Compositional and Structural Analysis of Nitrogen Incorporated and Ion Implanted Diamond Thin Films

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COMPOSITIONAL AND STRUCTURAL ANALYSIS
OF NITROGEN INCORPORATED AND ION
IMPLANTED DIAMOND THIN FILMS

by

Elias James Garratt

A dissertation submitted to the Graduate College
in partial fulfillment of the requirements
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COMPOSITIONAL AND STRUCTURAL ANALYSIS OF NITROGEN INCORPORATED AND ION IMPLANTED DIAMOND THIN FILMS

Elias James Garratt, Ph.D.

Western Michigan University, 2013

Significant progress in area of nano-structured thin film systems has taken place in recent decades. In particular, diamond thin film systems are being widely studied for their wear resistant, optical and electronic properties. Of the various methods researchers use to modify the structure of such films, three techniques in particular are of interest due to their versatility: modification of the growth atmosphere, growth on metalized substrates, providing an interfacial layer, and modification through post-growth ion implantation. The aim of this study is to investigate the effects each has to the structure and composition of elements. Different techniques are applied in each section; nitrogen gas dilution in a microwave plasma CVD system, diamond deposition on a metal interfacial layer and ion implantation in thin nanocrystalline diamond film. The forms of nanocrystalline diamond film resulting from such modifications are investigated using advanced spectroscopic and spectrometric techniques, as well as mechanical testing and surface mapping.

The impact of these characterizations will provide valuable perspective to researchers in materials science. Understanding the changes to the structure and properties of this class of thin films, which can be induced through various mechanisms,
will allow future researchers to refine these films towards technological applications in areas of hard coatings, electronics and photonics.
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CHAPTER 1
INTRODUCTION

Nano-structured materials are becoming ever more prevalent in society; from the utilization of silver nanoparticles to clean indoor air [1] to strain sensors based on carbon nanotubes [2] to the increasingly compact design of very large-scale interface (VLSI) circuits [3]. Among the myriad number of materials under investigation, nano-diamond materials are of particular interest due to the well-known superlative qualities of diamond: hardness, optical transparency, and thermal conductivity. Within the past few decades, diamonds have been synthesized in the laboratory through techniques utilizing plasmas formed in various kinds of chemical vapor deposition systems [4]. These techniques have produced a number of different kinds of diamond films, classified by diamond grain size from micro-crystalline to nanocrystalline and recently ultrananocrystalline diamond films, or UNCD [5].

Nano-diamond films are typically grown in a microwave-plasma chemical-vapor deposition (MPCVD) system, often within growth atmospheres comprised of highly ionized argon and methane. Adjustments to the characteristics of the growth atmosphere, such as the relative composition and flow of gases, have been shown to greatly impact the development of NCD films. In this way, the emergent properties of such films can be greatly altered; including optical transparency, electrical and thermal conductivity, and hardness [6,7]. NCD films grown in atmospheres comprised partially of nitrogen have been shown to have greater electrical conductivity than those without by several orders of
magnitude [8]. Additionally, there exists evidence that the presence of nitrogen gas within the growth atmosphere of NCD facilitates nitrogen uptake into the bulk of the material [9,10]. Based on these changes to NCD films solely as a result of alterations to the growth parameters, it can be inferred that the potential exists for NCD film properties to be manipulated either by further alterations to the growth parameters of NCD films, such as interface modification, or by well-known techniques, such as ion implantation.

The focus of this thesis will be on characterizing the structure and composition of NCD films modified through the addition on nitrogen to the growth atmosphere and metallization via various mechanisms. Alterations to growth parameters, such as chamber atmosphere and growth interface will be discussed as well as alterations the post growth ion implantation has on the molecular structure of resultant NCD films. Throughout the various studies performed, the focus will be on the evaluation of the structure, microstructure and composition of films which result from such alterations, and the implications such alterations may have on the adaptation of these films for use in a technological setting. It is important to understand that, to derive an accurate understanding of the films studied in this dissertation, a fairly large array of characterization techniques has been employed. Each technique employed is separate from the other, e.g. Raman spectroscopy probes the vibrational molecular structure while Rutherford backscattering examines composition and interfacial characteristics. However, when these data are correlated, an accurate description of the structure to property relationships in each sample can be established. This dissertation is broken up into three parts, the first dealing with the changes to composition and structure of NCD films grown with nitrogen gas diluted in the growth atmosphere, while the second part
examines the changes to composition, structure, microstructure and mechanical hardness of NCD films grown on a metalized silicon substrate with nitrogen gas diluted in the growth atmosphere. Finally, the third section focuses on the metallization of NCD bulk through direct ion implantation, and probes the changes in film structure and microstructure using electron and scanning probe microscopy.

1.1 Nitrogen Incorporation and Quantification

Starting with nitrogen addition to the growth atmosphere, it has been shown in the literature that the relative concentration of ionized gases affect the properties of the deposited NCD films [11]. Nanocrystalline diamond (NCD) films have been shown to have mild conducting properties, which increase as a function of nitrogen absorption reaching a saturation in the resultant film at 20% nitrogen dilution within the ionized growth atmosphere [12,13,14,15]. Some studies of nitrogen incorporated films have attributed this increase in conductivity, in part, to a gain of conduction states within the band gap; which is attributed to an increase of bonding disorder due to impurities within the grain boundaries [16]. Similarly, some studies of nitrogen incorporated films have attributed the increase of conductivity, in part, to the resulting narrowed energy gap within the sp2 ordered carbon structure [17]. This and similar evidence verifies that nitrogen incorporation results in an increase of the superlative characteristics of NCD thin films. The aim of section 3.1 in this dissertation is to quantify the amount of nitrogen incorporated within NCD films, at the saturation limit, grown under typical conditions favoring increased conductivity. Knowing the concentration of the nitrogen impurity within this material will allow researchers to adapt diamond films towards various applications, such as high temperature semiconductors.
1.2 The Effect of Metal Interlayers

Sections 4.2 and 4.3 characterize the effect of NCD growth on a metal interlayer within a CVD reactor atmosphere of increasing nitrogen content. Through these characterizations, the aim of these sections is to provide empirical data concerning the viability of NCD growth on interlayers which can enhance the superlative properties of such films. For example, films grown on an interlayer of tungsten and molybdenum have displayed smoother surfaces than those prepared by traditional seeding methods [18,19]. This improved smoothness was attributed to an increase in the concentration of nucleation sites. Additionally, with the addition of nitrogen alone in CVD reactor conditions otherwise optimal for the growth of ultrananocrystalline diamond (UNCD), differed largely from expected UNCD grain size values (approximately 2-5 nm) [5].

Investigation into the effect of diamond grain size after film growth in a nitrogen diluted gas admixture on metalized substrates was undertaken. Characterizations were performed to determine whether or not the combined effect of metal interlayers and nitrogen dilution can optimize NCD film properties for potential application as highly customizable, high temperature, semiconductors or microacuators.

1.3 Metal Ion Implantation in Nanocrystalline Diamond Films

Section 4.4, metallization of the NCD bulk region, discusses the process of metal ion implantation and characterizes the structure and microstructure of metalized NCD. The metal ion of interest in this chapter, chromium, is undergoing a significant amount of scientific interest due to recent studies which have noted considerable emergent properties in materials after the incorporation of chromium, such as the brightest single
photon source reported within monolithic single crystal diamond to date or ferromagnetization in ceramic semiconductors [20,21,22]. In contrast to diamond, neither NCD nor UNCD are made up of purely diamond phases of carbon; within each material there exists a percentage of graphitic phase, or sp², carbon as well as hydrogen. As such, the picture of ion incorporation and resultant elemental composition of these films will be different from that of single crystal diamond. The aim of this section, then, is to determine the structural changes occurring within the NCD film and at the surface for the purposes of establishing a dialogue, or stepping stone, to further research dealing with the viability of adapting this technique to the fabrication of optical devices.

In summary, this dissertation examines the effects of metalized substrates and NCD bulk on the properties of NCD films grown in either a nitrogen diluted or undiluted growth atmosphere. The properties of each film in terms of composition, structure and microstructure are examined within the context of film application as hard coatings or high temperature semiconductors. The following chapters will describe the aspects of the experiments performed and the underlying theory of the techniques used to characterize each film. Chapter 2 will discuss the principal aspects of the physics governing each characterization technique, while chapter 3 will provide the basic experimental set up supporting the data obtained in each measurement. Chapter 4 delves into the analysis of data obtained by each technique within the context of the objective of each experiment which was carried out. Finally, chapter 5 summarizes the results from each experiment.
CHAPTER 2
THEORY

This chapter will outline the theory governing measurements performed on NCD samples to characterize the composition, structure and microstructure of each film. The overriding method used throughout this dissertation to evaluate NCD films, ion beam analysis, is described in detail in the first section of this chapter. The section on ion beam analysis covers the physics governing particle scattering interactions, energy losses of ions within materials and practical considerations such as the position of a detector to obtain good measurement cross sections. The following sections generally provide a brief background concerning the physical principles used to obtain data from which compositional, structural and microstructural information about each films was derived.

2.1 Ion Beam Analysis

2.1.1 Particle Scattering Spectrometry

Ion beam analysis (IBA) techniques are very powerful research tools. Information about a given material; such as elemental composition and concentration, as well as crystallographic orientation, can be determined using ion beam analysis techniques. Collisions of energetic particles with stationary atoms within a target material are the foundation of IBA techniques which were first observed in laboratory by Geiger and Marsden under the direction of Sir Ernst Rutherford in 1909[23]. In 1957, the scattering of high velocity particles was reported as a materials analysis technique by Sylvan Rubin, et.al. [24] Currently, ion beam techniques such as Rutherford backscattering spectrometry
(RBS), elastic recoil detection analysis (ERDA), and resonant nuclear reaction analysis (RNRA) are used frequently in research to characterize materials.

It is beneficial to study NCD films by these techniques because IBA has the ability to directly quantify the concentration of constituent particles within a material. This is difficult if not, in a practical sense, impossible with other techniques given the amounts and properties of the element in question. For example, extremely low concentrations, below 1 at% of a given element within a sample, are not reliably detectable by techniques such as x-ray photoelectron spectroscopy or x-ray absorption fine structure spectroscopy, due to the weak signal emitted by such low concentrations of the element, but is possible with ion beam analysis. Additionally, using a single ion beam technique, it is possible to obtain information on not only the concentration of an element, but also the concentration at varying depth within the material. Using known reactions of energetic particles with specific elements; i.e. the $^{15}\text{N}(p, \alpha\gamma)^{12}\text{C}$ nuclear reaction, in which a sodium iodide (NaI(Tl)) or germanium (HPGe) detector is used to measure the $\gamma$-rays resulting from the nuclear interaction, parts per million [25] of specific elements can readily be determined. This reaction was utilized for the first part of this dissertation to measure the content of nitrogen within NCD films grown on chromium and silicon interfaces.

2.1.1.1 Kinematic Factor

RBS, and specifically non-Rutherford backscattering spectrometry (NRBS) and ERDA used in this study, were performed to obtain the concentrations of carbon, chromium and hydrogen within each sample. RBS is the elastic scattering of incident particles from atoms within the target material. Based on the energy, angle and depth
from which incident particles are scattered one may determine information pertaining to
the elemental composition of the target, relative distribution of elements within the target
and thickness. RBS can be described theoretically as the classical scattering of an
incident particle from a central force field, making the technique easy to understand. In
this case, the conservation of energy and momentum are used to directly derive the
equations which give values that are of central importance in setting up RBS
experiments, such as kinematic factor and cross section.

From basic kinematic equations of elastic collision between two objects, a useful
term called the kinematic factor (K) arises. K is be expressed as a ratio of final velocity
over initial velocity, or final energy over initial energy [26];

\[ K = \frac{v_f}{v_i} = \frac{E_f}{E_i} = \frac{m_2^2 - m_1^2 \sin^2 \theta + m_1 \cos \theta}{m_1 + m_2} \]  \hspace{1cm} (1)

The equation indicates that the final energy of a system can be determined solely from
the masses of the particles, \( m_1 \) (incident particle) and \( m_2 \) (target particle), involved and
the scattering angle, \( \theta \). Tabulations of the kinematic factor for values of \( m_2 \) at different
scattering angles are often used to design RBS experiments. In such experiments, it is
desirable to have as large an energy separation (\( \Delta E \)) as possible between incident ions
and ions scattered off the target atoms. Assuming \( m_1 < m_2 \), the largest change of
energy, and therefore K, is produced when \( \theta = 180^\circ \), however, due to the size of detectors
used in RBS, most experiments use scattering angles between 170° and 160°.

2.1.1.2 Detector

Detecting the scattered particles is the function of the surface-barrier solid-state
detector employed in many backscattering experiments. These detectors produce a
voltage pulse from the collection of electron-hole pairs produced when a scattered particle enters the depletion region of a reversed biased Schottky barrier diode. The height of each pulse is proportional to the incident energy of the particles and the pulses are sorted into separate voltage bins (or channels) by a pulse height analyzer. In this way each channel is directly proportional to the energy of the particle picked up by the detector. The energy resolution of such detectors can be anywhere between 10-20 keV [27].

2.1.1.3 Cross Section

In IBA experiments, the identity of the particle from which incident ions are scattered is determined from the energy of the particle which is sorted into separate voltage bins by a multi-channel analyzer. From the yields of detected particles obtained during an RBS measurement the differential scattering cross section, $Q_D$, is determined from the number of target atoms per unit area:

$$Q_D = \frac{d\sigma}{d\Omega} \, d\Omega \, N_t \, Q$$ (2)

where $d\Omega$ is the solid angle measured from the target to the detector, $N_t$ is atoms/cm$^2$, $Q$ is the charge on the sample obtained by integrating the beam current at the scattering chamber, and $\sigma(\theta)$ is the scattering cross section. The scattering cross section itself may be derived from the central force scattering between the incident particle and the target atom. For RBS measurements the collision between particles is well outside of the range at which nuclear forces may be experienced by the incident ion, therefore, Coulomb repulsion determines central force scattering.
Figure 1. Illustration of impact parameter (b) for incident particles, and scattered angle \( \theta \) and \( d\theta \). Decreasing impact parameter, or radial distance from the axis of symmetry from which particle separation distance, \( r \), is determined, results in an increasing scattering angle, \( \theta \).

Given that for incident particles whose perpendicular distance to a target is \( b + db \), the scattering angle is \( \theta + d\theta \). The scattering cross section may be defined about the axis of the incident ion beam as (Figure 1) [26]:

\[
2\pi b \, db = -\sigma \, \theta \, 2\pi \sin \theta \, d\theta \quad (3)
\]

For RBS, the central scattering force is through Coulomb repulsion between scattered and incident particles:

\[
F = \frac{1}{4\pi\varepsilon_0} \frac{Z_1Z_2e^2}{r^2} \quad (4)
\]

Where \( Z_1 \) and \( Z_2 \) are the atomic numbers of incident and target atoms respectively, \( e \) is the charge of an electron, \( r \) is the distance of the target atom to the incident particle, and \( r \) points in the direction of from the incident ion to the target atom. Solving for impact
parameter $b$ based on conservation of linear momentum and scattering from central force eventually yields [26]:

$$b = \frac{Z_1 Z_2 e^2}{m_1 v^2} \cot \frac{\theta}{2} \quad (5)$$

which, when combined with (5) yields the equation for cross section [26],

$$\sigma \theta = \frac{Z_1 Z_2 e^2}{4E} \frac{1}{\sin^4 \frac{\theta}{2}} \quad (6)$$

with $E$ equal to the kinetic energy of the incident particle with velocity $v_i$. In the laboratory frame, taking into consideration target recoils, the scattering cross section during a collision results in a more complicated equation [26]:

$$\sigma \theta = \frac{Z_1 Z_2 e^2}{4E} \frac{4}{\sin^4 \theta} \frac{1 - \frac{M_1}{M_2} \sin \theta}{1 - \frac{M_1}{M_2} \sin^2 \frac{\theta}{2}} ^{1/2} + \cos \theta^2 \quad (7)$$

Equations (5) and (6) for elastically scattered particles are applicable to experiments utilizing Rutherford backscattering, but for those involving nuclear forces such as; collisions that take place at high energies, scattering angles, or with low $Z_2$ atoms, this formula is not applicable. A non-Rutherford cross section is, in cases where the reaction remains an elastic collision between interacting particles, the observed cross section is > 4% from the predicted Rutherford cross section at angles between 160° and 180° [28,29,30]. In practice, the differential cross section for non-Rutherford backscattering interactions is derived from empirical data [31], and resources exist online [32] to calculate differential cross sections from experimental data. In general, the scattering cross section for Rutherford backscattering experiments such as the one treated in this thesis is dependent on the atomic number and masses of the incident and target.
atoms, the angle to which the incident ion is scattered, and the energy of the incident ions. One can then optimize the geometry of the chamber within which scattering takes place to obtain the best possible cross section.

