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Dielectric Properties of Nitrogen Incorporated Ultrananocrystalline Diamond Films

Salem AlFaify

Western Michigan University

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DIELECTRIC PROPERTIES OF NITROGEN INCORPORATED ULTRANANOCRYSTALLINE DIAMOND FILMS

by

Salem AlFaify

A Dissertation
Submitted to the
Faculty of The Graduate College
in partial fulfillment of the
requirements for the
Degree of Doctor of Philosophy
Department of Physics
Advisor: Asghar Kayani, Ph.D.

Western Michigan University
Kalamazoo, Michigan
August 2011
Deposition of Ultrananocrystalline Diamond (UNCD) films have been carried out and dielectric properties of nitrogen incorporated UNCD films were studied using spectroscopic ellipsometry (SE), UV/VIS spectroscopy, and reflectance spectroscopy. Dielectric functions of the films were correlated with their nanostructure, elemental concentration, and growth conditions. The films were grown in a 915 MHz microwave plasma chemical vapor deposition system with 0%, 10%, and 20% N\textsubscript{2} gas diluted into Ar/CH\textsubscript{4}/H\textsubscript{2} plasma. Samples were deposited on 6-inch Si substrates. For UV/VIS spectroscopy studies, samples were deposited on quartz substrates. The bonding structure was investigated by Raman spectroscopy and the surface morphology of the films was characterized by atomic force microscopy (AFM) and scanning electron microscopy (SEM). Determination of the elemental composition of the deposited films was carried out by ion beam analysis (IBA) measurements. To obtain the precise concentration of carbon, hydrogen, nitrogen, and impurities incorporated in the film, Rutherford backscattering spectrometry (RBS), non-Rutherford backscattering spectrometry (NRBS), elastic recoil detection analysis
(ERDA), and nuclear reaction analysis (NRA) were performed. IBA measurements were carried out using protons, helium, and oxygen ion beams. By exploiting the high cross section and the narrow width resonance of $^{15}\text{N} \ (p, \alpha\gamma)^{12}\text{C}$ nuclear reaction, $^{15}\text{N}$ content in the deposited films was precisely determined. To the best of our knowledge the precise measurement of N content in the UNCD film using the nuclear reaction $^{15}\text{N} \ (p, \alpha\gamma)^{12}\text{C}$ has been done for the first time. Our results showed that UNCD films incorporated with $^{15}\text{N}$ have $\sim 0.13$ at.% N, 90-93 at.% of C, and 7-9 at.% of H. From the spectroscopic ellipsometry investigations, dielectric functions of the UNCD films were found to increase for the samples prepared with N$_2$ gas added to the growth plasma. The UNCD film deposited with 0% of N$_2$ has a high degree of light transmission in the visible and IR regions, whereas the transmission decreased as N$_2$ content in the growth plasma was increased. Results obtained from UV/VIS and reflectance spectrosopes were in agreement with the SE findings on the UNCD films.
ACKNOWLEDGMENTS

At this stage of my life I have a lot to be thankful for and as the saying goes, if you do not take time to thank people, then you are not thanking God. Therefore, first and foremost I would like to express my deep gratitude and thanks to my research supervisor, Professor Asghar Kayani, with whom I really enjoyed my years of scientific research. His unique way of sharing knowledge and great expertise were proven to me time after time as very effective. Thank you, Dr. Asghar, and I will be glad to collaborate with you for many years to come.

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Much deserved appreciation and endless thanks are due to my wonderful wife and children for their love and support, and for being always by my side.

Heartfelt gratitude and thanks to my sisters and brothers-in-law for their tremendous encouragements and unshakable belief in me.

Finally I would like to deeply emphasize my gratefulness and thanks to my parents Mr. Ali AlFaify and Mrs. Afiah AlFaify for their unconditional love, support, patience, and understanding. I simply do not have enough words to thank them. I dedicate this dissertation to them.

Salem AlFaify
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CHAPTER 1
INTRODUCTION

1.1 Historical Review of Carbon Based Materials

There are many forms of nanocarbon, including fullerenes, nanotubes, nanowalls, and most recently, graphene and ultrananocrystalline diamond (UNCD), all of which have been actively researched in the recent years. The history of synthetic graphite can be traced back to the 19th century [1]; however, artificial diamonds were not synthesized until the middle of the 20th century. Since that time, carbon materials-related research has experienced multiple waves of interest by researchers in both academia and the industry. In the 1960s, carbon-based materials such as high strength carbon fibers, glass-like carbon, pyrolytic carbons, and others found their way into a board range of industrial applications. One of the particularly important applications of these classes of carbon is lithium ion rechargeable batteries, where nanostructured graphite is used as an anode [2]. In the mid-1980s, a family of buckminsterfullerene or buckyballs [3] was discovered, which laid the foundation for fullerene nanotubules [4]. These findings in carbon materials set the stage for global booming research on nanocarbon materials and related compounds and the interest has been growing ever since.
Between 1910 and 1920, Bolton and Ruff reported the synthesis of polycrystalline diamond film by using low-pressure chemical vapor deposition (CVD) [5, 6]. The first successful synthesis of diamond from graphite was recorded in the 1950s [7]. In the 1980s, CVD diamond films became widely known [8-10]. In 1991, D.M. Gruen proposed that the use of the carbon dimer molecule, C\textsubscript{2}, extracted from the fragmentation of fullerenes or hydrocarbons, can be used for the growth of a CVD synthesized nanodiamond [11]. Gruen explained that a direct insertion of rows of carbon dimer, which is highly reactive by its nature, will help construct the (100) surface of a diamond and that the growth would be accomplished virtually without the presence of hydrogen atoms [12]. In 1993, an experiment was conducted to test Gruen’s theory, and it was found that the crystalline phase of the diamond film with grain sizes of 3-5 nm could be obtained from fullerenes containing argon microwave plasmas [13]. The name, ultrananocrystalline diamond film, was chosen to distinguish it from other nanodiamond films produced by the CVD process with crystallite sizes in the range of 30-300 nm. The interest in nanodiamond materials has profoundly increased after the discovery of the process to make ultrananocrystalline diamond (UNCD) films [14-18].

UNCD films, due to their unique and exceptional properties, have been the subject of extensive experimental and theoretical investigations in recent years [19, 20]. Some of the properties of the UNCD films are given in Table 1.1. With the exceptional mechanical, electrical, and optical properties, this material has variety of
applications, such as microelectromechanical (MEMS) devices, nanoelectromechanical (NEMS) devices, high temperature diodes and biosensors, and others [21-25]. One interesting fact that is worth mentioning here is the similarity between the free energies of the formation of UNCD films and carbon nanotubes (CNT), which enable the possibility of simultaneous synthesis of UNCD/CNT as self-assembled, self-composite material [41]. This carbon composite material is experimentally challenging and is being explored using density functional tight-binding theory (DFBT) due to its potential applications in the fabrication of quantum dots on graphite-based quantum wires [42]. Table 1.2 summarizes in chronological order advancements and major events of the carbon-based materials, from the last century to the present.
Table 1.1 Some properties of Natural Diamond, CVD Diamond, and UNCD; Ref. [9] &[26-40]

<table>
<thead>
<tr>
<th>Properties</th>
<th>Natural D(Ia)</th>
<th>CVD</th>
<th>UNCD</th>
<th>Comparison</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness {GPa}</td>
<td>57-104</td>
<td>50-100</td>
<td>98</td>
<td>(Cu): 2.1, (SiC):3.15</td>
<td>Abrasive Coatings for cutting tools</td>
</tr>
<tr>
<td>Thermal Conductivity {[W/m/K] at 298K}</td>
<td>20-23</td>
<td>10-21</td>
<td>12-14</td>
<td>Water 5.6</td>
<td>Heat sink for electronic power devices</td>
</tr>
<tr>
<td>Thermal Expansion Coefficient (*10^-6/K) between 298-473K</td>
<td>0.8-1.2</td>
<td>≈ 2.0</td>
<td>≈ 2.0</td>
<td>(Cu):17, (SiO_2):5.5</td>
<td>Microelectronic circuit boards</td>
</tr>
<tr>
<td>Band Gap (eV)</td>
<td>5.45</td>
<td>≈ 5.5</td>
<td>≈ 2.2</td>
<td>(GaAs): 1.12</td>
<td>Microwave power devices &amp; MEMs, NEMs</td>
</tr>
<tr>
<td>Optical Transparency</td>
<td>UV(230nm) to microwave (mm)</td>
<td>Visible-IR</td>
<td>Semi-Opaque</td>
<td>electro-optical device Optical coating Lithography</td>
<td></td>
</tr>
<tr>
<td>Electrical Resistivity {[Ω . cm]}</td>
<td>10^{16}</td>
<td>10^{12} - 10^{16}</td>
<td>Heat sink for electrical devices</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rel. Dielectric Constant at 45 MHz -20 GHz</td>
<td>5.7</td>
<td>5.6</td>
<td>(GaAs): 11.7</td>
<td>RF electronic device</td>
<td></td>
</tr>
<tr>
<td>Sound Velocities{m/s} Longitudinal</td>
<td>18000</td>
<td>15700-17980</td>
<td>15700</td>
<td>Nickel 6040</td>
<td></td>
</tr>
<tr>
<td>Grain size {nm}</td>
<td>1 ~ &gt;10000</td>
<td>2-100</td>
<td>2-5</td>
<td>nanocrystalline nickel 28</td>
<td></td>
</tr>
<tr>
<td>Bonding Characters</td>
<td>Sp³</td>
<td>&gt;50% Sp²</td>
<td>&lt;0.1%Sp²</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


Table 1.2 Summary of historical overview of carbon-based materials including UNCD

