**
- Set argon gas flow to 75 sccm
- Turn on RF power (200W, 13.56 MHz)
- Open Turbo pump
- Cool down to about 40°C
- Pump down to about 1 x 10^-6 mbar
- Set argon gas flow to 12.5 sccm
- Pre-sputtering for about 2 min
- Open gun shutter
- Sputtering process

Figure A.1: Step by step guide for thin-film carbon deposition using the Hummer XII.