2.1.1.4 Scattering Chamber Geometry

In general, the geometric orientation of detectors within a scattering chamber is described in terms of the position and angle of the target (relative to the incident beam). Within this context, two geometries have been developed; IBM and Cornell geometries. An illustration of each geometry is given in Figure 2. The equations associated with each are derived from the orientation incident, reflected and scattering vectors relative to each other and the sample. IBM geometry places the incident, reflected and scattering angles all in the same plane, described by the equation

\[ \alpha + \beta + \theta = 180 \quad (8) \]

while Cornell geometry is a three dimensional scattering geometry in which the scattering and exit angles lie outside the plane of the incident angle. It is described in terms of the angle \( \beta \) by equation;

\[ \cos \beta = -\cos \alpha \cos \theta \quad (9) \]

While IBM geometry offers a simplified setup, the more complicated Cornell geometry setup has the advantage of better depth and mass resolution due to its larger scattering angle.
Using either Cornell or IBM geometries, adjusting the incident angle to increase the path length within a shallow region of the target allows one to probe the concentration in a narrow range.

2.1.1.5 Energy Loss and SRIM Computer Code

Depending on the thickness of the target, considerations must be made to account for the energy loss of ions as they pass through a target. Several models of energy loss within target material have been created, and vary based on a statistical approach to the energy straggling experienced by incident ions passing through a target.

Based on the thickness of the targets used in this study, the energy loss model covered in this section will refer to theory developed by Vavilov [33]. Within the context of a thin target backscattering energy losses are considered negligible and the value of the kinematic factor is given simply by the kinematic factor, $K$. In the case of thick targets
the same model is applied; the thick target is divided into thin slabs and the total energy loss is calculated recursively (the energy of the previous slab applied to the next) from the path that the incident takes through the target. The energy is calculated for each slab in the order in which it was encountered and applied as the initial energy of the next layer. Exiting the material follows the same recursive procedure. This process is illustrated in Figure 3.

**Figure 3.** Illustration of recursive approach to energy loss within thin and thick targets. Incident particles lose energy within each layer. The remaining energy of the particle is applied as the initial energy of the particle in the next layer, which subsequently decreases as the particle passes through that layer.

Energy losses within a target vary with the material being studied, and as such the accuracy of RBS data depends on accurate stopping power. To obtain stopping power data this experiment utilized the stopping range of ions in matter (SRIM, www.srim.org) computer code extensively [34]. Briefly, SRIM is a Monte Carlo simulation of interactions between ions and target materials. For most targets, it utilizes the Bragg rule to determine the stopping power of a target made up of any combination of elements.
However, it does contain a library of compounds for which the effects of chemical bonds have been taken into account. Below are plots generated by SRIM software of ion trajectories and recoil collisions of 3.5 MeV He ions within NCD, the target material of this study.
**Figure 4.** SRIM calculations of 3.5 MeV helium beam incident on a typical NCD target. The series of figures on the left illustrates the cascade approach, described in the text, while the series of figures on the right illustrates a monolayer-step approach. Figures with a black background show helium ion trajectory, the figures with data in orange show atom recoils due to collisions with helium. Finally, the 3D figures (bottom) show the profile of damage to the NCD lattice due to collisions in the form of lattice atom displacements and vacancies.

These plots were generated for a low number of trials (5000) for the purposes of illustrating the function of SRIM software. Therefore, statistics on the number of recoils and distribution are not entirely accurate. SRIM software has available models to calculate ion trajectory and interaction based on the projected mean free path of ions within the target as well as monolayer calculations which parse collisions at each monolayer. In Figure 4, cascade (mean free path) and monolayer calculations are illustrated. While monolayer collisions generally yield more accurate data, cascade type calculations are much faster and yield results accurate to within a few percent of those from monolayer type calculations [35]. Within these plots, ions are calculated independently from a single scattering point to develop statistical plots of the overall ion
beam trajectory within a target. One may then consider the plots generated to be representative of incident ion behavior over the entire beam area on the target. The accuracy of stopping power models employed in this software has been quoted to be approximately 4% for protons and helium ions, and about 10% for heavier ions as of the latest software version [36]. Based on these calculations of stopping power (corresponding to energy loss) simulations of RBS spectra can yield valuable information such as target thickness and concentration of elements within a given range within the target.

The ability of experimentalists to develop accurate models of ion beam interactions within a target and correlate these models with real data to develop simulations of RBS spectra illustrates the depth and power of RBS and IBA techniques to evaluate materials. In terms of this study, NRBS combined with ERDA and RNRA was able to characterize elemental distribution and concentration clearly within NCD, leading to a more complete understanding of the architecture, composition and interfacial quality, of NCD films produced on metalized substrates and within a nitrogen diluted plasma. The next section will approach profiling nitrogen content within NCD films grown in a $^{15}\text{N}_2$ diluted growth plasma using resonant nuclear reaction analysis.

2.1.2 Resonant Nuclear Reaction Analysis

Nitrogen is notoriously difficult to quantify (in low concentrations) using techniques found in most materials science laboratories, such as x-ray photoelectron spectroscopy. Therefore, a reaction unique to IBA techniques was utilized to profile the concentrations of nitrogen within control films and films grown on metalized substrates used in this dissertation. The IBA technique, resonant nuclear reaction analysis (RNRA),
used the $^{15}\text{N}(p,\alpha\gamma)^{12}\text{C}$ reaction to probe the amount of nitrogen incorporated into NCD samples. Figure 5 shows the full RNRA spectrum obtained from the control sample for resonant nuclear reactions obtained using proton beams of increasing incident energy. A magnified view of the section of interest for determining $^{15}\text{N}$ content shows two escape peaks on the left and middle, and the $\gamma$-ray peak denoting $^{15}\text{N}$ concentration on the right. The escape peaks are data artifacts produced when $\gamma$-rays originating from the $^{15}\text{N}(p,\alpha\gamma)^{12}\text{C}$ reaction interact within the NaI(Tl) detector, resulting in pair production and reabsorption of the $\gamma$-rays produced from positron annihilation (4.43 – 0.511 MeV for the middle peak and 4.43 – 1.022 MeV for the left escape peak). Increasing the incident beam energy in steps from 900 to 925 keV allowed protons to penetrate to a greater depth within the sample before reaching the resonance energy of 897 keV as illustrated in Figure 6. The reaction at 897 keV was chosen due to its high cross-section of 800 millibarns, and sharp energy width of 1.7 keV (corresponding to a 20 nm depth within the film) [37], allowing nitrogen concentration and profile to be obtained simultaneously. At this specific energy protons colliding with the nucleus of a $^{15}\text{N}$ atom cause the emission of a 4.43 MeV $\gamma$-rays and are detected by the NaI(Tl) detector, resulting in the peak on the left. The integrated area under the far right-hand peak is directly proportional to the concentration of $^{15}\text{N}$ within the sample; therefore an increase in this area represents an increase of $^{15}\text{N}$ content at the depth at which the nuclear reaction took place.
Figure 5. Full RNRA spectrum of background radiation and a representative sample for each incident beam energy. Since the peaks generated by proton-induced γ-ray emission lie well away (far right) from the background (left of center) need not be subtracted from the spectrum.
Figure 6. Detail of γ-ray and escape peaks due to interactions within the NaI(Tl) detector. The two escape peaks to the left of the 4.43 MeV γ-ray peak result from the reabsorption of γ-rays produced from positron annihilation within the NaI(Tl) detector.

The $^{15}$N concentrations were determined from the γ-ray yields obtained at proton beam energies ranging from 900 to 925 keV. The atomic percent of $^{15}$N as a function of incident beam energy was calculated as follows [38];

$$m = \frac{f \cdot Y_{AB} \cdot \epsilon_{B}}{Y_{st} \cdot \epsilon_{st} + f \cdot Y_{AB} \cdot \epsilon_{B} - \epsilon_{A}}$$  \hspace{1cm} (10)$$

where $f$ is the known atomic fraction of the standard reference material, Si$_3$N$_4$, $Y_{AB}$ and $Y_{st}$ are the yield of the target and reference material respectively, and $\epsilon_{B}$, $\epsilon_{A}$ and $\epsilon_{st}$ are the stopping powers of the carbon-hydrogen bulk, nitrogen, and reference material respectively [38].
To obtain the stopping cross-section values for the carbon-hydrogen bulk and Si$_3$N$_4$ the Bragg rule approximation was applied, treating the stopping contribution of each element within the material separately and ignoring any of the secondary effects of bonding. The stopping cross section for Si$_3$N$_4$ was obtained as follows;

$$\varepsilon^{Si_3N_4} = 3\varepsilon^{Si} + 4\varepsilon^N \quad (11)$$

The stopping cross-sections for incident proton beams above were obtained as follows;

$$\varepsilon = \frac{\varepsilon_{low} \times \varepsilon_{high}}{\varepsilon_{low} + \varepsilon_{high}} \quad (12)$$

with $\varepsilon_{low}$ and $\varepsilon_{high}$ given by;

$$\varepsilon_{low} = A_1 e^{A_2} + A_3 e^{A_4} \quad (13)$$

$$\varepsilon_{high} = \frac{A_5}{E^A s \ln \left( \frac{A_7}{E} + \frac{A_8}{E} \right)} \quad (14)$$

where E is the energy of the incident beam, and A$_n$ are known stopping cross-sections [39].

The stopping range of the incident protons within the sample was determined by SRIM using the incident proton energy, as well as the composition and density of the films [40]. An increase in the energy of the incident beam corresponded to a linear shift of the resonance peak deeper into the material; this shift was calculated by taking the differences of the stopping ranges of protons for each 5 keV (corresponding to 70 nm) step.

This concludes the theoretical discussion of IBA techniques implemented in this dissertation to study the composition, interfacial quality and profile of elements within control NCD films and films grown on metalized substrates. The following sections will
deal, in less detail, with the spectroscopic, scanning probe, and mechanical characterization techniques used to complement the characterizations obtained through IBA.

2.2 Raman Spectroscopy

Raman spectroscopy is the study of light/matter interactions in the specific instance where a shift frequency is observed between the scattered and incident light from a given material. This frequency shift was first observed by C.V. Raman and K.S. Krishnan and reported as the visual discovery of a new form of secondary radiation in early 1928 [41]. In the case of Raman and Krishnan sunlight passed through a blue-violet filter, impinged upon various substances, and finally passed through a green filter displayed a feeble but robust, under purification, kind of radiation whereas Landsberg and Mandelstam [42] observed a satellite line to the Rayleigh scattering line. It was suggested that this new kind of radiation may be due to inelastic scattering of photons; which was found to be accurate.

Raman spectroscopy has been utilized in this dissertation to perform a comparative analysis of the carbon vibrational molecular structure, which reveals information about the molecular bond state of carbon within each film. Data obtained using this technique was analyzed based on previous Raman studies of NCD, and CVD diamond films in general. Since identification of bond states and comparative analysis was premise under which this data was obtained, a comprehensive analysis of the Raman spectra is not necessary. As such, this discussion of Raman theory, as it pertains to deriving the origins of the Raman signal and interpreting the spectrum produced based on
the observed intensities, will be the focus of this section. Specifically, the origin of the Raman signal due to polarization of a molecule will be the topic of this section.

2.2.1 Raman Signal, Inelastic Scattering and Polarization

A Raman signal is produced when incident optical electromagnetic (EM) radiation impinges upon a given material and undergoes inelastic scattering. Due to this inelastic scattering the emergent EM wave is shifted in frequency from the incident wave; EM waves shifted in this way are said to have undergone either Stokes scattering [43], for a frequency shift down, or anti-Stokes scattering for a frequency shift up (Figure 7).

In either case, inelastic scattering of incident EM radiation has taken place. Inelastic scattering in this way can be said to have perturbed the system – from which one may derive information about its condition; such as vibrational states unique to each molecular configuration, or its spin state (through examining the magnetic component of the

\[ \Delta E_i = h \nu_o \]

\[ \Delta E_c = -h(\nu_o - \nu_v) \]

\[ \Delta E_i = h \nu_o \]

\[ \Delta E_c = -h(\nu_o + \nu_v) \]

Figure 7. Energy diagram of Stokes and anti-Stokes type Raman scattering. Both Stokes and anti-Stokes scattering, and inelastic scattering event, are extremely rare occurrences compared to elastically scattered light (Rayleigh scattered). Anti-Stokes scattering results from photon absorption by an electron in an excited state.
measured signal) [44]. Exposure of a sample to optical EM radiation establishes a polarization within the greater (macroscopic) and local (microscopic or molecular) environment. The equation describing this polarization in either case is given as:

\[ P = X^{(1)}E + X^{(2)}E^2 + X^{(3)}E^3 + \cdots + X^{(s)}E^s \cdots E + \cdots \]  

(15)

where \( P \) is the polarization, \( X \) is the susceptibility, and \( E \) is the electric field; the superscripts of the symbol \( X \) refer to the order of the system, for instance \( X^{(1)} \) is first order and \( X^{(3)} \) is third order. \( E \) is given as an initial electrical field times the exponential of the difference between the positional and time components of the EM wave:

\[ E = E_0 e^{-i(k\cdot r - \omega t)} \]  

(16)

where \( k \) is the wavevector and \( \omega \) the frequency. A complete theoretical treatment of the polarization effect is described using a statistical quantum mechanical treatment of the time evolution of the vibrational, translational, or rotational eigenstate energies of the molecular system and their relation to the surrounding environment. Such a treatment lies outside of the scope of this study and as such this section will restrict itself to the derivation of the first order term susceptibility (often referred to as the polarizability) tensor.

In full matrix language, the first term in the polarization equation is written:

\[
P = \mu^{(1)} = \begin{pmatrix} \mu_x & \alpha_{xx} & \alpha_{xy} & \alpha_{xz} & E_z \\ \mu_y & \alpha_{yx} & \alpha_{yy} & \alpha_{yz} & E_y \\ \mu_z & \alpha_{zx} & \alpha_{zy} & \alpha_{zz} & E_z \end{pmatrix} = \alpha E
\]  

(17)

where \( \alpha \) is the polarizability tensor. The quantum mechanical expression of the polarizability for transition between the ground and final molecular eigenstates (as seen
in Stokes shifting) is dependent on the frequency of the incident and molecular electrical fields referred to as the (thermalized) Kramers-Heisenberg equation [45]:

$$\alpha_{bc}(\omega_i, \omega_j)_{gf} = \frac{g | \mu_b | n \ n | \mu_c | f}{\omega_{ng} - \omega_i} + \frac{g | \mu_c | n \ n | \mu_b | f}{\omega_{ng} + \omega_j} \quad (18)$$

where g and f refer to the ground and final molecular eigenstates, n is an intermediate ‘virtual’ state, \(\omega_i\) and \(\omega_f\) are the frequencies of the incident and molecular EM fields, and \(\alpha_{bc}\) is, the polarizability term which allows for the production of a Raman signal.