<table>
<thead>
<tr>
<th>Time</th>
<th>Advancement and Major Events</th>
<th>Comment</th>
<th>Citation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1959</td>
<td>synthesizes of nanodiamond by applying shocking wave to carbon</td>
<td>placing carbon around explosive materials</td>
<td>[43]</td>
</tr>
<tr>
<td>1960</td>
<td>production of carbon tubes from graphite layer</td>
<td>arc discharge method</td>
<td>[44]</td>
</tr>
<tr>
<td>1963</td>
<td>ultradispered diamond powder produced by carbon detonation</td>
<td>formation of carbon from explosive products</td>
<td>[45]</td>
</tr>
<tr>
<td>1966</td>
<td>a large hollow cage molecule is proposed</td>
<td>suggested that molecule can be fashioned out of graphene</td>
<td>[46]</td>
</tr>
<tr>
<td>1970</td>
<td>proposed of Spherical Molecule C_{60}</td>
<td></td>
<td>[47]</td>
</tr>
<tr>
<td>1973</td>
<td>prediction that molecule C_{60} would be stable</td>
<td>Hackle calculation suggested closed electronic shell for C_{60} configuration</td>
<td>[48]</td>
</tr>
<tr>
<td>1980</td>
<td>nanotubes observed for the first time</td>
<td>arc discharge method</td>
<td>[49]</td>
</tr>
<tr>
<td>1983</td>
<td>synthesize of dodecahedrane C_{20}H_{20}</td>
<td>molecule with same symmetrical form as C_{60}</td>
<td>[50]</td>
</tr>
<tr>
<td>1984</td>
<td>report on the stability of even-atom carbon clusters, C_{60}</td>
<td>mass spectrometry study on laser-ablated carbon plumes</td>
<td>[51]</td>
</tr>
<tr>
<td>1985</td>
<td>discovery of Bucky ball C_{60}</td>
<td>C_{60} is found on mass spectrum of laser-evaporated graphite</td>
<td>[3]</td>
</tr>
<tr>
<td>1987</td>
<td>nanodiamond particles found in meteorites</td>
<td>size of diamond nanoparticle found to be around 5 nm</td>
<td>[52]</td>
</tr>
<tr>
<td>1990</td>
<td>fullerene produces in large quantities</td>
<td>process of evaporation of graphite electrodes in an arc discharge</td>
<td>[53]</td>
</tr>
<tr>
<td>1991</td>
<td>discovery multiwall carbon nanotubes MW-CNT</td>
<td>MW-CNT deposited on the negative electrode during DC arcing of graphite</td>
<td>[4]</td>
</tr>
<tr>
<td>1991</td>
<td>prediction of hyper fullerenes</td>
<td></td>
<td>[54]</td>
</tr>
<tr>
<td>1992</td>
<td>observation of carbon onions</td>
<td>obtained by heating of nanotubes by electron beam in a microscope</td>
<td>[55]</td>
</tr>
<tr>
<td>1993</td>
<td>discovery of single wall carbon nanotubes SW-CNT</td>
<td>arc process in the presence of Fe or Co catalytic particles</td>
<td>[56][57]</td>
</tr>
<tr>
<td>1994</td>
<td>fullerene found in meteorites</td>
<td></td>
<td>[58]</td>
</tr>
<tr>
<td>1994</td>
<td>conversion of nanodiamond to carbon onions during annealing</td>
<td>annealing temperatures 1300-1800 k depending on the particles size</td>
<td>[59]</td>
</tr>
<tr>
<td>1994</td>
<td>UNCD films</td>
<td>CVD method with microwave-activated carbon/rare gas plasmas</td>
<td>[60]</td>
</tr>
<tr>
<td>1996</td>
<td>ropes of SW-CNT</td>
<td>mass production of SW-CNT by laser ablation methods</td>
<td>[61]</td>
</tr>
<tr>
<td>1996</td>
<td>conversion of carbon onions to nanodiamond by electronic beams</td>
<td></td>
<td>[18]</td>
</tr>
<tr>
<td>1998</td>
<td>CVD synthesis of aligned nanotubes films</td>
<td>MWCNT growth in the presence catalytic particles</td>
<td>[62]</td>
</tr>
<tr>
<td>2001</td>
<td>nanotubes single crystals</td>
<td>order of single crystals in microns size</td>
<td>[63]</td>
</tr>
</tbody>
</table>
1.2 Statement of Research Objectives

Diamond is famous for its superlative physical and chemical properties, which promote it as an excellent choice for a number of different mechanical, optical, biological, and electronics applications [64][65].

At room temperature, undoped single crystal diamond is insulating and has a band gap of 5.45 eV. Some of the physical characteristics of naturally existing diamond and thin films of diamond are shown in Table 1.1. Other than those qualities, diamond and thin films of diamond have highly saturated carrier velocities, high intrinsic charge carrier mobility, high electric field breakdown strength, high thermal conductivity and are highly transparent in the visible-IR region. These properties make diamond an ideal candidate for electronics applications. Moreover, diamond is used for other applications because of its bio-compatibility with human tissues, chemical inertness, radiation hardness and potential negative electron affinity. Some of the potential applications for diamond are in high power electronics, radiation detectors, optoelectronic devices, and field emission displays [39].

In general, diamond is favored over other wide band-gap semiconductors [66] because of its electronic properties; however doping diamond can’t be done with shallow impurities. In addition, wafer-size substrate of single crystal diamond is expensive and is rarely available. Due to such limitations, the use of diamond materials in electronic devices is limited. Boron as a deep acceptor is the common dopant for diamond layers [67]. Producing diamond with n-type conductivity is
difficult and has been largely unsuccessful. Doped diamond is necessary for semiconductor devices and has been predicted as a better electron and photon emitter, and electron or ion impact-induced emission, and would serve as a better inert electrode for electrochemical applications [68-70].

Chemical vapor deposition (CVD) is a widely used method to fabricate thin films of diamond. Most diamond CVD processes, however, could produce polycrystalline films on non-diamond substrates, like silicon. Coarse-grained diamond films possess most of the inherent mechanical properties of single crystal diamond but are unsuitable for applications that require smooth surfaces over a large area.

Ultrananocrystalline diamond films are new and promising materials of diamond. These films are called ultrananocrystalline due to their fine-grains structure with a grain size of 3-5 nm. Because of such a nanostructure, UNCD film has a smooth surface.

UNCD films are usually deposited in a microwave-enhanced plasma CVD system (MPCVD) [71, 72] using a hydrogen-poor Ar / CH₄ gas mixture. The structure of UNCDs is due to the high rate of renucleation that occurs as a result of the special plasma gas chemistry [73].

Doping of UNCD is an essential requirement for its use in the electronic applications. Since the discovery of the UNCD film in 1993, researchers have been trying to dope it. Theoretical studies on the film suggest nitrogen as a possible dopant to produce n-type material. Experimental studies on N doping in UNCD have
produced conflicting results [74, 75]. However, nitrogen incorporation in ultrananocrystalline diamond film, made by introducing 1%-20% of nitrogen gas into the growth plasma mixture during the MPCVD process, gives rise to the electrical conductivity of the film by five orders of magnitude to be around 143-250 $\Omega^{-1}$ cm$^{-1}$ and have been confirmed to be n-type diamonds by Hall measurements [39]. The initial properties of the nitrogen incorporated ultrananocrystalline diamond (N-UNCD) film signal that this film could overcome the limitations shared by the other diamond materials and make it the suitable diamond for electronics, as well as a broad range of other applications.

The work presented in this thesis is an exploration/investigation of the dielectric properties of the UNCD and the nitrogen incorporated UNCD films with respect to the growth parameters, the growth resulting nanostructure, and the elemental concentration. The properties are investigated for the UNCD film incorporated with N as different concentration of $N_2$ gas is added to the film plasma mixture during the growth process. To correlate the properties of N-incorporated UNCD (N-UNCD) film with the N and the other elemental content trapped in the film, ion beam analysis (IBA) has been carried out for the deposited films. One of the main objectives of this work is to develop a method to precisely determine the N content incorporated in the UNCD films during the growth process. To achieve this objective, a resonance nuclear reaction analysis (RNRA) was utilized. In particular, the $^{15}$N(p, $\alpha\gamma$)$^{12}$C nuclear reaction was used for the first time on specially prepared samples. The nanostructure of the UNCD film as nitrogen with other impurities
incorporated in it has been correlated with the optical transparency and electronic transport properties to investigate the structural effects on the properties.

Powerful and comprehensive set of techniques were used to establish the nanostructure of the UNCD film in order to draw conclusions about its properties. Since UNCD films are also being considered for a variety of technological applications that require knowledge of different material properties in the film, this work allows for a pedagogical choice of growth parameters to get the best film for the applications at hand. It also allows for the subsequent study of other material properties of nitrogen incorporated UNCD, such as the investigating of the mechanical properties, to be understood in terms of changes in the nanostructure.
CHAPTER 2
DEPOSITION OF ULTRANANOCRYSTALLINE DIAMOND FILMS

Diamond thin films are deposited in a number of very different ways, such as microwave plasma-enhanced chemical vapor deposition (MPECVD), hot filament chemical vapor deposition (HFCVD), pulsed laser deposition (PLD), arc-jet, and others, each with its own unique advantages and limitations. The method used to deposit the UNCD thin films for this study is MPECVD, and therefore, is the only technique discussed in depth here. The mechanism of CVD diamond growth is not completely understood, however, it is well established that H\textsubscript{2} and hydrocarbon gases such as CH\textsubscript{4}, CH\textsubscript{3}, C\textsubscript{2}H\textsubscript{2}, etc. play an important role in the complex CVD growth environment [53].

2.1 Synthesizing Mechanisms of UNCD Films

The main building block of UNCD films is the grain made of pure diamond crystal, which sizes on the order of nanometers. These crystals are usually much smaller than those of polycrystalline diamond films synthesized by H\textsubscript{2}/CH\textsubscript{4} initiated plasma. Nanocrystalline diamond film is often grown in a lower hydrogen concentration environment. Noble gases, such as Ar, are sometimes used in place of H\textsubscript{2}. When a
noble gas such as Ar is added to a H$_2$/CH$_4$ discharge, the plasma chemistry changes. Ionization, dissociation, and species concentrations are modified and that changes the emission intensity of various species of the plasma. When H$_2$ input is reduced and replaced by Ar, the C$_2$ emission is increased in the plasma, which gives rise to the Swan band shown in Figure 2.1.1. This increase in the C$_2$ emission is due to the increased C$_2$ ground state population in the plasma, since excitation and quenching (competing de-excitation mechanism) rates can be expected to change only marginally under these conditions [68].