To translate this polarizability term into the context of vibrational eigenstates of the molecule one must first introduce the Born-Oppenheimer approximation [46] to solve the Hamiltonian of the molecular system. In this, the kinetic energy term of the nuclei within the molecule is neglected, since the velocity of the nucleus compared to that of the electrons is relatively low and the spatial coordinates of these nuclei with respect to the electron cloud are fixed (or parameterized) incrementally to derive the electronic energy eigenstates of the system. The kinetic energy term for the nuclear components of the system is then reintroduced and the Schrödinger equation is solved with respect to nuclear motion. Within this second step the vibrational, rotational and translational elements of molecular motion are separated by applying the Eckart conditions [47] which minimizes the coupling between external (translational/rotational) and internal (vibrational) molecular motion. The electronic polarizability is then [44]:

$$\alpha_{bc}^{el} = \alpha_{bc}^{el}_0 + \frac{\partial \alpha_{bc}^{el}}{\partial Q_i} \Delta Q_i + \frac{1}{2} \frac{\partial^2 \alpha_{bc}^{el}}{\partial Q_i \partial Q_j} \Delta Q_i \Delta Q_j + \ldots \quad (19)$$

where \(\Delta Q_i\) are the normal displacement coordinates. The first term in the electronic linear polarizability corresponds to Rayleigh scattering while the second and
third terms correspond to fundamental scattering and scattering from first overtones \((i = j)\) and combination states \((i \neq j)\). From these values of the polarizability, the framework of the linear polarizability theory of Raman scattering has been established [48]. Further developments in Raman scattering theory lead to the realization that as the optical excitation wave moves from non-resonant to resonant regions within a material, the dispersive behavior of the Raman scattering cross section takes on a different analytical forms [49]. This covers the basic principles under which Raman measurements are based. For a more complete explanation of the detail involved in obtaining Raman measurements, the reader is referred to the literature referenced throughout this section and later in the dissertation. Raman spectroscopy is a valuable and powerful tool for assessing the molecular state of elements within a given system. For the of NCD films developed on silicon and metalized silicon substrates, Raman spectroscopy can yield valuable information about the relative vibrational state of molecules, indicating a shift in the fundamental molecular architecture between films. In addition to other techniques which probe the molecular structure of materials, a picture of the overall structure/property relationship within NCD films can be developed.

2.3 Atomic Force Microscopy

In terms of film application as a smooth, hard, coating to protect parts and devices from wear it stands to reason that the surface of the film should be evaluated. While IBA and Raman techniques described previously are effective in determining the composition and molecular structure of films altered by metallization or nitrogen gas dilution, they do not provide a picture of the microstructure of the film. Rather than draw inferences concerning the nature of microstructural changes based on these data, atomic force
microscopy, or AFM, was performed on NCD samples to determine the microstructural character of these films directly. AFM is an effective tool for characterizing the microstructure of thin film samples. This section was designed to give the reader a brief insight into the forces which govern the outcome of AFM measurements. For a more in-depth understanding, the reader may refer to the sources cited in this section.

AFM itself is a more complicated offshoot from scanning tunneling microscopy. Invented by Binnig [50] and introduced in 1985 by Binnig, Quate and Gerber [50] it has become a widely used tool in micro and nano-engineering. The core principle of AFM is surface characterization through the generation of a three dimensional topological map. AFM can create images with details down to the atomic scale in some cases [50]. In this study, AFM was performed on the surface of NCD/Si and NCD/Cr/Si to obtain a comparative picture of their surfaces. Although such a basic measurement does not make full use of the capabilities of AFM, it provides an excellent point from which to assess the relative differences in roughness and grain size in each film. This section will focus on the basis from which AFM images are obtained within the context of the experimental parameters used to obtain those images.

2.3.1 AFM Non-Contact Mode

AFM images obtained in this study were taken by a Nano-R series AFM machine developed by Pacific Nanotechnology under ‘close contact’, or non-contact, mode. Operating in this mode the combination stylus/cantilever is allowed to oscillate in the z-direction within a defined amplitude just above the surface of a sample, as the system is moved laterally by piezoelectric crystals. The stylus used in AFM measurements is typically a square-pyramidal or conically shaped needle attached to the underside of the
cantilever. Reflective material coats the side opposite the stylus on the cantilever; laser light which strikes this material is then reflected onto a cluster of photodetectors. Deflections in the z-direction of the cantilever system from the average range of the oscillation amplitude are picked up by this cluster as changes in the relative intensity of reflected laser light and, correlated with the lateral position of the system at the point of deflection, are translated into a three-dimensional map of the sample surface. Images are produced within proprietary software developed by Pacific Nanotechnology. Since the stylus, or probe, never touches the sample surface in this mode of operation, deflections which produce the image are generated by long range forces ubiquitous in all materials; van der Waals and electrostatic forces.

### 2.3.2 Interaction Forces; Van der Waals

Van der Waals forces are weak, short range, forces which arise primarily due to dipole interactions between atoms and molecules within a material. They are divided into: Keesom forces (dipole-dipole interaction); Debye forces (dipole-induced dipole interaction) and London, or dispersive, forces (dipole-non dipole interaction) [51]. As a whole, the van der Waals forces are expressed as the sum of these forces over the sixth power separation distance between molecules:

\[
W(r) = \frac{-C_T}{r^6} = -\frac{C_K + C_D + C_L}{r^6} \quad (20)
\]

Each component of the above equation; \(C_K\), \(C_D\) and \(C_L\) is an expression for the individual components of the total van der Waals force, the Keesom \((C_K)\), Debye \((C_D)\) and London \((C_L)\).
2.3.3 Interaction Forces; Electrostatic

While the Van der Waals forces act to bring the probe closer to the surface, electrostatic forces act opposite to repel. Assuming that both the probe and the sample are conductive, the electrostatic effects come into play when the potential difference, \( U \), between the two is nonzero during an AFM scan of the sample. Given briefly in [50], the electrostatic force in terms of the probe and sample interaction is:

\[
F_{\text{electrostatic}} = \frac{-\pi \varepsilon_0 RU^2}{z}
\]  

(21)

The forces derived from both kinds of probe/sample interaction become non-negligible at a close enough approach, usually \( \sim 100 \text{ nm} \) from the surface, resulting in a push and pull which maps the surface of the sample.

This is the basic picture of how AFM images are produced through the interaction of forces at the surface of the sample between the tip and the sample itself. More detailed descriptions of the experimental methodology can be found listed in the references given in this section as well as the experimental setup used to obtain AFM images, given in chapter three. The characterizations obtained through this method allowed for the direct quantitative analysis and correlation of microstructural change between films grown on metalized substrates and for films metalized through ion implantation with data gained through the other techniques which have been discussed and those yet to be dealt with.

2.4 Secondary Ion Mass Spectrometry

This section returns to the concept of particle scattering (or IBA) to obtain information about the composition and profile of elements within a given material.
Through understanding the composition and profile of elements found within NCD samples, researchers have been able to correlate changes in the properties of these materials through direct statistical inference, allowing for further refinement of such films within a technological context. The IBA techniques described previously rely on the scattering of ions from a target to obtain information related to, among other qualities, composition. While the reliability and effectiveness of these techniques are superb, examining the same set of data from another perspective is useful in drawing accurate statistical inferences about a system. Particularly, for films grown in a nitrogen diluted plasma, a comparison of elemental profile using multiple techniques can supply confirmation needed to draw accurate inferences about relationships between composition and film properties. Secondary ion mass spectrometry (SIMS) relies on the dynamic action of colliding ionized particles into a target surface to obtain similar information. An illustration of the process discussed above is given in Figure 8 below. Whereas RBS is essentially nondestructive due to the high energy of incident ions, SIMS utilizes lower energies and larger incident ions to pick up and examine the debris of collisions. The compositional profile of nitrogated NCD samples grown on silicon was performed using SIMS to verify data obtained by RNRA and NRBS on the same samples.
Figure 8. Visualization of particle sputtering during SIMS measurement. Low keV sputtering particles incident on the sample are used to blast the surface. Particles with sufficient energy to overcome the surface binding energy and pass through the surface-vacuum interface have a chance to ionize. Ionized particles are then accelerated through an electrostatic field and detected by a time of flight detector.

2.4.1 Measurement Conditions

Within the realm of SIMS measurements, the kind utilized for this study is referred to as dynamic SIMS; in which the progressive erosion of the target and the detection of subsequent ionized particles is used to determine the profile of elements within the target [52]. The equation governing particle detection in SIMS measurements in general illustrates the strong dependence of secondary ion intensity on a number of parameters, such as ionization probability of target (or matrix) elements, crystal orientation, angle of incidence, and incident ion energy. Briefly, the measured secondary ion intensity is given by:

\[
i_\hat{A} \propto I^p \ Y \ \alpha_A \ \eta_A \ \theta_A \ x_A \quad (22)
\]
where $I^P$ is the primary ion intensity (ions/sec), $Y$ the sputter yield (number of target atoms removed per ion), $\alpha_A$ is the ionization probability, $\eta_A$ the combined transmission efficiency of the extraction optics, and $\theta_A$ is the isotopic abundance of a given element within the target. To obtain the quantity $x_A$ (the atomic fraction of element A) one must have prior knowledge of the other quantities in the target (i.e. $\alpha_A$ or $\eta_A$), that is, one must obtain this information from a reference, typically unique to the target in question. A reference sample may be obtained by implanting an element of interest within a sample whose matrix is identical to that of the target and performing SIMS. The ratio of the measured intensities; $i_A^s$ and $i_M^s$ ($i_M^s$ is the secondary ion intensity of the reference sample), can then be compared between the reference sample and the target to calibrate the measurement. Overall, this equation illustrates the myriad parameters that SIMS measurements depend on. As this technique was utilized as supplemental data to verify the nitrogen compositional profile, an in depth discussion of the theory governing this technique will not be covered in this dissertation. Readers interested are directed to sources cited within this section for a more thorough analysis. What follows is a slight elucidation of the probability of obtaining target particles yields, which is of interest in this study as this probability changes based on the properties of the elements present in a target, e.g. electronegativity or ionization probability.

2.4.2 Ion Yields and Cross Section

The bombardment of a surface by keV energy ions triggers a series of collisions which often result in the release of particles, atoms in the case of dynamic SIMS, from that surface. This process is referred to as sputtering. Of the particles sputtered from a target by an ion beam, the intrinsic yield of secondary ions is low, about 1% [53]. Taking
into account the probability of ionization, $\alpha$, in addition to the sputtered yield, $Y$, one obtains the sputtering yield $Y^\pm$ (where ‘+’ refers to positive ions and ‘-’ refers to negative ions):

$$Y^\pm = Y\alpha^\pm \quad (23)$$

with the $Y$ characterized as the total number of ejected particles over the number of particle impacts.

### 2.4.3 Surface Binding

As ions are freed from the material matrix their movement from the surface layer to vacuum constitutes a transition from one space to another. At the interface region between these spaces there exists factors which affect the yield of secondary ions. Aside from the physical properties of the bulk material itself, which play a role in the total yield of secondary ions, the electronic properties of this interface region; ionization potential, electron affinity, and sputtered atom velocity determine the outcome of ionization. For example; positive ion formation has shown an exponential decrease with increasing ionization potential, while negative ion formation increases exponentially with electron affinity [54,55]. To obtain an expression for the ionization yield for sputtered atoms transitioning through the surface and vacuum interface in the case of sputtering from metals or semiconductors, one must consider the parameters of the sputtered atom velocity and work function (energy difference between the Fermi level and vacuum level). Positively charged, sputtered, atoms must overcome the difference between ionization potential and work function, while negatively charged atoms must overcome the difference between work function and electron affinity [54]. The transition of sputtered atoms through the interface region may be considered theoretically in terms of
electron tunneling through a potential barrier. The probability of tunneling then depends on the surface region’s Fermi energy level of the surface region, the energy of the sputtered atom, and the lifetime of the initial state of the sputtered atom [54]. In this case the ionization probability for positive and negative ions is expressed as a ratio of energy difference to velocity:

\[
\alpha^+ \propto e^{-\frac{I-\Phi}{c v_\perp}} \quad (24)
\]

\[
\alpha^- \propto e^{-\frac{(\Phi-A)}{v_\perp}} \quad (25)
\]

where \(I\) is ionization potential, \(A\) is electron affinity, and \(c\) represents a constant [54,56].

Thus it can been seen that ionization through the sputtering of atoms by a ion beams is a fairly complex process that is not entirely understood, but for which there is a significant amount of supporting experimental and theoretical work. As such it is considered a versatile and reliable method to obtain depth profiling, concentration, and composition of a given material. However, given the electronegativity of nitrogen, the elemental of interest in the study of nitrogen profiling, SIMS cannot be relied upon for an unassailable assessment of the concentration of nitrogen within the film. Therefore, within this dissertation it is used as a check to verify the nitrogen profile, but not concentration, within NCD films grown in a nitrogen diluted growth atmosphere.

### 2.5 Near-Edge X-Ray Absorption Fine Structure

The premise upon which this dissertation was performed is the technological application and viability of diamond thin films in industry and, eventually, everyday life. To this end, it is of interest to understand the molecular structure, and quality of bonding, of carbon at the surface of grown films. AFM has been discussed as one of these
techniques which can assess the microstructure of these films through interaction between slight forces present at the interface between a sample surface and a small probe. This technique, however, tells us little of the quality and molecular bond states between elements as this surface. X-ray absorption fine structure (XAFS) is a spectroscopy technique which utilizes high energy x-rays to probe the core electron shell of atoms. Depending on the mode in which scattered x-rays are collected, one can obtain data about the electronic structure, and therefore molecular bonding states, of matter within the first few nanometers within a sample. This analysis technique utilizing x-rays was first described by Kossel [57] who developed a treatment for the absorption edge, which is a part of every XAFS measurement. Later, Kronig [58] developed a theory to explain the molecular structure past the absorption edge and the stage was set for the development of the techniques known collectively as x-ray absorption fine structure. Within the body of XAFS techniques, near-edge x-ray absorption fine structure (NEXAFS) probes the electron transitions from K-shell (or p orbital) of low-Z elements, particularly carbon, within the first few nanometers of a material. Information, such as the bond length or orientation of molecular bonds [59,60], can be derived from the shapes and locations of peaks within a NEXAFS absorption spectra, making it a useful non-destructive technique to examine the molecular state of solids or organics.

In this dissertation, NEXAFS was utilized to verify the presence of the diamond, sp$^3$, structure and assess the general quality of the sp$^3$ bonds between films. To gain a general understanding of the source from which NEXAFS data is obtained, this section will cover the parameters governing the calculation of cross section in NEXAFS.
measurements. For an in-depth analysis of measurement conditions used to obtain NEXAFS spectra, the reader is referred to references given in this section.

### 2.5.1 Cross Section

NEXAFS measurements depend on the absorption and subsequent emission of energy from electrons in the K-shell orbitals of low-Z elements. The intensity of photoelectrons emitted by a given material i.e., the signal strength is indirectly given by the absorption cross section which is dependent on the population state of a given condensate. The population state can be described by the Fermi Golden Rule, given below. The ‘rule’ expresses the population in terms of finding an electron in an allowed excited state of a given condensate, whose wavefunctions are described by ‘f’ (final state) and ‘i’ (initial state) under perturbation by a harmonic time dependent oscillator ‘V’.

\[
P_{if} = \frac{2\pi}{\hbar} f V i e^{\frac{1}{2}\rho_f(E)} \tag{26}
\]

where \(\rho_f(E)\) is the energy density of the final state and \(f\) is an allowed state in the continuum of states for the system. The harmonic potential expressed in the above probability is a perturbative term originating from an exciting agent, the incident x-ray field. The total cross section is then expressed in terms of the population of excited state electrons over the total incoming flux of photons:

\[
\sigma = \frac{P_{if}}{F_{ph}} \tag{27}
\]

Within the context of the absorption cross section alone, the population state probability and flux of photons are expanded to expose the elements of the cross. With the potential expressed as a time-dependent term, \(V t\), as:
\[ V \, t = V e^{-i\omega t} = \frac{e}{mc} A \cdot p \]  

(28)

the population state probability term becomes [61]:

\[ P_{tf} = \frac{\pi^2}{2\hbar^2 e^2 m^2} A_0^2 \, f \, e \cdot e^{i k x} \cdot p \, i \, \rho_f(E) \]  

(29)

where \( p \) is the sum of linear momentum operators of a target material electron and \( k \) is the wavevector of the incoming x-ray. Assuming that the interatomic travel distance \( x \) is less than the wavelength of the perturbing x-ray, only the dipole momentum operator is significant and therefore for the cross section may be expressed as [62]:

\[ \sigma = \frac{4\pi^2 \hbar^2 e^2}{\omega c h^2 m^2} A_0^2 \, f \, e \cdot p \, i \, \rho_f(E) \]  

(30)

with the dipole element \( p \) expressed as [63]:

\[ p = i \hbar \nabla = \frac{i \hbar}{E_f - E_i} \nabla V \]  

(31)

with \( V \) the attraction potential of the system.