![Figure 2.1.1 Optical emission spectra for Ar/CH$_4$ plasma. The peaks prominent between 450 nm and 650 nm are due to the Swan band emission of C$_2$, and the peak at 378 nm is due to CH in the plasma. For the peaks assignments see ref. [76].](image)
The rise in C₂ population is correlated with the observed increase in growth rate, and thus supports that C₂ is a growth species for UNCD synthesis. Therefore, dicarbon (C₂) is believed to be the key growth species for ultrananocrystalline diamond [77] instead of methyl (CH₃) and acetylene (C₂H₂), which are believed to be the important species in traditional CH₄/H₂ polycrystalline diamond growth. A two-step C₂ addition mechanism for growth from a CH₄ precursor in Ar plasmas for a (110) H unreconstructed surface was proposed by Gruen et al. [78]. As shown in Figure 2.1.2, UNCD growth process is summarized as follows:

a) C₂ adds to the unreconstructed monohybrid surface by inserting itself into first one C-H surface bond without abstraction of the terminating hydrogen bond (step 1). From the Hartree-Fock calculation, C₂ can insert into a C-H bond with no activation barrier forming a stable H₃C-CH=C molecule.

b) The C₂ molecule then rotates about the newly formed bond to insert its other carbon into the C-H bond across from it, thus forming a (100) oriented surface dimer row (step 2), producing an adsorbed ethylene-like structure (III).

c) A subsequent C₂ molecule then inserts itself into the adjacent surface C-H bond, parallel to the newly inserted surface C₂ dimer (III), to produce a surface with two adjacent ethylene-like groups (V), (steps 3 and 4).

d) The original state of the (110) surface is finally recovered by the formation of a C-C single bond between adjacent ethylene-like groups and produces a new layer on the diamond surface via step 5 (formation of a singlet diradical, structure VI, directly from structure V).
This direct insertion growth mechanism for C\textsubscript{2} is unique in that it is not dependent on the abstraction of hydrogen atoms from the surface. Specifically, the path for the formation of a C-C single bond between adsorbed, two-carbon moieties via step 5 does not involve any gas-phase atomic hydrogen.

**Figure 2.1.2** Diamond (110) surface growth mechanisms with C\textsubscript{2} as growth species; a schematic representation of the proposed mechanism for direct two step C\textsubscript{2} addition to the (110) - (1×1): H diamond surface [78].

In a theoretical study of UNCD growth conducted by Gruen at el. [79], the reaction of a singlet C\textsubscript{2} with the C=C bond of the C\textsubscript{9}H\textsubscript{12} cluster leads to the formation of diamond critical nuclei. The nucleation rate of the diamond increases dramatically
when the $C_2$ concentration in the plasma reaches a critical level of $10^{12}$ cm$^{-3}$. Such condition favors low hydrogen content plasma.

As a consequence of the special growth mechanism of the UNCD film, it has featureless morphology with a RMS surface roughness on the order of a few to tens of nanometers. In addition, UNCD films are grown by continuous high heterogeneous renucleation rates which ensure the formation of smooth and phase pure films. The high secondary nucleation rates make the transition from microcrystalline to nanocrystalline diamond films. A typical scanning electrons microscopy (SEM) image of UNCD film is shown in Figure 2.1.3 to illustrate the surface morphology of the film.

![Figure 2.1.3 Typical SEM image of UNCD film](image)

Nitrogen and hydrogen addition to the growth plasma of UNCD film have a profound effect on the properties of the film. Adding hydrogen to the Ar/ CH$_4$/ H$_2$
plasma seems to cause the $C_2$ density to linearly decrease due to the conversion of $C_2$ species into hydrocarbons [80]. On the other hand, the effects of adding nitrogen to the growth plasmas of diamond films are not well understood although a large number of studies have been conducted to find the chemical species responsible for the incorporation of nitrogen into diamond. Many researchers on the deposition of nitrogen doped diamond films reported the presence of HCN and CN molecules in the plasma [81-85]. The chemical routes in which CN and HCN produced in the plasma are:

\[
C_2H_2 + N \rightarrow CN + CH_2 \quad (2.1.1)
\]
\[
C + N_2 \rightarrow CN + N \quad (2.1.2)
\]

Other reactions involving atomic nitrogen and hydrocarbons could lead to the appearance of CN and HCN molecules in the plasma as well [86, 87]. It is commonly considered that CN and not HCN is responsible for the incorporation of nitrogen into diamond, even though both species may be presented in the plasma, however, the exact mechanism is not fully clear yet [85].
2.2. Microwave Plasma Enhanced Chemical Vapor Deposition (MPECVD) System

2.2.1 The Deposition Reactor of the MPECVD System Used for the Growth of UNCD Films

UNCD films deposition was carried out in the clean room of the Center for Nanoscale Materials (CNM) at Argonne National Laboratories (ANL) using a state-of-the-art 915 MHz microwave plasma CVD reactor from Lambda Technology. This system is custom built for depositing mainly UNCD materials, so a detailed description of the reactor is given in this section.

Figure 2.1.4 Cross-Sectional view of the reactor chamber of MPCVD. Figure has been provided by Lambda Technology: the equipment manual serial #2007-03 and doc. 17569 (http://www.microcure.com).
A cross-sectional view of the microwave plasma reactor is shown in Figure 2.1.4. The cavity side wall (1) consists of a 17.8 cm inside diameter cylindrical brass tube. This brass tube is electrically connected to a water-cooled base plate assembly (2-7) and water-cooled sliding short (21) via finger stock (9); thus, the cylindrical volume is bounded by the sliding short. The side walls and the base plate form the cylindrical cavity applicator make up the electromagnetic excitation region. As selected, the electromagnetic resonance mode, TM_{012}, or TM_{013}, 915 MHz or 2.45 GHz (CW) microwave power respectively, is coupled into the cylindrical cavity applicator through a mechanically tunable coaxial excitation probe (11) located in the center of the sliding short. The sliding short can be moved up and down along the reactor axis to control the applicator height, \( L_s \), and the depth of coaxial excitation probe, \( L_p \), is also independently adjustable. Thus by changing the probe depth and the cavity height, the applicator can be excited and matched to the desirable electromagnetic resonance. The base plate assembly consists of a water-cooled and air-cooled base plate (2), an annular input gas feed plate (3), a gas distribution plate (4), a 12.5 cm quartz dome (5), the water cooling assembly in the holder-baseplate (6), and the substrate itself (7). The base plate, the annular gas plate, and the gas distribution plate introduce a uniform ring of input gas into the quartz dome volume. A hemispherical-shaped discharge (12) is positioned over and is adjusted to be in direct contact with the top of the substrate surface by varying \( L_p \) and \( L_s \) to excite and match the TM_{013} plasma-loaded resonant mode. The discharge can be viewed and the substrate temperature measured by an optical pyrometer through the screened side window.
The gas flow pattern regulator (15), which is placed on the top of the water cooling stage, is an electrically conducting disk with a ring of holes circumferentially surrounding the substrate. A quartz tube (17) is placed around the water stage bottom plate to regulate the flow of gas into the plasma through the flow pattern regulator and finally out of the reactor. The substrate position is varied up or down by inserting different metal spacers (16) and the substrate temperature is independently controlled by placing graphite and boron nitride disks (22) in between the water cooling stage and the substrate.

2.2.2 Variable Space Model of MPECVD System

The experimental output of a CVD reactor is a function of many variables [88]. In a reproducible and understood deposition experiment each of the reactor variables are known and controlled. The reactor variable space model shown in Figure 2.2.1 summarizes these experimental variables into three groups: (i) input variables, $I$, (ii) internal variables, $X$, and (iii) output variables, $O$. The variables that can be controlled by the experimental operator are known as the input variables. In addition, these variables can be influenced by the reactor geometry. The input variables are divided into three sub-groups: (a) the reactor geometry variables, $I_1$, such as the substrate holder setups, reactor size and geometry, etc., (b) deposition process variables, $I_2$, such as substrate material, seeding procedure, deposition time, etc., and
(c) controllable input variables, \( I_3 \), i.e., deposition pressure, gas flow rate, substrate temperature, etc. The internal variables describe the internal reactor states including plasma density, electromagnetic field strength, and gas temperature. The desired process outputs are known as the output variables.

![Diagram of variable space](image)

**Figure 2.2.1** Model of the Variable Space of the reactor in MPCVD system, see ref. [88].

Table 2.2.1 organizes the experimental variables as defined in the reactor variable space model in a subset of experimental deposition variables, which is normally chosen for depositing UNCD films. The Reactor geometry variables, \( I_1 \), are fixed by the reactor designer. However, the substrate holder setups were allowed to be independently modified so that substrate temperature can be varied. Deposition time, \( t \), was varied from 2 to 3.5 h. The controllable input variables, \( I_3 \), are incident
microwave power $P_{\text{ine}}$, pressure $p$, substrate temperature $T_s$, total gas flow rate $f_t$, and gas concentrations $c$ shown in percentage of standard cubic per minute as Ar/CH$_4$/H$_2$/N$_2$ (% sccm). The measured internal variables $X$ were defined as the plasma volume, $V_d$, the power absorbed by the reactor, $P_t$, and the absorbed power density that is given by $(P) = P_t / V_d$. The power absorbed $P_t$ is known as the difference between the incident microwave power $P_{\text{ine}}$ and the reflected power $P_{\text{ref}}$, i.e. $P_t = P_{\text{ine}} - P_{\text{ref}}$. The reactor output variables, $O$, are the film uniformity over the 6 inch diameter substrate, film thickness estimated by the film growth rate, film morphology and structural quality. To check the output variables, Raman spectroscopy, scanning electron microscopy (SEM), and atomic force microscopy (AFM) were systematically used to insure the presence and qualities of diamond layer in all deposited UNCD film.
Table 2.2.1 Descriptions of deposition process variables. Table’s idea and parameters were taking from ref. [88]

<table>
<thead>
<tr>
<th>Input Variables I</th>
<th>Deposition Process I₂</th>
<th>Controllable Input I₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor Geometry I₁</td>
<td>(I) Substrate material and size. (II) Substrate seeding procedure, fixed. Seeding was carried out by immersing the substrate in slurry of diamond powder mixed in acetone and agitated using ultrasonic vibration. (III) Deposition time, variable: t = 2-3.5 h.</td>
<td>(I) Gases concentrations, variable: Ar/CH₄/H₂/N₂. (II) Incident microwave power, variable: P_{inc}=2.1-2.3 kw (III) Deposition pressure, variable: p = 80-120 mbr. (IV) Substrate temperature, fixed: Tₛ = 750°C (V) Total flow rate, variable: fᵢ = 200 – 410 sccm</td>
</tr>
<tr>
<td>(I) Reactor configuration, variable: substrate holder setups. (II) End-feed excitation, fixed. (III) Electromagnetic mode and cavity tuning, fixed at TM₀₁₂. (IV) Dome geometry, fixed.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Internal Variables X</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I) Plasma volume, Vₐ, approximately constant at 144 cm³. (II) Absorbed microwave power, variable: Pᵢ = 2.1-2.3 kw. (III) Absorbed power density, variable: &lt;P&gt; = Pᵢ Vₐ.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Output Variables O</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I) Film growth rate, calculated from total weight gain (II) Film uniformity, inspected by AFM and SEM (III) Film morphology, inspected by SEM and AFM (IV) Film structural quality, inspected by Raman spectroscopy</td>
</tr>
</tbody>
</table>

2.3 Deposition of UNCD Films for this Study

2.3.1 Seeding Procedures

The initial stage of diamond thin films growth begins with the creation of diamond nuclei on the deposition surface. This process is called seeding and it is a key for producing high quality, continuous and smooth diamond films. Although this
process has been extensively studied and established [89-90], it is as yet poorly understood. Seeding processes are usually used in order to enhance the nucleation of UNCD films. There are two exclusive routes by which nucleation can take place: heterogeneous or homogenous. Homogenous nucleation occurs when the substrate and the growing film are the same material, i.e. diamond is grown on diamond. Heterogeneous nucleation occurs when the substrate and the growing films are comprised of different materials such as diamond on silicon. In this work, diamond films on Si and on quartz have been studied.

The most commonly used technique for enhancing the diamond nucleation density is mechanical abrasion of the substrate surface by diamond powder. Abrasion can be accomplished either mechanically or by immersing the substrate in slurry of diamond powder mixed in acetone and agitated using ultrasonic vibration. This technique has been found to be effective in raising the nucleation density to $10^7 - 10^{11}\text{cm}^{-2}$ [90].

Direct seeding occurs when diamond powder or other carbonaceous residues left on the surface act as nucleation sites. Although this has been found to increase the nucleation density, the fact is that enhanced nucleation also proceeds if one uses non-diamond materials on the surface as well. The degree to which both effects contribute to the overall nucleation enhancement is currently unclear. To test the above mentioned hypothesis, samples were also deposited on a tungsten (W) interlayer (between 10-20 nm in thickness) as a nucleation-enhancement layer on Si. The W layer was deposited using a magnetron sputtering system that is available at the CNM
at ANL. Sputtering is carried out using a RF power of 150 watts and an Ar flow of 30 sccm at room temperature. Metal interlayers have been used to promote adhesions of diamond thin film [90, 91].

2.3.2 Experimental Procedures and Growth Conditions of UNCD Films

After manually loading the substrate onto the substrate holder, the reactor was first pumped to 5 m Torr by a mechanical pump. Source gases with appropriate chemistry and flow rate were introduced into the reactor and the pressure was gradually increased by controlling a throttle valve. When the pressure reached approximately 15 mbr, microwave power of 800 W ignited the discharge. Then desired processing pressures (80-120) mbr were achieved by controlling the throttle valve. Absorbed microwave power was adjusted between 2.1-2.3 kW in order to cover the 6 inch diameter substrate with the plasma discharge. The substrate temperature was independently controlled and kept around 700°C. Argon, methane, hydrogen, and nitrogen were used as source gases and their flow rates were controlled by a multiple channel flow controller.

During an actual deposition experiment, all the experimental input variables such as flow rate, running time, microwave power, etc. were monitored and recorded versus running time by computer software. Film growth rate, $W$, in (mg/h) was determined by measuring the total weight gain of the substrate, $W_t$, during the
experiments and divided by the deposition time, $t$. The average linear growth rate ($\mu$m/h), $d$, was determined from $d = (W/g) / (A \cdot D)$, where $A$ is the deposition area, $D$ is the diamond density, and $g$ is gravitational acceleration. Film uniformity, morphology, and qualities were determined by several characterization techniques such as SEM, AFM, and Raman spectroscopy which will be shown later. Uniformity is defined by the difference between the maximum and minimum thickness measurements divided by the average thickness measurement over the 6 inch diameter substrate. Table 2.3.1 shows the deposition conditions of the eight samples investigated for this research along with their assigned specified names appearing hereafter.

Table 2.3.1 Deposition conditions of the UNCD samples on different substrates deposited with different 14N2 and 15N2 concentrations

<table>
<thead>
<tr>
<th>Thin Film ID</th>
<th>Deposition Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gases flow rates Ar/CH4/H2/N2 (sccm)</td>
</tr>
<tr>
<td>15N-UNCD/Si</td>
<td>160/3/0/40</td>
</tr>
<tr>
<td>15N-UNCD/Cr/Si</td>
<td>160/3/0/40</td>
</tr>
<tr>
<td>UNCD/W/Si (0% N2)</td>
<td>400/1.5/8/0</td>
</tr>
<tr>
<td>14N-UNCD/W/Si (10% N2)</td>
<td>160/3/0/20</td>
</tr>
<tr>
<td>14N-UNCD/W/Si (20% N2)</td>
<td>160/3/0/40</td>
</tr>
<tr>
<td>UNCD/SiO2 (0% N2)</td>
<td>400/1.5/8/0</td>
</tr>
<tr>
<td>14N-UNCD/SiO2 (10% N2)</td>
<td>160/3/0/20</td>
</tr>
<tr>
<td>14N-UNCD/SiO2 (20% N2)</td>
<td>160/3/0/40</td>
</tr>
</tbody>
</table>
CHAPTER 3

BASIC CHARACTERIZATIONS OF UNCD FILMS

The synthesis of UNCD films is a function of many parameters, as emphasized in the previous chapter. Therefore, it is important to confirm the identity and qualities of the deposited UNCD films. Several known and well-established characterization techniques such as Raman spectroscopy, scanning electron microscopy, and atomic force microscopy are carried out. These basic characterizations are used to determine the bonding structure, morphology, and topography of the deposited UNCD films.

3.1 Raman Spectroscopy of UNCD Films

3.1.1 General Overview of Raman Spectroscopy on Diamond Films

Raman scattering is the inelastic scattering of incident photons by matter [92]. As shown in Fig 3.1.1, when light scatters off of a solid material, the photons may either lose part of their energy by exciting phonons in lattice vibrations (Stokes), or they may gain energy by absorbing phonons (anti-Stokes). The scattered photon is shifted in wavelength by the phonon energy (called the Raman shift). Typically, the
Stokes signal is more intense at room temperatures, and so is generally examined [93]. In classical theory, the Raman shift could be explained by assuming that the electric field of an electromagnetic wave (laser beam) that interacts with a material will induce an electrical dipole moment given by the following equation:

\[
\vec{P} = \alpha_0 E_0 \cos(2\pi \nu_0 t) + \frac{1}{2} \left( \frac{\partial \alpha}{\partial q} \right)_0 q_0 E_0 \left[ \cos(2\pi (\nu_0 - \nu_m) t) + \cos(2\pi (\nu_0 + \nu_m) t) \right].
\]  

(3.1.1)

where \(E_0\) is the vibrational amplitude and \(\nu_0\) is the frequency of the laser. Here \(\alpha_0\) is the polarizability constant, \(\nu_m\) is the molecule vibration amplitude, and \(q_0\) is related to the nuclear displacement due to the electrical moment \(\vec{P}\). In equation 3.1.1, the first term represents Rayleigh scattering while the second one corresponds to the Stokes (\(\nu_0 - \nu_m\)) and anti-Stokes (\(\nu_0 + \nu_m\)) Raman scattering. It is obvious that if \(\left( \frac{\partial \alpha}{\partial q} \right)_0 \) is zero, then the vibration induced is not Raman active.

\[\]
The inelastically or Raman-scattered photons carry information that is the signature of the bonding characteristics of the material. Raman spectroscopy is a widespread tool used for fast and non-destructive characterization of materials and is used frequently to evaluate carbon thin films. Raman spectroscopy and its related applications encompass rich theory originating from classical and quantum treatments of the light interaction with the matter [94, 95].

RS is widely used to obtain the quality of diamond films, i.e., whether or not the diamond films possess a significant amount of sp$^2$ bonded carbon. However, difficulty arises in interpreting Raman spectra for films that are composed of a mixture of sp$^2$ and sp$^3$ bonded carbon [96]. In particular, the scattering efficiency of graphite (sp$^2$ bonded carbon) is approximately 50 times higher than that of sp$^3$ bonded diamond [97], and therefore RS does not yield a quantitative sp$^3$/sp$^2$ ratio. However, this difference in scattering efficiencies has the benefit that Raman spectroscopy is ideal for detecting sp$^2$ carbon in diamond films [98]. The choice of the wavelength of the laser excitation is very important since the intensities and peak positions of some nanodiamond carbon is dependent on the wavelength used [99]. The Raman cross section of non-diamond carbon relative to diamond decreases with decreasing wavelengths of the excitation source [100]. Two possible explanations have been suggested for this effect. The first is that a resonance effect occurs for the non-diamond carbon at higher wavelengths. In this case, the laser excitation wavelength is close to the energy of electron transitions, causing an increase in the signal intensity. The second theory is ascribed to an absorption effect, where graphite and other non-
diamond carbon have a different absorption depth than that of diamond [101, 102]. As the excitation wavelength is changed, the relative interaction volume is changed, causing a change in signal intensity. In addition to lowering the cross section of the non-diamond carbon signal, a lower excitation (UV Raman) also eliminates the so-called D-band of graphitic carbon, which lies close to the diamond peak [100]. This enables the unambiguous examination of the quality of the diamond. Furthermore, the background fluorescence (which occurs when the excited state molecule or electron decays to the lowest level by non-radiation transitions and then emits radiation) is suppressed at shorter excitation wavelengths [95]. These effects make UV Raman the method of choice for monitoring and characterizing both high- and low-quality diamond films [100].