To obtain the theoretical cross section of the material of interest, sp\(^3\) bonded carbon, one must obtain the operators of the system. A Hamiltonian needs to be set up according to the nature of wavefunctions corresponding to each region within the system. The operators of this system can then be determined from the eigenfunctions of this Hamiltonian [63]. To simplify the description of the cross section, the optical oscillator strength term, \( f \), is defined for the transitions of the molecular system to excited states. In terms of the optical oscillator, the cross section is written:

\[ \sigma = C \frac{df}{dE}; \quad C = \frac{2\pi^2 e^2 \hbar}{mc} \]  

(32)

\[ f = \frac{2}{\hbar \omega} \, f \, e \cdot p \, i \, \rho_f(E) \]
Thus the picture of NEXAFS theory defined thus far for the absorption cross section allows us to determine what bound states within the molecular system the incident x-rays are exciting electrons from. In the final description, the cross section is written:

$$\sigma \ E = \frac{2\pi^2 e^2 \hbar}{mc} \cdot f \cdot \rho_f(E) \quad (33)$$

where $\rho_f(E)$ may be expressed in terms of the energy density of bound or continuum states.

Translating the description of the cross section to typical absorption spectra seen in NEXAFS is relatively straightforward. The cross section itself directly corresponds to the height of each peak (a bound state or Rydberg, resonance), while the width of those resonances (peaks) may be described over the reciprocal of the energy density of the final excited bound state. Additionally, the widths of these peaks correspond to discrete resonance lifetimes of the molecular vibrational excited states. Since the lifetime of these excited states is susceptible to the localized electronic state of the molecule, impurity concentrations within a system can affect the lifetime of these excited states and will appear as variations in peak width; subsequently showing up in NEXAFS spectra. As such NEXAFS is also a useful technique to probe the relative quality of the molecular bond state in materials, as used in this study. The absorption cross section, obtained from the measured energy density of the bound excited state and optical oscillator strength, can be found as the area of the Gaussian line shape in this spectra and the width of each peak corresponds to the excited state lifetime of each transition (Figure 9).
Figure 9. Arbitrary K-shell absorption spectra for carbon. Optical oscillator strength is given as the darkened area under the peak while the excited state lifetime is the width of the peak.

Studies utilizing this technique and reviews are available in literature [64,65,66,67].

At this point only a small fraction of the myriad parameters governing the measurement x-rays ejected during excitation of a system by the same particles has been presented. However, analysis of the spectra obtained by this technique did not require an understanding of these conditions. The absorption peaks appearing in NEXAFS spectra of this study are identified via previous literature on the subject, therefore, further detail concerning methods to precisely determine the origins of NEXAFS absorption peaks based on the elemental and chemical composition of materials are omitted from this
section. It is clear, based on the sensitivity of electron transitions to the molecular potential that NEXAFS is a precise method by which one can determine the chemical phases of a material. For the purposes of identifying the relative quality and presence of diamond phases in films altered through metallization of the growth surfaces and direct ion implantation, it has been an indispensable technique.

2.6 X-Ray Diffraction

Focus will now shift, from the surface to the bulk regions of the films studied in this dissertation. As these films are inherently crystalline, albeit polycrystalline, one technique stands out as directly applicable to identify their structure, x-ray diffraction (XRD). Additionally, this technique was utilized to study diamond peak orientation on films grown on metalized silicon substrates, in atmospheres diluted with increasing amounts of nitrogen. The technique employs basic considerations of reflection of energetic photons in a crystalline lattice to produce a diffraction pattern that, among other things, reveals the crystalline nature of the material in question. When correlated with data probing the molecular structure of carbon or composition of elements at various regions (surface and bulk) within each film, one can derive, or infer through descriptive statistics, contributions to crystalline order of each.

There are two types of XRD analysis, powder XRD and thin film XRD. The theoretical equations below were derived mainly for powder XRD, but are applicable to thin film as well. For example, the crystallographic phases in powdered samples are somewhat averaged; in obtaining a powder of a solid sample the long range crystalline order is destroyed and crystallographic planes become randomly oriented. However, in thin film XRD there may be significant anisotropic growth of certain crystalline phases.
due to preferential growth of that phase on a given substrate. A model which assumes an essentially equal probability for the occurrence of the characteristic crystalline phases for a given material will result in systematic error of that model when applied to a thin film exhibiting anisotropic growth. Despite this, for the purposes of identification of specific crystallographic orientation and crystalline phases within NCD/Si and NCD/Cr/Si films, powder XRD theory is able to provide a sufficient theoretical background.

2.6.1 Bragg Scattering

The basic equation used to describe the kind of elastic scattering that takes place in XRD measurements can be derived from an examination of the geometry of the lattice planes of any crystalline material. However, a derivation from the point of view of the incident beam of x-rays encountering a lattice electron also ultimately yields the same equation. In lieu of an extensive derivation of the Bragg Law from first principles in either case the equation itself is provided here in favor of a more in depth enumeration of the various factors affecting the measurement of scattered x-rays originating from both the target material and beam itself. The Bragg Law is governed by the elastic scattering of x-rays from the planes of a crystalline lattice within a target material (Figure 10). Through constructive interference of x-rays scattered from lattice planes separated by lattice spacing defined by the parameter $d_{hkl}$ analysts may obtain a diffraction pattern of the lattice. This constructive interference occurs only when the x-rays reflected at a scattering angle $\theta$ are a multiple of the wavelength of the incident beam wavelength. Therefore the Bragg law equation is typically written;

$$2d \sin \theta = n\lambda \quad (34)$$
Figure 10. Bragg scattering from lattice planes a distance \( d \) apart.

where \( \theta \) is the Bragg scattering angle and \( n \) is an integer. The illustration above provides a simplistic view of the origins of the resultant diffraction patterns. This equation effectively describes the position of x-ray scattering peaks in terms of the angular incidence of the incoming beam. Spacing between crystallographic planes, given by \( d_{hkl} \) is defined by the Miller indices \( hkl \). For a basic cubic lattice, the reciprocals of these indicies, \( a/h, a/k \) and \( a/l \) describe the intersection of lattice planes with points within a unit cell of the lattice. The letter ‘a’ is the length of each side of the cube with the endpoints of each side corresponding to the position of an atom in the crystal lattice. ‘d’ is then given, in terms of a cubic lattice, as:

\[
d = a/ \sqrt{h^2 + k^2 + l^2} \quad (34)
\]

2.6.2 Determination of Chemical Phases

Determining the crystal phases of a sample is a relatively straight forward process requiring little to no modeling whatsoever. Large databases accessible online contain diffraction patterns for most any material an analyst may need to identify. All the analyst needs to do is a simple comparison of the measured diffraction pattern to the patterns
available. The only unconditional requirement to this approach is that the measured pattern be due to Bragg reflection of x-rays with the sample. Information from these databases may not necessarily be absolute, however, the presence or absence of expected crystallographic phases in a given material does not entirely rule out the possibility of it being the correct material. Neither does the presence of additional crystallographic phases (peaks). Furthermore, the growth conditions of the sample itself have direct influence on the resultant diffraction pattern. Amorphous phases commonly seen in carbon films tend to produce a broadened pattern due to the absence of long range crystalline order. Considering this, nearest neighbor ranges for a given atom within the amorphous matrix may exhibit crystalline order and the associated diffraction pattern for that material. Elemental composition, bonding types, and spatial distribution (representative of regular or distorted lattice) of constituent atoms within the crystallite can also have a significant effect on the diffraction pattern produced as well. During crystalline growth distortions in the crystalline structure like microstrain (or microscopic stress resulting in a deformation), edge or screw dislocations, (distortion of the lattice around the area where an extra half-plane is introduced, or slippage of a block of planes along a lattice vector), twin planes (plane common to two individual crystals about which each is symmetrically arranged), and stacking faults (a disturbance in the regular sequence in which unit cell structures are arranged about each other) may arise. These distortions also reveal themselves in the diffraction peaks one obtains from XRD measurements.

An XRD spectrum, highly dependent on the ordering of crystals within a material, was integral in this study of CVD grown films. Interesting differences were revealed in these films, grown under standard conditions for the production of NCD, through the
identification of the different chemical phases of carbon, chromium and nitrogen. Particularly, correlation between XRD results with NRBS and RNRA measurements of the films developed a very interesting picture of resultant films in terms of chemical phase and elemental distribution within the films; to be covered in chapter three.

2.7 Nanoindentation

The evaluation of these films in terms of their structure was performed under the context of them being viable materials for engineering. Under this context, the hardness of the control group of samples and those grown on metalized substrates were evaluated through the process of nanoindentation. This process grew from a desire to study the mechanical properties of hard thin films being developed in the 1980s [68], and as such there is a direct correlation to studying the hardness of NCD films used in this study. This section will focus on the basic principles behind nanoindentation, the factors affecting measurements, and the interpretation of data resulting from these measurements.

Quite simply, nanoindentation is the process of pressing a very small tip into the surface of a sample to obtain the elastic modulus and hardness of that sample. Nanoindentation is an indirect measure of the area of contact between the sample and tip at ‘full load,’ or maximum load specified by the user. The mean contact pressure, and thus the hardness, is then derived from this area. The validity of the derived value of hardness depends largely on the analysis procedure used to process raw data. Among these procedures, the Oliver and Pharr method is a widely accepted technique, applied to many different systems but originally considered in the case of Berkovich tips [69,70]. Since the hardness measurements used in this study were obtained using a Berkovich tip
a discussion of the Oliver and Pharr method and the basic equations governing nanoindentation in general will follow.

2.7.1 Hardness

The significance of the values of hardness derived from indentation of a sample requires an understanding of the method used to obtain this value. ‘Hardness’ in regards to these kinds of measurements is defined by as an absolute value; the least value of pressure beneath a spherically shaped indentation tip necessary to produce a permanent set at the center of the area of contact between the indenter and the sample surface. This definition by Hertz [71,72] has been further amended to remove practical difficulties in adhering to this definition [73,74,75]. The material response to pressure through contact with an indenter produces two kinds of effects which directly relate to hardness, elastic and plastic responses. Plastic responses result in permanent deformations, like shaping or molding the material, while elastic responses are non-permanent deformations from which the material recovers. Material hardness is, then, directly proportional to the flow of the stress of the material’s during compression which results in an elastic-plastic response leaving an indentation on the surface.

Hardness is directly proportional to flow stress, and can be expressed as [76]:

\[ H \approx C \cdot Y \]  \hspace{1cm} (35)

where Y is the flow stress of the material and C is the constraint factor which depends on parameters of the indenter, such as geometry, and the sample. This definition of hardness is a two-way street, however, and the value from hardness can be defined from the point of view of the indenter. The most common definition of hardness, used in many nanoindentation experiments, is the Meyer hardness [76] expressed as:
where $P$ is the load placed on the sample through the indenter, and $A$ is the projected area of indentation.

### 2.7.2 Berkovich Indenters

A Berkovich indenter, or a triangular pyramid shaped tip (Figure 11), was used in this study to obtain measurements of hardness. This type of indenter will be the focus of the next few sections to derive the hardness value of the films studied within this context.

Below is an illustration of a typical Berkovich tip shape where $\theta$ is the face angle of a pyramidal side, typically $65.27^\circ$.

![Berkovich Indenter Tip](image)

**Figure 11.** Berkovich type indenter tip. The geometry of the indenter determines the area of contact created in the sample from which the depth of indentation, and subsequently the hardness, is determined.

### 2.7.3 Berkovich Indenter Geometry

To derive the hardness from load applied to a sample and the projected area left by an indentation, the geometry of indenter used must be accounted for. This study used
pyramid-shaped indenters referred to as Berkovich indenters which are commonly approximated to a conical shape for ease of calculation. Although they are not true cones it has been shown through modeling that this simplification of shape can still produce satisfactory results under certain conditions [77].

At this point it is useful to define the term ‘circle of contact’ in terms of its relation to the equation for the hardness value ‘H’. The circle of contact is used to derive the projected area left by the indentation, the projected area then having the value ‘A’ which is used to determine hardness. For a Berkovich indenter, the projected area is given by the formula:

$$A = 3 \frac{3}{\pi} h_c^2 \tan^{2} 65.27 \ ^\circ \quad (37)$$

where 65.27° is the standard face angle of the Berkovich indenter and $h_c$ is the depth beneath the initial point of contact of the indenter with the surface. Since the Berkovich indenter is being approximated to an axial symmetric conical shape it should be noted that a conical semi-angle of 70.3° and the Berkovich indenter give the same area to depth ratio through the relation:

$$\tan 70.3 = \frac{3}{\pi} \frac{3 \tan^{2} 65.27 \ ^\circ}{\frac{1}{2}} \quad (38)$$

2.7.4 Berkovich Type Load-Displacement Curves

Conical indentations leave somewhat characteristic load vs. displacement curves (Figure 12). The method applied to deriving hardness values from Berkovich indenters exploit features in this curve due to the elastic material response. A characteristic load-displacement curve is given below which demonstrates the behavior of the sample between increasing and decreasing force, or load, on the sample in an ideal case.
**Figure 12.** Representative load-displacement curve for a Berkovich indenter. Quality of indentation is determined from the shape of the curve as well as material response. At the tip of the load/unload curve the value of maximum depth and maximum pressure applied are derived, which are directly applied to calculations of hardness.

The analysis of load displacement curves obtained using a Berkovich indenter is an ideal case and relies on two assumptions: unloading is purely elastic and no plastic deformation takes place during this phase of indentation and the slope of the fully unloaded impression is that of a flat sided cone (or pyramid). Therefore, a correction factor $\beta$ is applied to contact stress slope, $\frac{dP}{dh}$, to obtain more accurate values of hardness:

$$\frac{dP}{dh} \rightarrow \frac{1}{\beta} \frac{dP}{dh_{measured}} \quad (39)$$

The range of values for $\beta$ is usually between 1.02 and 1.08 [78] but the most common value used is 1.034 [79].
Based on these considerations, the hardness of a material is determined from the area of the circle of contact and the maximum pressure (load) under which the indentation is applied (with appropriate corrections). Using such measurements, the evaluation of NCD films altered by metallization of the silicon substrate is taken one step further to correlate structural changes to the structure and microstructure with a change in the hardness resulting from growth on this metalized surface.
CHAPTER 3
EXPERIMENTAL METHODOLOGY

Within this section the conditions by which the data used in each study was obtained is elucidated. Methods which appear in multiple studies, e.g. non-Rutherford backscattering spectrometry (NRBS) and elastic recoil detection analysis (ERDA) are performed under identical experimental setup conditions for each study. As ion beam analysis (IBA) techniques are the primary method used to examine the films in each study, they are described in the greatest detail. All other techniques are complementary, strengthening the conclusions and providing a means to obtain an overall characterization of the films studied in this dissertation. Perhaps most importantly, the growth conditions of the samples referred to throughout the remaining sections is given in the first section of this chapter.

3.1 Sample Growth

Samples characterized for this study were prepared in batches in collaboration with research partners at the Center for Nanoscale Materials (CNM), Argonne National Laboratory (ANL). Using techniques developed at this facility, NCD films were grown on large, 20 cm, wafers of silicon, chromium coated silicon and tungsten coated silicon. Table 1 below lists the chamber conditions of the microwave plasma chemical vapor deposition system (MPCVD) in which each film was grown. Metal coatings were deposited by magnetron sputtering in a physical vapor deposition system, separate from the MPCVD system before film growth. These coatings were deposited at low pressure
using an automated process developed at ANL. All samples grown for this dissertation were not seeded prior to film growth on any substrate or metalized substrate. The nitrogen gas diluted in films with no interlayer and a chromium interlayer were done with isotopic ($^{15}$N$_2$) gas so that advanced ion beam analysis, proton-induced $\gamma$-ray emission, could be used to determine the quantity and distribution of nitrogen within the resultant films.