3.1.2 Raman Spectroscopy of UNCD Films

All samples deposited for this study have been characterized by Raman spectroscopy to insure their qualities as UNCD films. Raman data were collected using Renishaw’s Via Reflex Raman microscope located in the CNM at Argonne National Laboratory. Different laser sources supply the tool for suitable wavelengths selection. All spectra and optics specifications were handled through Wire 2 software.
Several plots of the Raman spectra of UNCD films deposited with varying N$_2$ content in their growth plasma were obtained at visible and ultraviolet wavelengths. Figure 3.1.2 shows Raman spectra taken with (a) 633 nm and (b) 325 nm lasers. In the visible Raman excitations (top figure) four dominant peaks are seen: the substrate signal silicon peak which usually appear around 520 cm$^{-1}$, the diamond peak at 1333 cm$^{-1}$, which is the signature of sp$^3$-bonds in the UNCD layer, the D-band peak around 1340 cm$^{-1}$, and the G-band peak that takes place around 1540-1590 cm$^{-1}$.

Both D-band and G-band peaks are due to the sp$^2$ bonds associated to the amorphous carbon portion presented in the film, particularly at the grain boundaries. G-modes in Raman spectra are well known for disordered carbon films while D-modes originate due to the graphite-like structure. Both modes arise from the in-plane stretching modes of the sp$^2$-bonded carbon at the grain boundaries (GBs) of UNCD [103]. It is important to notice that diamond peaks are on the shoulders of D peaks, which are broad and are more enhanced due to the visible Raman excitations [97]. However, in the UV Raman spectra shown in Figure 3.1.2 (b), diamond peaks appear more enhanced due to the dispersions of D-peaks at higher excitations of energy of the Raman laser. This makes UV Raman a more suitable tool for looking at sp$^3$ bonds in the nanodiamond films. In both UV and visible Raman, distinct and sometimes strong peaks appear around 1140 cm$^{-1}$ and 1480 cm$^{-1}$ respectively. The origins of these peaks were a topic of debate among researchers. Because of their usual appearance in Raman spectra of UNCD, many researchers assigned them as signatures of the UNCD layer in the film, specifically the peaks at 1140 cm$^{-1}$. However, one recent
study that looked deeply into the topic concluded that Raman peaks in the nanodiamond film that appear around 1140 cm\(^{-1}\) and 1480 cm\(^{-1}\) should be assigned to the modes arising from trans-(CH)\(_x\) [104]. It is well known that UNCD films have some hydrogen content in their textures, as will be shown later in the structural studies of this work. Thus, peaks present around 1140 cm\(^{-1}\) in Figure 3.1.2 (a) and (b) were assigned to the trans-(CH)\(_x\) modes due to the incorporation of hydrogen atoms in the UNCD films.

\[\text{Figure 3.1.2 Raman spectra for UNCD films- (a) visible laser, (b) UV laser.}\]
To investigate the effects of nitrogen incorporation in the UNCD films, it is more convenient to look at several parameters, such as the intensity ratio of D to G peaks (\(I_D/I_G\)) in visible Raman. Moreover, position, dispersion, and width of Raman peaks (specifically G-peaks) provide valuable information on structural changes in UNCD films when incorporated with different contents of nitrogen.

Figure 3.1.3 (I) gives the \(I_D/I_G\) ratios as a function of N content incorporated in the UNCD films. Increase of the \(I_D/I_G\) ratio means an increase of the graphite-like structure in the grain boundary. The theoretical model of the disorder carbon materials [105] suggested the increase of the \(I_D/I_G\) ratio promotes more clustering of sp\(^2\) configured carbon into aromatic rings (graphite-like structure). To confirm the \(I_D/I_G\) result, Figure 3.1.3 (II) shows the G-peak position versus the \(I_D/I_G\) ratio. Variations of the G-peak position with respect to nitrogen content are considered an important parameter that is related to the bonding strength [106]. From both visible and UV Raman spectra of UNCDs film, G-peaks positions shifted upward with the higher N content incorporated in the UNCD films. This blue shift-like of Raman G-peak positions with N content incorporated in the UNCD is attributed to the increasing of sp\(^2\) clustering in the film, just as the \(I_D/I_G\) data of these films suggested.
I.

![Graph I](image)

**ID/IG**

UNCD/W/Si films

**N₂ content in growth plasma (%)**

II.

![Graph II](image)

**G-position (cm⁻¹)**

**ID / IG**

UNCD/W/Si films

**Figure 3.1.3** Raman spectra for UNCD films: (I) $I_D/I_G$ ratio, (II) $I_D/I_G$ vs. G-positions.
The $I_D/I_G$ ratio behavior of the UNCD films shown in Figure 3.1.3 suggests an increase of the grain boundaries sizes of the film as more N content is incorporated. Most of the sp$^3$-bonded carbon is in the nanosized grain composed of 3-5 nm randomly oriented diamond crystallite separated by ~ 0.2 nm grain boundaries [107]. Larger sizes of grains and grain boundaries in UNCD films have been seen due to the nitrogen addition into growth plasma [108]. The $I_D/I_G$ ratios behavior of the UNCD films with varying N content can be further confirmed by measuring these ratios against the width of their respective G peaks in Raman spectra. In Raman spectra, widths of G peaks (FWHM-G) are related to the bond length and angle distortion [109-110]. In this study, FWHM-G as a width measurement of the G peaks width was obtained by the use of Gaussian fits. Gaussian line shape fits are used widely in disorder materials due to random distributions of phonon life times [105] [110][111]. Figure 3.1.4 shows the G-peak width is gradually decreasing as N content and $I_D/I_G$ ratios are increasing in the UNCD films. This indicates an increase of the more ordered phase in the film which could explain the larger sizes of graphitic clusters and diamond grains with an addition of N content to the plasma mixtures of the film.
Figure 3.1.4 Raman spectra for UNCD films: FWHM G-peaks vs. $I_D/I_G$ ratio.

One more parameter worth of mentioning is the dispersion of G peaks (G-disp.) due to a change of the excitation laser wavelength. This parameter is related to the shape and size (topology) of the sp$^2$ clusters [109]. In amorphous carbon materials, the G band tends to change position and intensity as the photon energy of the excitation laser changes in wave number [112]. This originated from the selection rule of the wide band gap states ($\pi$- states) resonances in the highly vibrated sp$^2$
groups [105]. Results in Figure 3.1.5 show less dispersion of G peaks for the films deposited with higher N content. That means UNCD films deposited with more N gas in their plasma will have more order phase in their nanostructures. Thus larger graphite-like structures (sp² clusters) will be more prominent in films textures. Similar conclusions have been reported for nitride amorphous carbon materials [113].

![Graph showing G peak dispersions of UNCD films](image)

**Figure 3.1.5** G peak dispersions of UNCD films deposited with varying N content along with amorphous carbon and nanocrystalline graphite films taken from ref. [113] for comparative analysis.
3.2 Scanning Electron Microscopy (SEM) of UNCD Films

Scanning Electron Microscopy (SEM) is a powerful tool that uses electrons instead of light to form images. The high resolution (~50 nm), high magnification (50-200,000), and high depth of field makes SEM one of the most widely used techniques to study surface morphology of materials. In a typical SEM machine, an electron beam travels through electromagnetic fields and lenses, which focus the beam down toward the sample. Secondary electrons emitted by the sample surface are used then for the construction of the images. Thus, samples under study should be conductive or weakly conductive. To overcome this limitation, the sample is coated with a thin layer of silver or gold to prevent charging effects [114][115].

For the UNCD samples prepared for this study, SEM data were taken by FEI Nova 600 NanoLab instruments located in the clean room of the CNM at Argonne National Laboratory. The tool is a dual-beam instrument that integrates ion and electron beams for focused-ion-beam (FIB) and scanning electron microscope (SEM) functionality in one machine. The convergence of the SEM and FIB at short working distance allows precision milling, etching, deposition, and analysis at high resolution.

SEM analyses of three UNCD films deposited respectively with 0%, 10%, and 20% of N2 gas leaked into their growth plasmas will be reported here. Images of these UNCD samples are shown in Figure 3.2.1. SEM images of the films show granular structure separated by highly energetic twisted GBs [71]. These grains are grouped in clusters. Moreover, it is clear that these films are continuous and uniform on the
surface. Multiple images on the surface of UNCD films have shown the solidity of the aforementioned qualities. A recent theoretical study established a 1-D Monte Carlo model of the growth mechanism of the CVD diamond suggesting that UNCD’s complex grain structures, crystallites number, their average sizes, and surface homogeneity are functions of renucleation probability [116]. From experimental experiences, taking clear images for N-incorporated UNCD films using regular SEM equipment seems to be difficult. One reason for such difficulty is the increase in electron scattering activities during the scanning of the films surfaces. This will lead to the assumption that the grain and grain boundary sizes increase as nitrogen is added in the growth plasma for the material preparation. Such assumptions can be explained in terms of the theoretical model developed for nitrogen incorporation in the UNCD film. According to that model, a CN molecule bonds with the growing diamond surface so that nitrogen remains on the surface. When the growing surfaces of diamond meet, a grain boundary is formed with much higher concentrations of nitrogen than that of bulk diamond crystals. Additionally, this model predicts that nitrogen on diamond surfaces does not provide a stable nucleation site; hence, CN acts to suppress the renucleation rate of diamond grown via a C\textsubscript{2} mechanism. According to the model, the grain boundaries could be larger because of nitrogen segregation at the grain boundaries. Such a mechanism has not been conclusively proven yet [117-119]. A close look at the images shown in Figure 3.2.1 reveals some changes in the UNCDs surface structures as more N\textsubscript{2} gas is used in the growth plasmas. Apparently, the grains network clusters in more spherical-like shapes (3-D
spheres) as the N\textsubscript{2} content increased in the film plasma. That suggests changes in grains and GBs sizes and shapes which is in direct correlation with the Raman results on the shown UNCD samples.

![SEM micro-images of UNCD/W/Si films deposited with (I) 0% N\textsubscript{2}, (II) 10% N\textsubscript{2}, and (III) 20% N\textsubscript{2} in the plasmas mixtures.](image)

**Figure 3.2.1** SEM micro-images of UNCD/W/Si films deposited with (I) 0% N\textsubscript{2}, (II) 10% N\textsubscript{2}, and (III) 20% N\textsubscript{2} in the plasmas mixtures.
The SEM technique can also be used to take a cross-sectional image of the film. However, sample preparation is required to have a cross-sectional view. The SEM cross-sectional view gives detailed information about internal structures and thicknesses of different layers in films materials. Figure 3.2.2 shows a cross-sectional view of structural forms of the UNCD film deposited with 20% N₂ in its growth plasma. The UNCD layer thickness is measured to be 540 nm. A close examination showed the nature of the film grains which are grown in the outward direction from the nucleation sites on the substrate surface. Measuring the films’ thickness by SEM techniques proved reliable, however preparing the sample to such measurement could be destructive. Other techniques to measure the thickness of the UNCD films deposited for this study are shown in later chapters of this work.

Figure 3.2.2 Cross section image of UNCD film.
3.3. Atomic Force Microscopy of UNCD Films

The atomic force microscopy (AFM) technique invented in 1986 is a method to measure surface topography at the nanometer scale [120]. In the AFM tool, a small (few $\mu$m in height) cantilever with a tip of a few nanometers is attached to a precision positioning device at one end for scanning. AFM resolution is limited by the end radius of the cantilever tip. As the AFM tip scans over a surface, intermolecular forces between the cantilever tip and the samples surface attract or repel the tip, causing it to deflect from its original position. Then, a laser-based sensor is used to detect the vertical deflection of the cantilever, thus detecting the topography of the surface. A feedback system is used to move either the tip or the sample with precise positioning using a piezo-electric device to maintain a constant force between the tip and the surface (see Figure 3.3.1). The AFM can be used either in contact mode or noncontact mode. In both modes, surface topography characteristics were obtained by measuring the deflection of the cantilever [120-122].
For the UNCD films used in this study, the AFM analysis was carried out in the clean room of CNM at ANL using a scanning probe microscope (PSIA XE-HDD). XE-HDD was designed for the sole purpose of thin film materials and it excels in obtaining superior images of such materials. Figure 3.3.2 presents the AFM images taken for three UNCD films deposited respectively with (I) 0%, (II) 10%, and (III) 20% of N₂ concentrations in their synthesis plasma. To analyze these AFM images, Gwyddion software was used. This software is an open source of modular program designed for visualization and data analysis for scanning probe microscopy [123].
Figure 3.3.2 AFM images of three UNCD samples deposited with varying N$_2$ content in their growth plasma (I) 0% N$_2$, (II) 10% N$_2$, and (III) 20% N$_2$. Inset figures are zoomed sections of the AFM images to show spatial distribution of grain clusters in each sample.
When analyzing AFM images of UNCD films, it is possible to correlate changes in the films surfaces as functions of N content incorporated in the films. Results of the root mean square (RMS) surface roughness analysis are shown in Figure 3.3.3. The RMS surface roughness data of each sample were obtained from scanning areas of 0.25 μm², 1 μm², and 4 μm² respectively. The RMS roughness is clearly increasing as N₂ is added to the film plasma. Moreover, there is more variation of the surface roughness in the UNCD film deposited with 20% of N₂ as the scanning area is increased, which indicates more variation in the film thickness. The RMS results suggest changes in the surface nanostructures of UNCD film, as more N₂ gas is used in the deposition plasma of the film.

![Figure 3.3.3 RMS surface roughness of UNCD films deposited with varying concentrations of N₂ in their growth plasma.](image)

**Figure 3.3.3** RMS surface roughness of UNCD films deposited with varying concentrations of N₂ in their growth plasma.
For further confirmation of the RMS results, a high resolution scan on each UNCD films, as shown in Figure 3.3.2 (insets in the lower-left corners), were obtained. These scans show spatial distributions of grain clusters and grain clusters boundaries for the UNCD samples. Results of the analysis of these AFM scans are listed in Table 3.3.1. Grains statistics in Table 3.3.1 show increasing trends of grains and grains boundaries sizes in UNCD films when deposited with more nitrogen gas diluted to their plasma. Increases in grain size will promote larger grains clusters in the films surface, which gives rise to larger surface roughness and thickness variations as seen in the UNCD film deposited with the highest percentage of N₂ gas. Moreover, measurements of grains clusters radial sizes in x- and y- directions, as presented in the last two rows of Table 3.3.1, indicate changes in the grains cluster shape as more N₂ gas is used for the film deposition. For UNCD films deposited in N₂ free plasma, grain clusters tend to have coin-like shapes (Δx ≈ Δy), while UNCD films deposited with a plasma mixed with a high concentration of N₂ gas has grain clusters in more uneven (Δx ≠ Δy) ball-like shapes. The AFM results agree with the conclusions drawn from Raman and SEM studies on the same UNCD films. A high resolution transmission microscopy (HRTEM) study conducted by Bhattacharyya et al. (2001) on nitrogen-incorporated UNCD films concluded that higher N₂ gas in the growth plasma of the UNCD film will promote increases in the sizes of grains and grain boundaries of the film [108].
Although N incorporation into UNCD films increase surface roughness of the film, its RMS roughness is still in the submicron level (nano-level), which is very small as compared to sub-microcrystalline diamond and microcrystalline diamond [124], therefore, N-incorporated UNCD film still retains the smoothness and surface quality, which is a unique quality attributed to UNCD films.

<table>
<thead>
<tr>
<th>Grains Statistics</th>
<th>UNCD/W/Si films deposited with different nitrogen content</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0% N₂</td>
</tr>
<tr>
<td>Average grain size, z_{avg} (nm)</td>
<td>3.2</td>
</tr>
<tr>
<td>Maximum size of grains, z_{max} (nm)</td>
<td>5.4</td>
</tr>
<tr>
<td>Grain boundary maximum size, b_{max} (nm)</td>
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</tr>
<tr>
<td>Grain Cluster Equivalent disk radius, (r_{eq})(nm)</td>
<td>21.67</td>
</tr>
<tr>
<td>Grain Cluster zero basis volume, V₀ (m³)</td>
<td>4.8 X 10^{-24}</td>
</tr>
<tr>
<td>Grain Cluster maximum bounding size D_{max}(nm)</td>
<td>50.54</td>
</tr>
<tr>
<td>Grain Cluster radial size, Δx (nm)</td>
<td>24</td>
</tr>
<tr>
<td>Grain Cluster radial size, Δy (nm)</td>
<td>18</td>
</tr>
</tbody>
</table>
CHAPTER 4

STRUCTURAL CHARACTERIZATIONS OF UNCD FILMS
USING ION BEAM ANALYSIS (IBA)

4.1 Introduction to Ion Beam Analysis: Techniques and Instrumentations

Ion beam analysis (IBA) is an important set of modern analytical techniques involving the use of high energy ion beams, in the energy range of MeV, to probe composition and to obtain elemental depth profiles in the near-surface region of solids. All IBA methods are quantitative and allow the detection of elements in the sub-monolayer range. The depth resolution is typically in the range of a few nanometers to a few ten nanometers. Ion beam analysis (IBA) encompasses a number of techniques including Rutherford backscattering spectrometry (RBS), non-Rutherford backscattering spectrometry (NRBS), nuclear reaction analysis (NRA), elastic recoil detection Analysis (ERDA), particle induced X-ray emission (PIXE), and particle induced γ-ray emission (PIGE). Ion channeling is another IBA technique that utilizes fast ion beams to align accurately with major axes of a single crystal; the atoms off the lattice sites gives visible extra scattering that is the signature of the damage to the crystal.
The quantitative analysis of IBA spectra requires a use of models to simulate the experimental results. SIMNRA, data furnace, IBA and Rutherford manipulation programs (RUMP) are some of the software programs available for the analysis of RBS, ERDA, NRBS and NRA. To obtain a complete picture of the elemental compositions and trapped impurities in the UNCD films, RBS, NRBS, ERDA, NRA, and PIGE techniques were used in this project.

The Rutherford backscattering technique uses elastic collisions between a target and incident ions of energy $E_0$ to determine the target elements and their concentration in the material. The scattering geometry for RBS is shown in Figure 4.1.1 A surface barrier silicon detector placed at scattering angle $\theta$ will detect the scattered particle with energy $E_1$. Knowing the initial energy of the incident particle, $E_0$, one can determined the mass of the target atom by using the conservation of momentum.

The kinematic factor, $K$, is defined as the ratio between the scattered particle’s energy $E_1$ and the incident particle’s energy $E_0$. Using the conservation of momentum, $K$ can be calculated for a particular scattering angle $\theta$ using the masses of the incident ion and the target atom [125]

$$K = \left[ \frac{(M_2^2 - M_1^2 \sin^2 \theta)^{1/2} + M_1 \cos \theta}{M_1 + M_2} \right]^2$$

(4.1)
where $M_1$ and $M_2$ are the masses of the incident and target particles respectively. There is a limit to how well RBS can resolve two target atoms of similar mass. This is due to the limited energy resolution of silicon surface barrier detectors and the difference between the kinematic factors of the two atoms. The energy separation $\Delta E$ of the particles scattered by two different atoms of mass difference $\Delta M$ at a fixed $\theta$ is given by [126]:

$$\Delta E = E_0 \left( \frac{dK}{dM_2} \right) \Delta M$$  \hspace{1cm} (4.2)$$

where $dK/dM_2$ is the change in the kinematic factor due to the change in the target mass. Thus, the energy separation of two heavier atoms of mass difference $\Delta M$ will be larger using a He beam than a H beam due to the fact that changes in the kinematic factor for He is larger than for H. Since the detector has a minimum energy resolution, one can calculate the mass resolution, $\delta M$ by using equation (4.2), letting $\Delta E$ be equal to the minimum energy resolution $\delta E$ of the detector and solving for $\Delta M$.