Table 1. Sample Growth Conditions

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Gas flow rates: Ar/CH$_4$/H$_2$/N$_2$ (sccm)</th>
<th>Interlayer</th>
<th>Pressure (mbar)</th>
<th>Power (kW)</th>
<th>Temperature (°C)</th>
<th>Time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCD/Si 20%</td>
<td>160/3/0/40</td>
<td>None</td>
<td>80</td>
<td>2.3</td>
<td>750</td>
<td>2</td>
</tr>
<tr>
<td>NCD/Cr/Si 20%</td>
<td>160/3/0/40</td>
<td>Chromium</td>
<td>80</td>
<td>2.3</td>
<td>750</td>
<td>2</td>
</tr>
<tr>
<td>NCD/W/Si 0%</td>
<td>400/1.5/8/0</td>
<td>Tungsten</td>
<td>120</td>
<td>2.1</td>
<td>750</td>
<td>3.5</td>
</tr>
<tr>
<td>NCD/W/Si 10%</td>
<td>160/3/0/20</td>
<td>Tungsten</td>
<td>80</td>
<td>2.3</td>
<td>750</td>
<td>2</td>
</tr>
<tr>
<td>NCD/W/Si 20%</td>
<td>160/3/0/40</td>
<td>Tungsten</td>
<td>80</td>
<td>2.3</td>
<td>750</td>
<td>2</td>
</tr>
</tbody>
</table>

The overall study can be characterized as two parts of an ongoing investigation. The first part concerns the growth and characterization of films utilizing ion beam techniques in conjunction with complementary methods of film evaluation. The second part deals primarily with modification, and initial characterization, of NCD films using ion implantation with metal ions. In the second part samples were implanted according to the table below. Samples studied in this experiment were taken from the NCD/W/Si 0% batch, deposited under conditions given in table 1. Annealing was performed at 600°C for
one hour in an argon atmosphere to relax defects out of the nanocrystalline diamond (NCD) matrix. This temperature was chosen as it is below the temperature at which the NCD film breaks down. The range of ions within these films was predicted by SRIM calculations to be between 10 to 60 nm using plots generated in SRIM (Figure 13 below). Both plots are of the range in which 68 keV chromium ions stop which in the film, the first a three dimensional plot illustrating both lateral and longitudinal straggling, or spread, of chromium ions just before they stop. The second is of longitudinal straggling along. As a control, to assess the differences in microstructure, one implanted film from each fluence ‘group’ was left un-annealed.

**Table 2. Implantation Table of 68 keV Cr Ions in NCD/W/Si 0% Films**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fluence (atoms/cm$^2$)</th>
<th>Anneal (°C)</th>
<th>Time (hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCD/W/Si 0%</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>NCD 68 keV Cr</td>
<td>$10^{11}$</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>NCD 68 keV Cr</td>
<td>$10^{11}$</td>
<td>600</td>
<td>1</td>
</tr>
<tr>
<td>NCD 68 keV Cr</td>
<td>$10^{16}$</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>NCD 68 keV Cr</td>
<td>$10^{16}$</td>
<td>600</td>
<td>1</td>
</tr>
</tbody>
</table>

This covers the full domain of samples used in this dissertation. Each sample was evaluated in groups using the techniques described in the following section, and data was correlated between each technique as well as control groups in experiments briefly described in the introduction.
Figure 13. Implantation range of chromium in NCD. Each plot was generated using a Monte Carlo algorithm in the SRIM computer code. With an increasing number of simulated ions the curves become more Gaussian and reflect the occurrence of a large amount of particle straggling, or spread, immediately before the particles come to rest (Bragg peak). The implanted depth within each sample is thus controlled by the energy of the incident ions.

3.2 Ion Beam Analysis Measurements

To assess the presence of impurities and determine the total concentrations of elements, IBA measurements were performed using a six megavolt tandem Van de Graaff accelerator located at Western Michigan University shown in Figure 14. Elemental profiles were measured via NRBS and RNRA. Alpha particles of 3.5 MeV, chosen to exploit their enhanced cross section [80] with carbon, were projected onto a 2 mm diameter circular area on the sample. IBM geometry, in which incident and scattering angles are observed within the same plane, was utilized to analyze each sample. The incident (α) and exit (β) angles of 0° and 20° respectively were set with respect to the surface normal of the sample so that backscattered ions were detected at a
scattering angle of 160°. Total charge collected on the sample was 16 µC from a beam of 20 nA.

![Image](image108x317to540x641)

**Figure 14.** The six megavolt tandem Van de Graaff accelerator at WMU. Pictured here is the Alphatross source on the far left, Duo Plasmatron (center) and tank in which particles are accelerated to high energy.

NRBS and ERDA measurements all follow the same experimental setups illustrated below (Figure 15 and Figure 16). Uncertainties in elemental concentrations determined via NRBS measurements were determined from event, or count, statistics as

\[ \frac{1}{\sqrt{\sigma}} \]

where \( \sigma \) is the count under each peak. When determining sample or layer thickness from simulations of each experimental spectra, uncertainty in the final
calculated value was determined from the resolution of the detector used (Si surface barrier detectors, resolution ~20 keV per channel).

**Figure 15.** Experimental setup for NRBS measurements. Alpha particles incident normal to the sample surface are scattered in many directions, but only particles scattered at a scattering angle of 160° with respect to the incident beam will be detected.

**Figure 16.** Electronics setup for NRBS and ERDA experiments. A current pulse from the silicon surface barrier detector (Ortec BA-014-050-150) is converted to a voltage pulse within the pre-amp (Ortec 142IH). This signal is amplified in the amplifier (Canberra Model 2020 Amplifier) and fed to the multi-channel analyzer (TRUMP PCI-8k) where the size (height) of each voltage pulse is...
sorted into separate bins, or channels to create the NRBS spectra for each sample.

To determine the hydrogen concentration, elastic recoil detection analysis (ERDA) was performed using 15 MeV O$^{4+}$. Oxygen was used instead of conventional alpha particles based on the mylar foil thickness and range of alpha particles within the foil. At 3.5 MeV forward recoiled alpha particles from carbon would have sufficient energy to pass through the foil, confounding measurements of hydrogen. To simplify the incident and exit angles used in this IBM geometry setup, the sample was oriented at 67.5° (incident angle $\alpha$) with respect to the surface normal of the sample (making the exit angle $\beta$ also 67.5°). This sets the scattering angle at with respect to the 45° after passing through a 13 µm Mylar foil. Total charge collected on the sample was 16 µC from a beam of 22 nA. An illustration of the setup explained above is given in Figure 17. The target elemental concentrations were determined using the n-simplex algorithm of SIMNRA [81], which develops a polynomial function to simulate the experimental spectrum. The set of target composition and profile parameters for NRBS and ERDA were adjusted until a single set of parameters could be used to accurately simulate both the spectra. Uncertainties in ERDA measurements was again determined by random error in each measurement, determined based on the reciprocal of the square root of the number of events measured ($1/\sigma$).
Figure 17. Experimental setup for ERDA measurements. Identical to NRBS except for the location of the detector, oriented at 45° with respect to the incident beam. The sample is positioned at 67.5° with respect to the incident beam to accommodate forward scattering for hydrogen atoms from the sample.

The concentration profile of nitrogen was obtained utilizing the nuclear reaction of $^{15}$N atoms with protons producing $\gamma$-rays, or RNRA. For these measurements, samples were oriented at incident and exit angles of 45° with respect to the surface normal, and emitted $\gamma$-rays were detected using a NaI(Tl) detector mounted at a scattering angle of 90° (as illustrated in Figure 18). Beam energies were iterated from 900 to 925 keV in 5 keV steps to obtain the concentrations of $^{15}$N as a function of depth. The electronics setup for this experiment differed from the NRBS and ERDA only in the addition of a 1000 V source (Bertan Association Inc. Model #353) hooked to the NaI(Tl) (Harshaw Chemical
Co.\(^1\) detector, illustrated in Figure 19 below. The NaI(Tl) detector efficiency decreases exponentially with increasing γ-ray energy. Therefore, to reduce the uncertainty in \(^{15}\)N concentration measurements, data was collected over large amount of charge deposited on the sample, resulting in long measurement times and increased area under each γ-ray peak.

Figure 18. Experimental setup for proton-induced γ-ray emission in samples. γ-rays radiate isotropically from the sample, but only those radiating at 90° with respect to the beamline are recorded by the NaI(Tl) detector.

\(^1\) Rexon TLD Systems and Components, Inc. now services all Harshaw Chemical Co. scintillation detectors.
3.3 Raman Microscope Measurements

The vibrational molecular states of carbon, particularly \( \text{sp}^2 \) states, were assessed using Raman spectroscopy. Measurements were carried out for this spectroscopy using a Renishaw Via Reflex Raman microscope having a laser source at 514 and 633 nm wavelengths (separate measurements) in CNM at Argonne National Laboratory. The basic setup of Raman measurements, as illustrated in Figure 20, scattered light from the sample is passed through a number of pre-monochromaters before being passed through a spectrometer to diverge the signal, then on to a detector where the diverged signal is fed to a computer readout. This setup allows technicians and researchers to distinguish the weak signal coming from inelastically scattered light (the Raman signal) from the much stronger signal coming from elastically scattered light (Rayleigh scattered).
Figure 20. Basic experimental setup for Raman measurements. Optical wavelength light originating from a laser source scattered from the sample is passed through several pre-monochromators (mirrors). These monochromators filter Rayleigh scattered light so the spectrometer may pick up the much weaker Raman signal. A spectrometer then separates the remaining light before it is sent to a detector for conversion to an electronic signal.

3.4 Atomic Force Microscope Measurements

Digital mapping of the surface of each film was performed using two separate AFM devices: a Digital Instrument (DI) Nanoscope IIIa multimode scanning probe microscope under tapping mode located in the Environmental and Molecular Sciences Laboratory at Pacific Northwest National Laboratory and a Pacific Nanotechnology SPM, Nano-R series, scanning probe microscope under close contact mode located at Kyushu University. The basic setup of these experiments is given in Figure 21 as well as a description of the method by which AFM images are generated. Uncertainty in each measurement was determined from the machine specifications. Error in the vertical
measurement reported in the literature published by Pacific Nanotechnology \[^{82}\] is ± 0.1 nm. Error in lateral measurement is reported to be ± 2 nm.

**Figure 21.** Experimental setup for AFM. Laser light scattered off a reflective coating on the cantilever tip and collected by a cluster of photodetectors generates the signal used to map the surface over which the tip is being passed onto the computer.

### 3.5 Secondary Ion Mass Spectrometry Measurements

To verify the nitrogen profile obtained with RNRA during the nitrogen quantification experiment, SIMS measurements were performed using a time-of-flight instrument (TOF.SIMS 5, IONTOF GmbH). As shown in Figure 22, a constant sputtering beam of 2.0 keV Cs\(^+\) and analysis beam of 50 keV Bi\(_3\)\(^{2+}\) were employed in tandem. The Cs\(^+\) beam sputtered an area of 300 \(\mu\text{m}^2\) while the Bi\(_3\)\(^{2+}\) beam analyzed an area of 100 \(\mu\text{m}^2\) at the center of the sputtered area.
Figure 22. A rough sketch of typical SIMS ToF experimental setup. A sputtering beam is used to sputter through the sample while an analysis beam assists in the ionization of ejected target particles. Ionized particles are accelerated down a beamline and detected by the time of flight detector.

3.6 Near-Edge X-Ray Absorption Fine Structure Measurements

NEXAFS, used comparatively to determine the quality of carbon bonding between films grown on metalized substrates, was performed in cooperation with research partners in Kyushu University at the SAGA Light Source located in Tosu City, Kyushu, Japan. After passing synchrotron radiation through two 10 μm slits in beamline 12 (BL12, shown in Figure 23 and Figure 24), the spectra of samples were recorded in total electron yield (TEY) mode in the energy range 280 ~ 345 eV.
Figure 23. A rough schematic of SAGA Light Source Synchrotron. Electrons are generated in a linear particle accelerator (far left) and introduced into the ring (center). X-rays are generated by bending magnets placed at the threshold of each beamline.
Figure 24. Within each beamline, x-rays are filtered through monochromators before impinging up on a sample located at the end of the beamline.

3.7 X-Ray Diffraction Pattern Measurements

XRD patterns were collected for NCD control films and those deposited on a metalized substrates using a Rigaku D/Max Rapid II micro diffraction system. In cooperation with researchers in EMSL at PNNL, x-rays were generated from a rotating Cr target ($\lambda = 2.2910 \text{ Å}$) and focused through a 300 μm diameter collimator onto the specimen surface, making an incident angle of approximately 10° (see Figure 25). Diffraction data recorded on a 2D image plate were integrated between 10 and 160° 2θ using the manufacturer’s software to give powder traces. Diffraction from the single crystal substrate gave rise to strong localized spots on the 2D detector, while that of the polycrystalline film produced annular rings. The sample was positioned to exclude the spots from the substrate in the integrated area. Phases present were identified by comparison with library patterns supplied by the International Committee for Diffraction Data using Jade v9.3 (Materials Data Inc., CA).
**Figure 25.** Basic experimental setup for XRD measurement. Kα x-rays are generated by impinging electrons upon a target like copper or chromium. These x-rays are directed to the target surface oriented at angle θ with respect to the incident x-ray direction. Reflected x-rays are then picked up by a diffraction plate detector located at an angle 2θ.

### 3.8 Nanoindentation Measurements

Nanoindentation tests were carried out to measure the hardness and young’s modulus of the deposited films under on NCD control films and those deposited on a metalized substrate. Measurements were performed using a Nanoindenter II machine located at the Electron Microbeam Analysis Laboratory, University of Michigan. Penetration depths using a Berkovich tip were limited to 100 nm or 20 mN of force. Elastic modulus and hardness were determined using the Oliver and Pharr method [83]. Calculations were performed using proprietary software.

### 3.9 Ion Implantation

Metallization of the bulk within NCD films was performed using a custom ion implanter developed at Western Michigan University. A source of negative ions by
cesium sputtering (SNICS) produced the beam of chromium ions, negatively charged (Cr⁻), which was directed onto NCD targets mounted on a mobile vertical plate (target holder) within the low energy beam line of the Van de Graff accelerator (Figure 26 and Figure 27). The position of the target holder in the vertical and horizontal planes (oriented perpendicular to the axis of the beamline) was calibrated and adjusted individually and then set into routine scanning mode through LabView software linked to stepper motors. The scanning routine moves the target holder through an ‘L’ type motion, allowing for uniform implantation of ions within samples mounted on the target holder. Implantation performed for this experiment forced chromium below the near surface region of NCD targets by setting the incident ion energy to 68 keV through manipulation of extraction magnet voltage. The type of defects created during implantation differed depending on the nature of the collision encounter but were consistent in variety across all films. Vacancies, formed by chromium ions expelling target atoms during a collision, and interstitial atoms (half of a Frenkel pair), formed from incident chromium ions embedding themselves within the material or material atoms being expelled from its lattice location and later trapped. A schematic and picture of the implanter described in this section is given below.
Figure 26. A simple schematic of implantation system. The load-lock system consists of a pneumatic valve separating the loading chamber from the beamline. The valve is closed during loading and open during implantation. An interlock system is used to ensure that neither power failure nor operator mistakes will allow the valve to close while the sample is in the beamline.
Figure 27. The ion implanter mounted on low energy end of the beamline. The bellows pictured in below the stepper motors on the far left and top center of the picture constitute the loading chamber. The pneumatic valve is located directly below this chamber. While samples are being loaded and unloaded these bellows must be straight to accommodate the size of the sample stage, therefore, the horizontal position of the stepper motor is set to center.
CHAPTER 4
RESULTS AND ANALYSIS

4.1 Nitrogen Quantification

Using the techniques outlined in the above sections; Raman, NRBS, SIMS and RNRA a lucid picture of the nitrogen concentration and its depth profile within the NCD films grown on silicon has been developed. Although previous studies [84,85,25] have evaluated the nitrogen content within NCD thin films using different ion beam analysis (IBA) techniques, there exist gaps in the literature which have yet to addressed. In the study by Samlenski, et al [25], isotopic nitrogen was added to NCD samples grown on homoepitaxially prepared CVD (111) and (100) diamond substrates in a methane/hydrogen primary gas admixture. Nitrogen concentration utilizing the 1.64 MeV resonance of $^{15}$N(p,αγ)$^{12}$C was performed to determine concentration between samples. Although it was concluded that nitrogen preferentially incorporates into (111) growth sectors resulting in greater amounts of nitrogen concentration in such sites, no characterization was reported to examine the molecular or morphological structure of the films. Additionally, the 1.64 MeV resonance, while having a high cross section with $^{15}$N, has a very broad energy width resulting in poor depth resolution.

Nitrogen concentration in a study by Birrell, et al [84], was evaluated using secondary ion mass spectrometry (SIMS), requiring the use of reference samples to quantify measurements. As nitrogen does not form stable negative ions by itself it must form compounds with atoms it is sputtered with; i.e. CN⁻ or NH⁻, an indirect
measurement of nitrogen content. Additionally, the fraction of nitrogen ions that remain positively charged cannot be detected by SIMS, confounding measurements [86,87].

Finally, in a study concerning nitrogen content in NCD films [85], the nitrogen concentration was estimated, based on nuclear reaction analysis (NRA) of deuterium with $^{14}$N, the concentration of nitrogen with the sample, to be 1 at%. However, due the overlap of peaks associated with the nuclear reactions between silicon and deuterium ($^{28}\text{Si}(d,p)^{29}\text{Si}$), and nitrogen and deuterium ($^{14}\text{N}(d,p)^{15}\text{N}$) further investigation to unambiguously determine the concentration of nitrogen within NCD is required.

Thus far nitrogen content in NCD diamond grown on silicon substrates in a microwave chemical vapor deposition system has not yet been evaluated via resonant nuclear reaction analysis. Given the wide spread attention being devoted to nitrogen incorporation via dilution in CVD growth atmospheres, especially those deposited on silicon and metallic underlayers, obtaining a direct measurement of nitrogen content and profile within such films provides clear data to support future refinement of such films within at technological context.

Films were deposited as described in section 2.1, listed as NCD/Si 20%. The characterization techniques employed in this section are NRBS, RNRA, SIMS, Raman spectroscopy and AFM. Descriptions of the underlying theory and experimental set up of each technique are covered in chapters 2 and 3.

4.1.1 Raman Analysis

Structural characterization via Raman analysis is shown within Figure 28. Raman spectroscopy has been employed in the past to confirm the UNCD signature carbon structures within amorphous thin films [88,89]. The peaks at 1355 and 1550 cm$^{-1}$ are the
$D$ and $G$ (disordered and graphitic) modes of sp$^2$-bonded carbon respectively, while the peak at 1140 cm$^{-1}$ and 1480 cm$^{-1}$ corresponds to C-H in-plane bending and C=C stretch of trans-polyacetylene [90,91,92]. The D and G modes are attributed to the breathing and stretching of planar carbon at the grain boundaries of NCD [93,94].

![Raman Spectra](image)

**Figure 28.** Raman spectral analysis of deposited film along with deconvolutions of each peak. The four peaks pictured are considered a ‘signature’ of the NCD or UNCD molecular structure despite the lack of a direct measurement of the Raman diamond signal at 1332 cm$^{-1}$.

### 4.1.2 AFM Mapping

To assess the surface structure of the film mapping of the surface was performed via AFM under tapping (non-contact) mode. Figure 29 below reveals the surface of the film to have an average grain size of approximately 100 nm. This result is not consistent with previous studies utilizing similar conditions of deposition, and given the size of these grains, this film does not fall under the definition of ultrananocrystalline diamond.
A number of factors may have resulted in this outcome, including a lack of seeding of the silicon surface. However, it is likely, given the greater concentration of nitrogen diluted in these films than in previous studies, that nitrogen is inducing these larger grain sizes through a change in the plasma chemistry.

Figure 29. AFM of the NCD film. Grain size was estimated by direct measurement using the Gwyddion computer code [95]
4.1.3 NRBS Spectra

Silicon nitride, Si$_3$N$_4$, was used as standard by which to validate, through comparison to the known concentration of $^{15}$N in Si$_3$N$_4$, the $^{15}$N measurements obtained via RNRA. The quality of the sample was verified by its NRBS spectrum, matching the known stoichiometry of 42.8 ± 0.1 at% silicon and 57.2 ± 0.3 at% nitrogen as seen in Figure 30. The NRBS spectrum obtained for the NCD sample overlayed with the spectrum simulated using SIMNRA is shown in Figure 31. The NCD sample displayed no diffusion of either silicon into NCD bulk, or of carbon into the silicon substrate. Due to the channeling of ions within the substrate, a decrease in the height of the silicon plateau towards the edge can be seen within Figure 31. Through NRBS the concentration of carbon was found to be 94.2 ± 0.5 at%. ERDA results determined hydrogen concentration to be 5.7 ± 0.03 at%. Additionally, the concentration profile of carbon was used to determine the thickness of the film to be 215 ± 13 nm based on the density of UNCD (3.3 g/cm$^3$)\textsuperscript{196}. 
Figure 30. Si₃N₄ standard used to validate $^{15}$N concentration measurements via RNRA.

Figure 31. Experimental and simulated spectrum of NRBS on NCD/Si with 3.5 MeV He$^{++}$. The energy in keV (x-axis) of the edge associated with each element is determined on the scattering angle and beam energy while the height of each peak is determined from the cross section of each element at 3.5 MeV He$^{++}$.
4.1.4 RNRA Depth Profile and Nitrogen Concentration

The resulting depth profiles of Si$_3$N$_4$ and NCD/Si are shown within Figure 32.

![Graph showing depth profile and nitrogen concentration](image)

**Figure 32.** The profile of nitrogen concentration as a function of depth in the representative sample and standard. Depth is determined from stopping power calculation of protons in an NCD matrix using SRIM while concentration is based on a conversion of the area under each 4.43 MeV $\gamma$-ray peak to an at%. Error was calculated from the event statistics of each 4.43 MeV $\gamma$-ray peak and, due to their small margin of error (2–5%) are not visible on this graph.

The concentration obtained throughout the Si$_3$N$_4$ sample was found to be in accordance with the natural abundance of $^{15}$N in Si$_3$N$_4$; 0.21 ± 0.01 at%. The depth profile of the film grown on silicon; beginning at approximately 30 nm into the film, displayed variation in $^{15}$N concentration between 0.18 and 0.22 ± 0.01 at% within the first 160 nm. An increase in $^{15}$N concentration is observed at a depth of 220 nm (0.31 ± 0.01 at%) which, based on the determined thickness of the sample, is in the interface region and is seen to decrease as function of depth. The average concentration of $^{15}$N was calculated to be 0.20 ± 0.01
at% within the sample. Uncertainty in the measurement was found to decrease with increasing nitrogen content, from a relative percent error of 5 to approximately 2.

4.1.5 Ion Straggling Issues

To determine the accuracy of the depth profile found for the film, energy straggling effects were calculated. By determining the depth at which the mean transmitted proton energy reaches 897 keV one may also determine the straggling energy of protons at this depth by finding the standard deviation from this mean value. SRIM was used to find the depth at which transmitted proton energies reached 897 keV; based on the statistics of these transmitted protons, the standard deviation was obtained. Figure 33 shows energy straggling converted to distance in nm vs. resonance depth in nm; and reflects increasing straggling as a function of depth. As beam energy increased, the 897 keV resonance moved deeper into the sample; corresponding to enhanced straggling of protons within the sample. This enhanced straggling resulted in a range of distances over which protons may reach the resonance energy, consequently lowering the accuracy of the depth profile within the sample. It should be noted the uncertainty in stopping power values of protons calculated by SRIM, and subsequently their calculated straggling range, is approximately 4% [36]. This is coupled with the additional uncertainty added through the application of Bragg’s rule, increases the total uncertainty in stopping power to approximately 24% [97]. Bragg’s rule was applied in this case since the data to utilize the core and bond method of stopping power calculation is not available for NCD materials. Still, from this estimation of particle straggling within NCD, it can be inferred that the yields obtained from 920 and 925 keV beams data from shallower regions within the film.
Figure 33. Energy straggling of protons converted to range in the y-axis versus expected resonance depth. Depth (x-axis) is once again calculated from the stopping power of protons in a NCD matrix while energy straggling was converted to a range in nm using straggling statistics generated in SRIM for each beam energy.

4.1.6 SIMS Depth Profile

To verify the $^{15}$N profile obtained via RNRA, SIMS depth profiling measurements were performed. Figure 34 shows a SIMS profile of the NCD film. The $^{12}$C$^{15}$N$^{-}$ signal was used as an indicator of $^{15}$N because both N$^{+}$ and N$^{-}$ are too weak to be detected. The C$^{-}$ signal shows a relatively stable value within the diamond layer, indicating that the components of the diamond film are reasonably constant from surface to the bottom. The $^{12}$C$^{15}$N$^{-}$ signal (green line) shows a relatively low but constant value within the bulk region. The high concentration of CN$^{-}$ (pink line) and oxygen (blue line) detected at the surface of the film is likely due to atmospheric contamination since the samples were
stored for extended periods of time in atmosphere. An increase of $\text{C}^{15}\text{N}^-$ in the interface region, consistent with RNRA measurements, was also detected by SIMS.

**Figure 34.** SIMS depth profile of the representative sample.

The trend in $\text{C}^{15}\text{N}^-$ concentration throughout the sample was found to be consistent for both RNRA and SIMS except at the interface region. However, the nitrogen profile determined by RNRA becomes less accurate with depth due to the straggling of protons within the sample. The resonances of the 920 and 925 keV beams corresponding to the nitrogen concentrations at 220 and 344 nm, respectively, which would indicate a very broad interface region, are due to this straggling effect. As such, the exact location and width of the nitrogen peak in the interface region as seen by RNRA appears inconsistent with SIMS.
4.2 Nitrogen Gas Dilution: Effect after Growth on Metal Interlayer

Following the surprising increase in grain size observed via AFM in the previous film, the next series of characterizations were performed with the intent of ascertaining the effects of nitrogen dilution in the growth plasma in conjunction with diamond grain nucleation on metal surfaces sputter deposited on silicon substrates. In particular, this experiment utilized tungsten as the metal interface due to research which has shown enhanced nucleation resulting in smoother film surfaces due to smaller grain sizes. Films were grown as stated in section 2.1, listed as NCD/W/Si 0%, NCD/W/Si 10% and NCD/W/Si 20%. The characterization techniques employed in this particular section were XRD and NRBS. The theory and experimental set up for each covered in chapters two and three.

4.2.1 XRD Patterns

Films investigated by XRD revealed a complex polycrystalline structure in films grown on tungsten. In Figure 36 below, the overlapping XRD patterns for each sample are given. In each sample, the x-ray scattering peak attributed to (111) diamond was located at a 2θ angle of 67.5°. The lower limit for grain size in each sample was calculated according to the Scherrer equation [98]:

\[
\tau = \frac{0.9 \cdot \lambda}{\beta_{1/2} \cos \theta_B} \quad (40)
\]

where \( \lambda \) is the wavelength of incident x-rays, \( \beta_{1/2} \) is the full width half maximum (FWHM) of the peak in question and \( \theta_B \) is the Bragg scattering angle. The Scherrer equation relies on the accurate calculation of the FWHM of the diffraction peak, which is confounded by a number of factors including stress, strain and line shape broadening by
instrumental uncertainty. Therefore, any calculation of average crystallite size using the Scherrer equation should be accompanied by correlating measurements, e.g. AFM. Based on Voigt peak fitting to the XRD pattern, given in Figure 35, the resolvable crystallite size was calculated. The factors affecting the uncertainty inherent in the determination of the FWHM were not fully accounted for, and, therefore, this calculation of crystallite size should be treated as a back-of-the-envelope determination of the potential diamond crystallite size. These values are given in Table 3. XRD Results vs. Growth Conditions below. As the crystallite sizes determined from this equation were not correlated with direct measurements of grain size, as can be obtained from AFM images, the values here are meant to further illustrate, in a quantitative fashion, the apparent loss of the (111) diamond peak which may be due to increasing strain on the diamond grains within the film accompanying increasing incorporation of nitrogen within the film.

Table 3. XRD Results vs. Growth Conditions. Accuracy in each measurement decreased as the peak height decreased, resulting greater uncertainty for the NCD/W/Si 20% sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallite Size (111) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCD/W/Si 20%</td>
<td>5</td>
</tr>
<tr>
<td>NCD/W/Si 10%</td>
<td>9</td>
</tr>
<tr>
<td>NCD/W/Si 0%</td>
<td>13</td>
</tr>
</tbody>
</table>
Figure 35. A comparative analysis of (111) diamond peak by Voigt function fitting. Diffraction peaks alone are Lorentzian in nature; however, Gaussian line shape is introduced through a number of factors affecting the crystalline lattice. Therefore, Voigt function fitting, which is recommended by literature to accommodate the dual nature of x-ray diffraction peaks, was used to simulate each peak.
With nitrogen gas dilution in the ionized growth atmosphere increasing from 0 to 20% a corresponding decrease in (111) diamond peak between samples is observed. The eventual disappearance of the (111) diamond peak into the background signal within XRD patterns is shown in Figure 35 above. This phenomenon may be attributable to a number of factors, including preferential diamond growth in the (111) sector, or increased strain on crystallites within the film due to increased nitrogen incorporation. As shown in Figure 36, the films contain a number of peaks associated with tungsten carbide WC (pink arrows) and W$_2$C (orange arrows) at 75°, 48° 60°, 99°, 104° 125° and 129° 2θ. Within the 10% N$_2$ sample, a (002) tungsten oxide (WO$_3$) peak also appears at 34.45° 2θ.
The addition of oxygen was not intentional, and is likely to have occurred during or immediately after sputtering while the sample was being transferred to the CVD chamber for film deposition. A large peak at approximately 130° 2θ is assigned to (220) diamond. The apparent maximum appears to shift between the samples, however, Voigt fitting of multiple peaks to each pattern, as shown in Figure 37, determined that the addition of tungsten carbide compounds (WC and W₂C) is responsible for this apparent shift in the center of the peak. After deconvolution of the single large peak the (220) diamond peak centers appear approximately at their expected 2θ positions, although the diamond peak was shifted significantly from its expected position in the case of the NCD/W/Si 10% sample, according to matching patterns obtained from the International Committee for Diffraction Data database.
Figure 37. A fitting of the (220) diamond peak. Multiple Voigt function peak fitting was used to separate out the contributions from WC and W₂C to the overall peak. The (220) diamond peak remained centered around 130.6° 2θ except in the case of the NCD/W/S 10% sample.
4.2.2 NRBS Spectra

To assess the interfacial quality and concentration of elements within each film, NRBS and ERDA were utilized. Figure 38 below shows the representative NRBS spectrum obtained for these films. Based on the density of diamond the thickness of each film was calculated to approximately 100 nm, indicating that growth rates for the films developed in a nitrogen diluted atmosphere were greater than the sample deposited in a hydrogen atmosphere. Between each film the hydrogen content remained constant at $15 \pm 0.9$ at%. The quality of the interfacial boundary between tungsten and silicon is abrupt, indicated by sharpness of the carbon and tungsten peaks with little to no mixing between tungsten and carbon in these films.

![NRBS Spectrum](image)

**Figure 38.** NRBS of NCD films grown on a tungsten interface. The tungsten peaks appears much larger than silicon or carbon due to the much larger cross section of tungsten with 3.5 MeV alpha particles.
4.3 Growth and Characterization of NCD on a Chromium Interlayer

Continuing the premise of NCD film alteration through substrate metallization and nitrogen dilution in the growth atmosphere, a novel interfacial layer, chromium, was chosen to examine any differences to the NCD film which can arise using different metals. As chromium has been used as an adhesive layer on different substrates, during the fabrication of many micro and nano devices, it was chosen as an interfacial layer. To tailor the characteristics of such devices or films, various metallic underlayers have been used [99,100,101] Among these, chromium has been used as interfacial barriers between iron and carbon during deposition to prevent the formation of graphitic phase film [102] and was shown to lead to the formation of useful microstructures in diamond films; i.e. mechanical interlocking of diamond grains into chromium carbides on steel substrates [103]. Further, earlier studies have demonstrated that one can enhance interfacial cohesiveness of resultant diamond films grown on steel substrates [104], as well as producing interesting structures [105] or compounds [106] whose overall effect may enhance or become a detriment [107] to the system. In this dissertation, a nano-crystalline diamond film deposited on a thin chromium layer over silicon at high substrate temperature has been fully characterized. Though chromium has been used as an interlayer during radio frequency chemical vapor deposition of DLC coatings [108], no similar study has been done of NCD. The NCD films in this study were deposited in a MPCVD system, within nitrogen diluted atmosphere (details of growth conditions are given in chapter 2). The presence of nitrogen providing growth enhancements of smoothness and morphology [109,110,111]. The properties of NCD films grown on a chromium interlayer to a control sample grown on silicon, and ascertains the effect of this
interlayer on NCD film properties, characterizing composition, structure, microstructure and interfacial characteristics.