RBS has good mass resolution for light elements, but poor mass resolution for heavy elements. For example, when He$^{++}$ strikes light elements such as C or O, a significant fraction of the projectile energy is transferred to the target atom and the energy recorded for that backscattering event is much lower than the energy of the beam. It is usually possible to resolve C from O, but difficult to resolve Hg from Au and Fe from Cr, even though all of these elements differ in mass by about 4 amu.
The RBS cross-section is a measure of the probability that an incident particle will strike a target particle and scatter into a detector placed at an angle $\theta$. It depends on both the scattering angle and the energy of the particle when it strikes the target. Assuming only the Coulomb interaction between the incident ion and the target particle and neglecting electron shielding, the cross-section can be described as [126]:

$$\sigma_R(E, \theta) = 4 \left( Z_1 Z_2 e^2 / 4E \right)^2 \left[ \left( M_2^2 - M_1^2 \sin^2 \theta \right)^{1/2} + M_2 \cos \theta \right]^{1/2} \left[ M_2 \sin^4 \theta (M_2^2 - M_1^2 \sin^2 \theta) \right]^{1/2}$$

(4.3)

$Z_1$ and $Z_2$ are the number of protons in the incident and target atoms respectively. $E$ is the energy of the incident ion and $e$ is the charge of an electron. If the target is thin, then $E$ can be taken to be $E_0$ and the energy loss of the incident ion in the solid can be neglected. This leads to another limitation of the RBS methods. It is more sensitive to heavy elements than for light elements, due to the larger scattering cross sections of the heavier elements. Therefore, RBS is particularly useful for obtaining concentration depth profiles for the heavier elements in the coating, but is somewhat limited in detecting the light elements such as C, O and N because of the quadratic dependence of the Rutherford cross section on the atomic number of the target atom.

In contrast, ERDA is a primarily IBA technique that is convenient for depth profiling of light elements in heavy matrix, such as H in Si films. A major difference between ERDA and RBS is that ERDA detects a recoil atom and not the scattering
projectiles. The ERDA geometry is shown in Figure 4.1.1 Analytical expression of ERDA is quite similar to that presented for RBS; however, the recoil angle is fundamentally different from the scattering angle of RBS. In the laboratory frame of reference, an incident ion projectile with energy $E_o$ just prior to colliding with a recoil atom of mass $M_2$ and charge $Z_2$ will drive the recoil atom to scatter at an angle of

$$\phi = \pi - (\alpha + \beta),$$

where $\alpha$ and $\beta$ are the incident and detection angles respectively from the surface normal to the sample. Using again the conservation of momentum, $K_{rec}$ (kinematic factor of recoil) can be calculated for a particular scattering angle $\phi$ using the masses of the incident ion and the target atom [126]:
Figure 4.1.1 Schematic configurations of back scattering and recoil scattering geometries in the lab frames. Corresponding back scattering and recoil scattering angles are $\theta$ and $\phi$. Incident and exit angles are respectively $\alpha$ and $\beta$ measured relative to the sample normal. For recoil scattering, the loss of incident beam energy ($E_0 - E'$) is due to the penetration into the sample for the distance ($x$). $E_3$ is the recoil atom energy after exiting the sample. The detected energy for the recoil atom $E_d$ is measured by a surface barrier detector after the recoil passed a stopper foil.

Nuclear reaction analysis (NRA) and non-Rutherford backscattering spectrometry (NRBS) are useful in the case of light element concentration.
determination. The phenomena of NRA and NRBS take place when the incident nuclei and target nuclei come so close to each other that nuclear forces start playing their role in the scattering process. In the first type, the target nucleus becomes unstable and by releasing a particle, that carries signature of the target nucleus, becomes a stable daughter nucleus. The spectral peaks resulting from this reaction typically rest on a very low or zero-background signal. In the second type, the nucleus of the target stays intact and scattering probability is enhanced. At certain energies, even resonant scattering can give rise to peaks that are signatures of the target nuclei. In both cases, scattering cross section is non-Rutherford. A limitation for NRA is that the reaction cross sections are generally known only for a few selected scattering angles, and thus may need to be measured using standard thin films of known stoichiometry [126].

NRA techniques are well-known for their superior sensitivity for specific isotopes. A special case of NRA techniques is particle induced γ-ray emission (PIGE), where a photon is detected. Nuclear reaction with γ-ray emission resembles secondary ion mass spectroscopy (SIMS), however, is nondestructive and quite rapid for multiple sample analysis [126]. Common PIGE reactions are \((p, \alpha\gamma)\) used for resonance nuclear reaction analysis (RNRA). RNRA with γ detection are particularly useful for depth profiling of light isotopes such as \(^{13}\)C, \(^{15}\)N, \(^{18}\)O, \(^{19}\)F, \(^{22}\)Ne, \(^{23}\)Na, \(^{24}\)Mg, \(^{27}\)Al, \(^{29}\)Si and \(^{30}\)Si [129-130]. RNRA theory is discussed in detailed fashion elsewhere [131-132].
Deposition of UNCD films with varying concentrations of N₂ in the growth plasma will affect the film properties. Hence, it would be important to determine the N content incorporated in the UNCD films along with the overall elemental concentration. NRA and RNRA will be exploited for N content determination due to their high sensitivities and better depth resolution [126]. For quantitative detections of nitrogen in nitride materials deposited with low concentrations of N₂, the most convenient resonant nuclear reaction is ¹⁵N(p, α₁γ)¹²C with resonance occurring at 897 keV with a narrow resonance width (Γ ~ 1.7 keV) and high cross section (σ ~ 800 mb) [133-135].

Geometry of RNRA with reaction ¹⁵N(p, α₁γ)¹²C is illustrated in Figure 4.1.2. When a proton with enough energy (higher than the threshold energy of ¹⁵N(p, α₁γ)¹²C reactions) hits a ¹⁵N atom in the sample matrix, the nitrogen atom will go through a nuclear reaction resulting in emission of a γ particle with a quantum well defined energy of 4.43 MeV. The resulting signal of such a reaction is proportional to the concentration of N atoms in the sample. The yield of γ rays as a function of bombardment energy can be quantitatively described as [136]

\[
Y(E_b) = \epsilon_{det} \Omega N_p \int_0^\infty \int_0^\infty C_N(x)g(E_b, E)f(E, E', x)\sigma(E')dE'dE dx \tag{4.5}
\]

where \(\epsilon_{det}, \Omega, N_p\) are respectively detector efficiency, detector solid angle, and number of the incident protons. \(C_N(x)\) is the concentration profile of nitrogen atoms as function of depth. \(\sigma(E')\) and \(f(E, E', x)\) are proton cross section at resonance energy and the probability of finding proton with energy \(E'\) at depth \(x\) respectively.

The factor \(g(E_b, E)\) is a measure of energy distributions of the incident protons. The
concentration of nitrogen $C_N(x)$ could be derived then from equation (4.5) by the use of the deconvolution inverse procedure (numerical method). The simplest approach to determine $C_N(x)$ for a material made of two compounds $A_m B_n$ is given by

$$C_N = \frac{C_{stn} Y \varepsilon_B}{Y_{stn} \varepsilon_{stn} + C_{stn} Y (\varepsilon_B - \varepsilon_A)}$$  \hspace{1cm} (4.6)

where $\varepsilon_A$, $\varepsilon_B$, and $\varepsilon_{stn}$ are the stopping power of pure A, pure B, and standard materials. Stopping powers are calculated using the Bragg rule [137-138]. The standard material is a sample with known nitrogen concentration $C_{stn}$. $Y$ and $Y_{stn}$ are yields of $\gamma$ rays radiated by the materials $A_m B_n$ and standard respectively.

Finally, the depth profile of nitrogen in the sample is determined by

$$x(E_i) = x(E_{i-1}) + \frac{2 (E_i - E_{i-1})}{\varepsilon(E_i) + \varepsilon(E_{i-1})}; \; i \geq 2$$ \hspace{1cm} (4.7)

Practically, the depth $x$ corresponds to successively increasing bombarding energies ($E_i$). Knowing the stopping power of the materials at the specific energy and assuming it is constant with small depth step, depth can be converted from (at/cm$^2$) units to (nm) if the material density is known.
Figure 4.1.2 Schematic of RNRA geometry of $^{15}$N incorporated sample. Protons from the beam with enough energy can trigger nuclear reactions in $^{15}$N atoms that result in $\gamma$ rays collected by the detector.

All IBA measurements carried out on the UNCD films of this study are performed at the Western Michigan University (WMU) accelerator laboratory. The accelerator lab in the department of physics at WMU houses a model EN 6 MV tandem Van de Graaff accelerator. It has two negative ion sources: an exchange source that makes negative ions from gases (duo-plasmatron), and a cesium sputter source that makes negative ions from solids (SNICS). In addition a state of art RF exchange ion source is available and it is used solely for the production of the He beam. With these ion sources and the accelerator, intense beams of protons and deuterons between 1 and 12 MeV can be produced, as well as a variety of heavier and isotopic ions including
helium, oxygen, fluorine, sulfur, nitrogen ($^{14}$N and $^{15}$N), copper etc. An experimental ultra high vacuum (UHV) stainless steel scattering chamber is permanently attached to the accelerator beamline. This chamber can be used for surface science experiments that require ultra high vacuum environments. An ion and turbo molecular pumps are installed on the chambers providing vacuums in the range of $10^{-8}$ – $10^{-9}$ Torr. Surface-barrier particle detectors mounted on shafts with a rotary feed through are used for RBS, ERDA, NRBS, and NRA measurements. This detector arrangement can provide variable scattering angles. For NRA measurements involving gamma emission a NaI scintillation detector is used. Following interactions of the ion beam with the target materials, the energies of emerging ions and particles are recorded using the laboratory data acquisition system which employs NIM and CAMAC electronics modules. Additional information about the WMU physics accelerator facilities can be found in the lab webpage [139]. Specifications of experimental setups for each IBA work done on the UNCD films will be given in the following sections of this chapter.

4.2 Rutherford Backscattering Spectrometry (RBS) of UNCD Films

4.2.1 Experimental Setup

RBS measurements on all UNCD films deposited for this study have been obtained by a He$^{++}$ beam with energy of 3.5 MeV and collecting the scattered projectiles with a standard Si surface barrier detector positioned at the scattering
angle $\theta = 160^0$. From the chamber geometry the incident angle $\alpha$ and exit angle $\beta$ were estimated to be $0^0$ and $20^0$ respectively. All samples were exposed to the same charge from the bombarding beam (50 $\mu$C) for consistency. The Si detector was calibrated using standard techniques and the spectroscopy amplifier gain was set at constant values for all runs.