The deposition parameters for the samples used in this study are listed in section 2.1, identified as samples NCD/Si 20% and NCD/Cr/Si 20% This section employs the greatest number of characterization techniques, with results from each data set correlated with those of others where appropriate. The techniques used in this section are: NRBS, RNRA, Raman spectroscopy, NEXAFS, XRD, AFM and Nanoindentation. The theoretical aspects governing each characterization technique as well as measurement conditions are covered in chapters two and three, respectively.

4.3.1 Raman Analysis

Raman spectra of the NCD films deposited on pure silicon substrate as well as with a chromium interlayer are shown in Figure 39. The peaks at 1370 and 1580 cm\(^{-1}\) are the \(D\) and \(G\) (disordered and graphitic) modes of \(sp^2\)-bonded carbon respectively, while the peak at 1155 cm\(^{-1}\) corresponds to a trans-polyacetylene (or C-H bonded) phase. The fourth peak at 520 cm\(^{-1}\) (circled, far left) is due to the substrate silicon (100) phase \([112,113]\). The \(D\) and \(G\) modes are attributed to the breathing and stretching of planar carbon at the grain boundaries of NCD \([114,115]\). Raman spectroscopy has been employed in the past to detect carbon structures within amorphous thin films \([116]\).

Raman spectra of the NCD films deposited on silicon substrate with and without a chromium interlayer were quite similar \([117]\). Normalized spectra, shown as an inset in Figure 39, confirmed this further. \(I(D)/I(G)\) ratios taken from the peak maxima of each mode were also consistent, at 0.50 and 0.52 for samples grown on silicon and chromium respectively, indicating the fractional volume of the lattice structures associated with \(sp^2\)
carbon are also similar. These results indicate an overall consistency of graphitic and amorphous phases of carbon between samples deposited on silicon and chromium.

Figure 39. Raman spectra for NCD samples grown on silicon with and without a chromium interlayer taken at 633 nm wavelength light. The prominent peaks in this spectra show the sp² bonded carbon structure in each film.

4.3.2 NEXAFS Absorption Spectra

NEXAFS studies were performed to confirm the presence of diamond within the NCD sample grown on chromium coated silicon. NEXAFS is an excellent technique to study bond states due to its sensitivity which is not influenced by grain sizes. The normalized absorption patterns of C1s transitions for both samples at photon energies
between 280 and 315 eV are given in Figure 40. The data was taken in collaboration with technicians at the Saga Light Source in Japan, while data analysis was performed at WMU. The x-axis, photon energy, was calibrated using a highly-ordered pyrolitic graphite target. In the pre-edge region a peak at 284.5 eV, attributed to the C1s $\rightarrow \pi^*$ transition [118] is observed. The absorption edge for diamond in both samples (C1s $\rightarrow \sigma^*$ transition) is located at approximately 288.5 eV. In order to confirm the shift of the absorption edge of diamond, observed within both samples, from 289.5 eV [118] separate measurements were taken of (100) oriented nitrogen doped NCD in total electron yield (surface sensitive) mode (Figure 41). The diamond absorption edge of NCD was consistent with both the NCD on silicon and NCD on chromium coated silicon samples. A slight shift in the secondary band gap associated with the $\sigma^*$ transition was also observed at 301.7 eV (from 302.5 eV) within the NEXAFS spectra of NCD samples. A shoulder at 287.2 eV, observed in both samples, has been assigned to different carbon bonding types under various conditions of sample preparation [119,120], and is likely due to carbon $\sigma$-type bonding with elements other than carbon [121]. Based on the identification of C-H bonding by Raman spectroscopy, this peak has been assigned to the C-H $\sigma^*$ transition. To examine the relative differences between the $\sigma^*$ transition peaks associated with diamond in both samples, multiple peak fitting was performed.

Figure 40 shows the fitted peak spectrum, which conforms closely to experimental data. The full width half maximum (FWHM) of the each $\sigma^*$ transition peak was found to be: 0.58 for NCD/Cr/Si; 0.59 for NCD/Si and 0.52 for NCD. Based on these values the FWHM, between each sample there is relatively little difference in local electronic structure of $sp^3$ bond types. Overall the NEXAFS spectra confirmed the
presence of sp$^3$ bond states within each film and indicated a relative consistency between films in terms of the ratio of their bonding states. Due to the small difference in the ratio of bonding states of carbon shown by Raman and NEXAFS data, the state of molecular carbon between the films is relatively unchanged.

**Figure 40.** NEXAFS absorption spectra for NCD on chromium coated and uncoated silicon; NEXAFS experimental and deconvoluted spectra of the pre-edge region of NCD on chromium coated silicon.
**Figure 41.** NEXAFS spectrum for NCD (100) oriented diamond. This spectra was taken to confirm the location of the $\sigma^*$ transition peak associated with sp$^3$ bonded carbon (or diamond) at 288.5 eV as opposed to the reported 289 eV in the literature. As each spectra was calibrated to the a highly ordered pyrolytic graphite standard, the reason for this shift remains unknown. However, this shift does not represent a significant problem in deriving information about molecular bond state and, therefore, does not interfere with the analysis performed in this section.

### 4.3.3 XRD Patterns

An XRD pattern of the films deposited on silicon substrate with and without the chromium interlayer is shown in Figure 42. XRD patterns for NCD grown on silicon confirmed strong diamond (111) and (220) peaks at 20 values of 67.8 and 130°.

In contrast, the NCD carbon film deposited on a chromium interlayer showed a much more complex structure with many peaks in addition to diamond (111) and (220) phases. Interestingly, different peaks observed in this pattern were identified to belong to two additional phases of Cr-C-N and CrN. The peaks at 53.8°, 59.5°, 64.6°, and 69.8°
associated with the lattice planes of (111), (040), (211) and (131) are of Cr-C-N. Similarly, the peaks at 57.2°, 67.1°, and 102.8° are identified to correspond to the lattice planes (111), (200), and (220) of CrN. The formation of CrN and Cr-C-N phases may be explained by the diffusion of chromium/nitrogen during the high temperature deposition of NCD. The presence of chromium oxide (Cr₂O₃) is evident by the occurrence of smaller peaks at 55.2° and 86.2°, which may be attributed to atmospheric exposure of the chromium during loading into the CVD chamber. Possible interfacial interaction between the layers NCD and chromium, and chromium and silicon (substrate) seem to have resulted in the formation of these multiple polycrystalline phases compared to the pure diamond phases observed on for the film deposited on the silicon substrate.
Figure 42. Overlapping XRD patterns for NCD grown on chromium coated silicon and silicon. Additional compounds overlapping with the (111) and (220) diamond peaks in the NCD/Cr/Si sample made unambiguously identifying diamond within this sample not possible.
4.3.4 Interfacial Quality and Concentration Profile

In order to understand the interfacial diffusion effects at the chromium, carbon and silicon interfaces, NRBS analysis was performed on these samples. The path of the ion beam used is illustrated as an inset in Figure 43. The NRBS experimental spectrum along with the overlapped simulation spectrum is shown in Figure 43. The chromium, silicon and carbon edges are represented in the spectrum at the energy values 2604, 1800 and 920 keV, respectively. Simulation of the experimental spectrum was performed utilizing the n-Simplex algorithm implemented in SIMNRA [122] The trailing edge of carbon (at 637 keV) and the leading energy edge of chromium (at 2604 keV) show a signature broadening indicating diffusion at the interfaces of the NCD layer and chromium as well as the chromium and substrate, respectively. The trend of chromium diffusion decreases towards the surface of the sample, from the chromium peak height at 2400 keV (30 at% of chromium) to the leading edge at 2046 keV (1 at% of chromium). By contrast the film grown on silicon (Figure 43) displays nearly vertical, sharp, leading and trailing energy edges for both carbon and silicon. This indicates minimal or no interfacial mixing between the silicon substrate and the film.

Correspondence between the energy width of the carbon peak and extended shoulder from the chromium peak indicate almost full diffusion of chromium through the film. Film thickness, based on target layer generated by SIMNRA, was found to be 384 ± 13 nm, with varying concentrations of carbon, chromium and oxygen. The small peak appearing at 1.0 MeV is an oxygen peak which correlates with XRD detection of Cr₂O₃ in the film, confirming the presence of oxygen in the chromium peak layers.
Figure 43. NRBS of films grown on chromium interlayer, illustrating the passage of the ion beam through the sample and silicon. The broadening of the carbon, silicon, and chromium peaks within the NCD/Cr/Si spectrum is indicative of a complex interfacial region in which diffusion of each layer takes place. In contrast the NCD/Si sample shows nearly vertical edges between silicon and carbon, indicating no detectable interfacial mixing has taken place.
The concentration of $^{15}\text{N}$ within the film was determined using RNRA at WMU using the 6 MV Van de Graaff accelerator. In correlation with the resonance peak of each beam, SRIM was utilized to determine the depth at which each peak occurred within the film based on the stopping power. Figure 45 below shows the concentration of $^{15}\text{N}$ at increasing depth within the sample. The concentration profiles are determined from a resonance peak originating from the interaction of 897 keV protons with $^{15}\text{N}$. Proton interaction with $^{15}\text{N}$ at this energy will produce 4.43 MeV $\gamma$-rays. The concentration of $^{15}\text{N}$ is then calculated from the yield of $\gamma$-ray particles from the equations given in chapter two.
The average concentration of $^{15}$N within the first 200 nm of the sample was found to be $0.48 \pm 0.01$ at%. The concentration increased to over $2 \pm 0.04$ at% from 205 nm to 320 nm. Uncertainty in the measurement was found to decrease with increasing nitrogen content, from a relative percent error of 5 to approximately 2. The trend in $^{15}$N concentration follows the diffusion profile of chromium seen in the NRBS spectrum. Within the calculated length of the extended shoulder both the chromium and nitrogen concentrations are relatively constant; with $^{15}$N varying between $0.36 \pm 0.01$ and $0.68 \pm 0.01$ at% and chromium staying at $1 \pm 0.16$ at%. In the region where $^{15}$N concentration increased to over 2 at%, the concentration of chromium was determined to increase to $30 \pm 1.2$ at%. In correlation with XRD data determining the presence of peaks associated with Cr-C-N and CrN, the corresponding rise in $^{15}$N content with rise in chromium content indicates that the greater overall concentration of nitrogen within this film compared to that found in NCD/Si (4.1.4 RNRA Depth Profile and Nitrogen Concentration) is due to the presence of chromium.
Figure 45. RNRA of sample grown on a chromium interlayer, exploiting the proton-induced \( \gamma \)-ray emission of \(^{15}\)N. Error in each \(^{15}\)N concentration measurement was based on event statistics, therefore, uncertainty was found to decrease with increasing yield, at low concentrations of \(~5\%\) relative error high concentrations of \(~2\%\) relative error.

4.3.5 Surface Mapping and Hardness

AFM was used in this work to study the microstructural changes of the NCD films and also to understand the effect of the interlayer. Figure 46 compares the grain size of the NCD films deposited on the silicon substrate without and with a chromium interlayer. The AFM topographical images show the grain size of the film grown on chromium interlayer (Figure 46) is larger than those of the silicon substrate without chromium (Figure 46). The estimated grain size for the film grown on chromium (250 ± 2 nm) is almost twice that deposited on the silicon substrate without a chromium interlayer.
(120 ± 2 nm). RMS roughness based on AFM images taken for both samples revealed an increase in the roughness of the film grown on chromium over that grown on silicon, from 7.4 ± 0.1 to 16.3 ± 0.1 nm. The formation of different CrN and Cr-C-N phases may have resulted in the nucleation of larger grains on the film deposited on chromium coated silicon over that of the film deposited directly on silicon.

(Figure 46a) NCD/Cr/Si sample AFM
AFM topographical images each sample. Grain size was estimated from directly measuring the diameter of each grain. Roughness was determined from proprietary Pacific Nanotechnology software.

In addition to the increased grain size and roughness of film grown on chromium compared to that deposited on silicon, nanoindentation tests on both films also revealed a striking difference between the hardness and elastic moduli of these films. The load-displacement curves obtained from the nanoindentation tests on both films are shown in Figure 47 (a and b). Interestingly, the curve obtained from the film deposited on silicon showed a greater variation during loading and unloading cycles, which is typically the signature of plastic deformation [123]. The film grown on silicon displayed a hardness and elastic modulus of 17 ± 2 and 207 ± 12 GPa respectively. In contrast, the film grown on chromium displayed a much higher hardness and elastic modulus; 45 ± 12 and 350 ± 43 GPa. Theoretical simulations coupled with experimental findings have predicted a
decrease in the elastic modulus with the addition of nitrogen in the grain boundary region under various conditions; however, the experimental values in this study differ from the predicted values [124,125,126,127]. This study clearly shows that the films deposited on chromium interlayer have higher hardness compared to those deposited on silicon substrate directly. This may be attributed to the formation of different hard phases (CrN, Cr-C-N or C-N) formed in the films on chromium layer. As oxygen was found only in the chromium interface layer, its contribution to the hardness value obtained is likely negligible. The addition of Cr-C-N and CrN phases of molecular chromium may be a contributing factor to the greater hardness of the film grown on chromium. As a comparison, CrN alone has a reported hardness of approximately 19.6 GPa [128] while the reported value for Cr-C-N ranges between 22.5 and 24.5 GPa [129,130].

Figure 47. Load-displacement curves for films grown on chromium coated silicon (a) and silicon (b). Plastic deformation is visible in the loading curve of the NCD/Si sample which resulted in lower than expected hardness value for the film grown on silicon.
4.4 Ion Implantation in Nanocrystalline Diamond Films

Towards the end of this research, ion implantation was performed as a prelude to continued research for the condensed matter group at Western Michigan University. Ion implantation, as a technique to alter the properties of NCD films, is of particular interest due to its versatility and relative ease of use. Ion implantation performed within NCD films using nitrogen at fluences just below the amorphization limit of diamond [131] demonstrated an enhanced electron field emission character within the implanted region [132]. Implantation using oxygen in UNCD [133] also indicated changes in the conductivity of the film. Both studies also indicated an amorphization of the film at fluences just above those in which electron field emission or conductivity enhancements were noted, indicating that the chemical morphology of these films may be contributing to their altered character.

Thus far no studies concerning a relatively large implantation species such as chromium has been conducted on NCD. Additionally, correlations between the changes to material property, microstructure and the relative shift of elemental concentrations of species such as hydrogen, present in UNCD and NCD films, have yet to be performed. Figure 48 is a SRIM simulation of chromium implantation within NCD which illustrates how ion implantation within NCD films can cause shifts in the concentration of elemental species within the implanted region. The investigations conducted in this study are focused on the effects of chromium ion implantation in nanocrystalline diamond films. The aim of this initial research was to assess the nature of ion damage in relation to NCD structural modification with increasing fluence.
Through funding awarded by the National Science Foundation and the Japan Society for the Promotion of Science, the microstructure of NCD samples implanted at 68 keV Cr ion with increasing fluence in each sample were analyzed in direct collaboration with partners in Japan. Focused ion beam (FIB) and TEM were performed and the High Voltage Electron Microscopy laboratory located on the Ito campus of Kyushu University, Japan. Sample preparation by FIB for TEM measurement was performed using a FEI Quanta™ 3D 200i. Electron energy loss spectroscopy (EELS), energy dispersive spectroscopy (EDS) and bright/dark field imaging were performed using a JEM-ARM 200F.

In a departure from previous sections, there is no extensive theoretical discussion or exact measurement conditions given for the TEM measurements taken in this section due to the limited amount of time available to perform these experiments. The data reported in this section was collected by experts in TEM measurements at Kyushu University under observation, while AFM measurements were performed using a Pacific Nanotechnology SPM, Nano-R series, scanning probe microscope under close contact mode.

4.4.1 Ion Implantation Issues in Diamond

Models have been developed to explain ion beam damage in metal lattices [134,135] and employed in diamond [136] to describe the onset of amorphous and graphitic phase structures in ion implanted diamond before and after annealing. The model employed in [136] has been contested [137], and it has been suggested that damage to diamond lattice comes from thermal spikes alone.
Figure 48. Monte Carlo simulation of individual ion distribution within diamond. Colors represent moving lattice atoms (orange for carbon, blue for hydrogen), the trajectory of incident ions (white), and thermal spikes (green).

A Monte Carlo simulation of diamond lattice damage due to thermal spikes is given in Figure 48. A study by Hickey et al. [138] determined, from bright field imaging of transition regions of silicon implanted diamond, that low temperature ion collisions produce more damage than room temperature and above collisions, likely due to dynamic annealing at higher implantation temperature. Furthermore, in diamond implanted beyond the critical fluence [131] at 303° K, high resolution TEM images, of the near surface area, showed a region of mixed diamond and the amorphous (implanted) layer. This layer contained pockets of diamond crystallites within an amorphous carbon matrix. Implanted layers deeper in the diamond sample displayed no such mixing between amorphous carbon and diamond. This finding indicates that lattice breakdown is not necessarily
uniform depending on environmental conditions and the energy state of incident ions during implantation.

The picture obtained thus far is that ion implantation in diamond is a complex, dynamic, process dependent on temperature during implantation and afterwards, ion beam species and beam energy (which changes as a function of depth). Within the context of CVD films containing a diamond crystalline structure this is still a rich and relatively unexplored field. By developing a picture of the basic material structure in implanted films; i.e. composition, microstructure, or localized electronic structure of molecules within the implanted regions, a framework within which further experiments may develop such films for technological applications can be realized.

4.4.2 Results and Analysis

4.4.2.1 Focused Ion Beam Milling

Films were prepared for TEM analysis by the ‘lift out’ focused ion beam (FIB) method (illustrated in Figure 49). The ‘lift out’ procedure is performed by first coating an area of interest, which will later become the sample, with a 5 μm layer of tungsten. Above and below this area, the sample is milled away leaving two ditches on either side of the area of interest. One side, either left or right, and the substrate underneath the sample is cut away. A probe, whose position relative to the sample is triangulated using a combination of the SEM ‘camera’ and the FIB ‘camera’ is brought close to the top of the sample and attached by another tungsten deposition. Finally, after the probe is secured to the sample top, the last side is cut away and the sample is lifted out and onto a ‘grid’ for analysis by TEM. The images below are representative of the ‘lift out’ process. It was determined during the course of preparing the reference sample and the film with $10^{16}$
ions/cm$^2$ that care must be taken in milling each sample. During the process of extracting the sample gallium ions implanted within the first 50 nm of the films caused amorphization of carbon within that layer. Later samples were protected with a thin (~50 nm) coating of gold by sputtering deposition to protect the sample during milling and extraction. Milling current was kept between 3.0 and 0.5 nA for large cuts, and between 0.5 nA and 200 pA for fine milling. Samples were thinned to approximately 100 nm and then subjected to extremely fine milling, or polishing, with 2 keV argon ions.
Figure 49. Scanning electron microscope images of samples being milled by FIB, lifted out of the sample and placed on a grid for measurement by TEM.

4.4.2.2 Transmission Electron Microscopy

Due to the time constraints on this set of measurements and the difficulty involved in preparation by FIB, TEM data was only obtained for the reference and NCD sample implanted to $10^{16}$ ions/cm$^2$ followed by heating at 600 ºC in an argon atmosphere.
Initial results of bright and dark field imaging on each show clearly defined amorphous and nanocrystalline regions bound between tungsten layers (Figure 50). The darkened regions in the bright field images are from regions where nanocrystalline planes within the grains are oriented perpendicular to the incoming light, blocking more light from getting through. The opposite effect is seen in dark field imaging where only unscattered light is received by the lens. The amorphous regions in the reference sample are attributable to gallium ion implantation during sample preparation, whereas for the chromium implanted sample the effect of gallium implantation has been ruled out by EDS and attributed instead to chromium ion implantation in this region.
Figure 50. Bright and dark field images of the reference sample and $10^{16}$ ions/cm$^2$ implanted sample heated to 600°C for one hour. Five regions are distinguishable in each image. For the reference sample the uppermost region is the silicon substrate, proceeding downward in order reveals a dark tungsten layer, two regions in the NCD film, and the remains of the protective tungsten coat. The film $10^{16}$ ions/cm$^2$ implanted sample follows the same sequent from left to right.
4.4.2.3 Electron Energy Loss Spectroscopy

Based on these images it is clear that; (1) implanted regions were clearly delineated from un-implanted regions and (2) ion implantation with high Z ions at relatively low dose results in an amorphous layer. The $10^{16}$ ions/cm$^2$ showed a clearly defined region corresponding to the predicted implantation depth. In order to examine the molecular state of atoms in each region, EELS was performed on the reference and $10^{16}$ atoms/cm$^2$ samples. The EELS technique is very similar to NEXAFS in that it examines the bonding state of a material through excitation of the inner shell electrons. However, instead of x-rays, electrons are used. EELS taken on the reference sample (Figure 51) revealed characteristic spectra of amorphous [139] and diamond phases [140] of carbon. An EELS depth profile (Figure 52), taken every 20 nm within the film, illustrates how ion implantation affects the microstructure within the implanted region compared to the bulk. This indicates that that the implantation technique employed can be performed reliably in correspondence with SRIM. An examination of the $10^{11}$ ions/cm$^2$ implanted samples (unheated and heated to 600 ºC) and remaining $10^{16}$ ions/cm$^2$ un-annealed samples is necessary to develop a complete picture of NCD film modification by ion implantation. By determining the molecular phases of carbon in the implanted regions of the $10^{11}$ ions/cm$^2$ implanted samples and comparing this to the implanted region of the $10^{16}$ ions/cm$^2$ implanted samples a complete picture of ion implantation with increasing fluence can be obtained. From this data, it will be possible to perform future experiments to precisely tailor the microstructure of NCD to suit each experiment.
Figure 51. EELS spectra of amorphous region in $10^{16}$ sample, background subtracted for green line spectrum.

Figure 52. EELS carbon molecular phase structure depth profile of reference NCD film. Each spectrum corresponds to increasing depth within the sample. Starting from the surface at the middle right of the picture and proceeding towards the tungsten interlayer, each spectra was taken 10 nm from the previous within the film.

4.4.2.4 Surface Mapping and Crystallite Recovery

To develop a picture of the ion implantation effect at the surface of implanted NCD films, AFM analysis was performed on un-implanted, implanted, and implanted/annealed films. In Figure 53 below, the surfaces of pristine, implanted and
implanted/annealed films are shown. As can be seen from the relative similarity of the AFM images obtained, the surfaces of each film were essentially unchanged due to both ion implantation and/or annealing. Calculated mean surface roughness for each film is; 5.7 ± 0.1 nm for the un-implanted sample (Figure 53a), 5.0 ± 0.1 nm for the implanted sample (Figure 53b) and 5.4 ± 0.1 nm for the implanted sample annealed at 600º C for one hour (Figure 53c). Average grain size for each film based on the AFM micrographs was estimated at; 60 ± 2 nm for the un-implanted sample, 55 ± 2 nm for the implanted sample, and 57 ± 2 nm for the implanted sample annealed at 600º C. Sputtering of constituent film atoms predicted by SRIM calculations is illustrated in Figure 54 below. In correlation with the AFM micrographs, atoms reaching the surface of the film with energy below the surface binding energy resulted in the development of disordered regions on the surface creating a smoothing effect [141], lowering the surface roughness. After annealing at 600º C the lattice structure is recovered by atoms filling vacant sites, thereby restoring crystallite size and resulting in increasing surface roughness.
(53a) Reference sample
(53b) $10^{16}$ ions/cm$^2$ implanted, un-annealed, sample

Figure 53. AFM mapping of the surface revealed little difference in the topographical features in each film. However, grain size estimation and roughness calculations determined a small but detectable amount of variation in grain size and roughness in each film. It cannot be ruled out, however, that this variation is simply from the examination of different regions on each film.
Figure 54. SRIM calculation of sputtered carbon and hydrogen by collision with 68 keV Cr ions. This graph predicts target ions with energy below the 4.7 eV vertical line lack sufficient energy to be ejected from the sample and remain ‘loose’ on the surface. This model appears consistent with the AFM data showing a loss and then recovery in grain size and surface roughness in the $10^{16}$ ions/cm$^2$ samples in relation to the reference sample.
CHAPTER 5
CONCLUSIONS

Throughout this dissertation the aim was to investigate the state of matter within nano-diamond films after controlled modification. The substantiation of how alterations in the properties of NCD films relate to changes in their structure and composition will guide the refinement of these films towards practical application as sensors, microactuators or high temperature semiconductors. The mechanisms of alteration used in this study were chosen based on ease of incorporation into tested methods of growth as well as previous studies which have verified their beneficial contributions to NCD film properties, i.e., increased conductivity through nitrogen incorporation. Nitrogen concentration and profile was evaluated after film growth in a nitrogen diluted plasma, film characteristics were thoroughly examined after growth on metalized substrates in nitrogen diluted plasmas and preliminary characterizations were performed on films whose bulk was metalized through ion implantation. What follows is an assessment of the results of each section in the order in which they were discussed.

5.1 Nitrogen Quantification

The quantification of nitrogen in NCD films grown on silicon substrates determined, within a small margin of relative percent error (4 – 5%), the concentration and profile of nitrogen. The overall concentration of nitrogen in the film was found to be 0.20 ± 0.01 at% using proton-induced gamma-ray emission, an RNRA reaction. In addition to the concentration of nitrogen within each sample, RNRA was also used to
determine its depth profile. While the results of the SIMS analysis confirmed previous measurements of a uniform distribution of nitrogen within the bulk of NCD film, RNRA was able to detect a small variation in the concentration of nitrogen within the bulk. Additionally, RNRA, in conjunction with a SIMS measurement, determined that nitrogen concentration increases in interface region with silicon. However, due to the straggling of protons within the sample RNRA was unable to resolve the width of the peak in this region. Utilizing a higher resolution detector, such as a HPGe detector, and proceeding through the sample in smaller energy increments, is recommended for future experiments in order to resolve sharp changes in the concentration of nitrogen within these materials. However, this study elucidates that multiple IBA techniques can give a lucid description of NCD samples for further research within these contexts. Additionally, using NRBS, the concentrations of carbon and hydrogen were found be 94.2 ± 0.5 and 5.7 ± 0.03 at% respectively, and the overall film thickness to be ~215 ± 13 nm.

Evaluation of the film microstructure by Raman spectroscopy displayed typical spectra associated with UNCD films. However, AFM mapping of the surface revealed a much different picture, one with grain sizes exceeding 50 nm in diameter. In addition to other factors such as the seeding method used to prepare the silicon substrate, the large percentage of nitrogen diluted within the deposition chamber altered the growth plasma and resulted in the larger grain sizes. Further investigation into the effect of nitrogen addition to the growth plasma of CVD deposited NCD, as well as deposition surface, was evaluated from films grown on metal interlayers in the next section.
5.2 Nitrogen Gas Dilution: Effect after Growth on Metal Interlayer

It became clear from the previous investigation that nitrogen has a dramatic effect on the growth of polycrystalline diamond within each film. Growth rates of the films grown in a nitrogen diluted atmosphere were greater than those in hydrogen, while the degree of interfacial mixing between films remained consistently below the detection threshold. XRD patterns revealed an apparently decrease of (111) diamond crystallite size with increasing nitrogen content, although these calculations of crystallite size have not been confirmed by AFM or other techniques. The (220) diamond reflection remained largely unaffected by the increase in nitrogen content, though detection of this peak was confounded due to the presence of tungsten carbide compounds overlapping with the diamond peak.

In comparison to NCD films grown on a silicon surface, calculations using the Scherrer equation indicate a lower bound for crystallite size much smaller than the average grain size of the films grown in the previous study. Additionally, crystallite size was found to decrease with increasing nitrogen content in the case of the (111) diamond peak. This points to the addition of a tungsten interlayer as a factor by which the size of resulting film grains may be further controlled despite the changes to the plasma chemistry brought on by increasing amounts of nitrogen dilution. A further examination of the effects which metal interlayers can bring about will be assessed in the next section.

5.3 Growth and Characterization of NCD on a Chromium Interlayer

Stemming from the evaluation of the effect of nitrogen gas dilution in the growth atmosphere of NCD grown on tungsten interlayers, $^{15}\text{N}_2$ diluted up to 20% in the growth atmosphere of NCD grown on chromium was performed and the resultant film was
characterized. Spectroscopic analysis clearly showed the formation of NCD structure in both films. However, bulk film analysis by XRD detected the presence of polycrystalline forms of chromium, carbon and nitrogen; CrN and Cr-C-N; as well as chromium and oxygen (Cr$_2$O$_3$) indicating the presence of chromium and incorporation of nitrogen into those films. NRBS detected diffusion of the chromium interlayer through the film in correlation with XRD findings. RNRA results coupled with XRD and NRBS indicated an interdiffusion of nitrogen, chromium and carbon. AFM surface mapping determined a large increase in grain size over the film grown on silicon alone, and nanoindentation tests revealed that the hardness of the film grown on chromium is more than twice that of the sample grown on silicon. Based on the data obtained by AFM, correlated with XRD, NRBS and RNRA data, it can be inferred that diamond grains began to nucleate from chromium compounds which formed during the growth process, resulting in the larger grain sizes seen in AFM images. Furthermore, although the hardness of the film grown on chromium was found to be greater than that of the control film on silicon, this difference may be affected by thickness of films and the depth to which each indentation was performed.

5.4 Ion Implantation in Nanocrystalline Diamond Films

Chromium implantation was performed in NCD samples to develop a picture of gradual film modification using ion beams. TEM analysis revealed an amorphous region within the NCD film implanted to a fluence of $10^{16}$ ions/cm$^2$. The interface between the amorphous region and the NCD matrix is very well defined; indicating that chromium implantation within these films can be performed with precision. The implanted range is consistent with SRIM calculations based on the width of the amorphous region within the
$10^{16}$ ions/cm$^2$ sample. AFM images indicated that small amounts of the sputtering of carbon and hydrogen predicted by SRIM calculations had a quantifiable effect on the topography of each film. Consistent with smoothing behavior, surface roughness was found to decrease from un-annealed to implanted samples and increase after annealing indicating a recovery of crystallinity. This illustrates the use of ion implantation as a tool to engineer materials. Further measurements of the $10^{11}$ implanted samples as well as the relative concentrations of hydrogen in implanted/annealed films will develop a more complete picture of the effects of heavy ion implantation on the properties of resultant NCD films.

5.5 Final Statements

The results for each study demonstrate how the overall effects of interface and bulk modifications before and after NCD growth greatly alter the structure, and subsequently, the properties of the film. While strictly adhering to proven growth techniques, and changing the nitrogen dilution up to 20% in the growth plasma, the grain size was found to increase for films developed on silicon surfaces, an effect which was found to be reduced when the same parameters are applied to films developed on tungsten interfaces. However, applying the same parameters to films developed on a chromium interface determined that, not only was the nitrogen incorporation increased drastically within the film, the microstructure changed significantly compared to films developed on silicon alone and additional chromium complexes developed during film growth (this also took place to a lesser degree on films developed on tungsten). Overall, the indication is that the metal interfaces chosen can have a dramatic effect on the properties of resultant films when all other deposition parameters are kept constant.
In the case of ion implantation it was seen through TEM images that even at relatively low doses, heavy ions have a great impact on the film microstructure after annealing, turning it from $sp^3$ bonded carbon to $sp^2$ or amorphous phase carbon. In the end what this study illustrates is only a few amongst the dearth of ways that diamond can be manipulated and shaped to fit the designs of researchers. From the properties that emerge in these the underlying components their relation to structure were identified and quantified, adding to the repository of information collected about such systems. Future research can then make use of this information while refining nano-diamond systems for use in technological applications.
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