4.2.2 Results and Discussion

For meaningful Interpretation of IBA experimental data, SIMNRA and RUMP programs are used [140]. Using real parameters such as the solid angle of the detector, scattering angle, and the incident and exit angles of projectiles along with the predetermined parameters of the ion beam energy, allow for the data simulation. These simulations will serve as quantitative methods to understand RBS spectra of the materials under investigations. Figures 4.2.1: (a), (b), and (C) present RBS results of UNCD/W/Si Films deposited with varying N$_2$ gas in their plasmas. Distinct features seen in RBS spectra of all UNCD films are the carbon peak that appears around channel 214 sitting on the Si substrate background. A peak of the W layer is around channel 787. Integrations of area under peaks reveal atomic concentrations of the respective elements that are usually obtained by simulating the spectra with SIMNRA. The depth scale ($10^{15}$ atoms/cm$^2$) is characteristic of the RBS measurement, which only determines the number of target atoms per cm$^2$ visible to
the analysis beam. If the sample density is known, this scale is readily converted to a linear depth scale. Otherwise, knowledge of elemental stopping cross sections of the projectile ions can be used to estimate the layer thicknesses of the film structure [141]. Moreover, the peak shapes and edges are related to layer orientation and interface mixing in the film structures. Therefore, RBS results could be utilized to obtain valuable information about the interface mixing between the different layers of the sample. The results of the IBA analysis obtained for the UNCD films are listed in Table 4.2.1. Our results show that the thicknesses of UNCD and W layers for each sample have 3% deviations when compared to thicknesses obtained by Reflectometry Spectroscopy (RES) for the same sample (Chapter 5). For film material thickness measurements, there are several techniques such as TEM, SEM, RES, SIMS, XPS, and AES [142]. However, each method has its strength and limitations. RBS is considered an accurate method and it is a nondestructive technique. Moreover, it has depth resolution up to 5 nm [143]. High depth resolution RBS is usually achieved by helium ion beams and by adopting special geometry for the sample and detector.

From Table 4.2.1, it could be seen that there is intermixing across the UNCD film layer structures. Although it is a very small atomic percentage, W atoms apparently have reached well into the UNCD layer of the film. Thickness of interface regions and the percentage of the atomic intermixing in the UNCD film structures can be determined by simulating the RBS date, which is strength of the technique.
Figure 4.2.1 (a) RBS result of UNCD films/W/Si deposited with 20% of N\textsubscript{2} gas in the growth plasma.
Figure 4.2.1 (b) RBS result of UNCD films/W/Si deposited with 10% of N\(_2\) gas in the growth plasma.
Figure 4.2.1 (c) RBS result of UNCD films/W/Si deposited with 0% of N₂ gas in the growth plasma.
Table 4.2.1 Summary of RBS results on UNCD/W/Si films deposited with varying percentages of N2 concentrations

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elemental Concentration (at. %)</th>
<th>UNCD Thickness $d$</th>
<th>W Thickness</th>
<th>UNCD/W interface Thickness</th>
<th>W/Si Interface Thickness</th>
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<tr>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
<td>at./cm$^2$ (10$^{15}$)</td>
<td>(nm)</td>
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<td>NA</td>
<td>1900</td>
<td>149.7</td>
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</tbody>
</table>

As part of the preparations for the PIGE studies on N content determination, UNCD films were deposited with 20% of isotopic $^{15}$N$_2$ gas in the growth plasma. RBS spectra of $^{15}$N-UNCD/Si, $^{15}$N-UNCD/Cr/Si, and standard (Si$_3$N$_4$) samples were obtained before the PIGE measurements. Figures 4.2.2: (I), (II), and (III) show these RBS spectra for the $^{15}$N-UNCD films and the standard nitride film. The RBS spectrum of Si$_3$N$_4$ film was simulated with 42.8 at % Si and 57.1 at% N to confirm the stoichiometry of silicon nitrite. RBS results of $^{15}$N-UNCD films along with the amount of N content in the standard silicon nitrite film was used to characterize and
understand PIGE spectra obtained for the $^{15}$N-UNCD films as will be shown later in this work. Table 4.2.2 shows a collection of the RBS results obtained for the two $^{15}$N-UNCD samples and the Si$_3$N$_4$ film.

![RBS spectrum](image)

**Figure 4.2.2 (I)** RBS result of $^{15}$N-UNCD/Si/Cr film deposited with 20% of isotope $^{15}$N$_2$ gas in the growth plasma.
**Figure 4.2.2 (II)** RBS result of $^{15}$N-UNCD/Si film deposited with 20% of isotope $^{15}$N$_2$ gas in the growth plasma.
RBS_3.5 MeV He$^{++}$ with scattering angle $\theta = 160^0$

Figure 4.2.2 (III) RBS result of the standard Si$_3$N$_4$ film.
Table 4.2.2 Summary of RBS results on the \(^{15}\text{N}\)-UNCD/W/Si films deposited with 20% of \(^{15}\text{N}_2\) concentrations and the standard film Si\(_3\)N\(_4\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elemental Concentration (at. %)</th>
<th>UNCD Thickness (d)</th>
<th>UNCD/Si interface Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C H N</td>
<td>at./cm(^2) ((10^{15}))</td>
<td>(nm)</td>
</tr>
<tr>
<td>(^{15}\text{N})-UNCD/Si (20% N(_2))</td>
<td>95 8 NA</td>
<td>3480</td>
<td>302.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elemental Concentration (at. %)</th>
<th>Si</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{15}\text{N}_3)N(_4)/Si (standard)</td>
<td>42.8</td>
<td>57.1</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elemental Concentration (at. %)</th>
<th>UNCD Thickness (d)</th>
<th>Cr Thickness</th>
<th>UNCD/Cr Interface Thickness</th>
<th>Cr/Si Interface Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C H N</td>
<td>at./cm(^2) ((10^{15}))</td>
<td>(nm)</td>
<td>at./cm(^2) ((10^{15}))</td>
<td>Cr at.%</td>
</tr>
<tr>
<td>(^{15}\text{N})-UNCD/Cr/Si (20% N(_2))</td>
<td>90 9 NA</td>
<td>5500</td>
<td>478.3</td>
<td>160</td>
<td>7.1</td>
</tr>
</tbody>
</table>
4.3 Elastic Recoil Detection Analysis (ERDA) of UNCD Films

4.3.1 Experimental Setup

ERDA measurements on the samples have been carried out by 15 MeV O\(^{4+}\) ions at scattering angle of \(\theta = 45^0\). IBM sample geometry was chosen for all runs with the beam incident angle \(\alpha = 67.5^0\) and the exit angle \(\beta = 67.5^0\). All samples were exposed to the same charge from the bombarding beam (20 \(\mu\)C) for consistency. The forward scattering detector solid angle was calculated and found to be 9.1065 x10\(^{-4}\)sr. A mylar foil with thickness of 13 \(\mu m\) was installed in the front of the detector to stop unwanted recoils and scattering.

4.3.2 Results and Discussion

ERDA results are shown in figure 4.3.1. According to the results, UNCD films contained atoms of H in the range of 7-9 at. %. In addition, the atomic percentage of H increased slightly in the film with the addition of N\(_2\) gas to the film plasma. During the growth process, the UNCD film deposited with 0% N\(_2\) was deposited with 3% of H\(_2\) gas in the plasma mixture, whereas, samples of UNCD for 10% and 20% N\(_2\) were deposited with 0% of H\(_2\) dilution. However, H was found trapped in the N incorporated samples as well. Owing to the fact that N\(_2\) introduction to the growth plasma of UNCD increases
Figure 4.3.1 ERDA results of three UNCD/W/Si films deposited with 0%, 10%, and 20% of N$_2$ gas content introduced into the films growth plasmas. H at. % increased slightly with increasing of N$_2$ content.
the volume of grain boundaries where H can passivate the dangling bonds, it is possible for the N incorporated samples to trap more hydrogen than the undoped ones. This H incorporation is probably from CH₄ used in the growth process or it might have come from the water vapors in the chamber. In general, UNCD films are grown in H₂ poor or even H₂ free plasma conditions; however, literature has shown the H contents in the UNCD films were in range of 3 to 15 at.% [144].

4.4 Resonance Nuclear Reaction Analysis (RNRA) of UNCD Films

4.4.1 Summary of the Work

The main aim of conducting RNRA studies using PIGE on UNCD samples is to find the concentration of nitrogen. For our initial studies we carried out NRA measurements on ¹⁴N incorporated UNCD films using a beam of 1.1 MeV deuterium ions (D⁺) which was directed on the samples at an angle of 60° from the surface normal. Reaction products were detected at a scattering angle of 170°. The detected particles for these measurements were protons from ¹⁴N (d,p)ⁱ⁵N and ¹²C(d,p)¹³C nuclear reactions. Results of NRA measurement on the samples were inconclusive which leads to the consideration of the ¹⁵N (p, aγ) ¹²C reaction. For RNRA measurements, UNCD films were deposited with isotope ¹⁵N₂ gas in the growth plasma. The deposited films for this study were UNCD films ¹⁵N-UNCD/Si and ¹⁵N-UNCD/Cr/Si. Each sample was deposited with 20% of ¹⁵N₂ gas leaked into their
growth plasma. RBS and ERDA data were collected for these samples which are discussed earlier. For RNRA, protons of energies varying from 880 keV to 1010 keV were used to take data for the specially papered UNCD films and the standard Si$_3$N$_4$ film. Detected particles in RNRA measurements were gammas from the $^{15}$N (p, $\alpha_1$γ) $^{12}$C nuclear reaction. As explained earlier in this chapter, the $^{15}$N (p, $\alpha_1$γ) $^{12}$C nuclear reaction has a resonance that occurs at 897 keV with a narrow resonance width ($\Gamma \sim 1.7$ keV) and high cross section ($\sigma \sim 800$ mb). Therefore, to obtain $^{15}$N profiles at different depth in the sample, the beam energy was increased in steps of 2 keV. Charge density of 100 $\mu$C and a current of about 120 nA were maintained on the target for each run. The gamma particles were detected by a NaI detector mounted at scattering angle of 90°. Calibration for the detector was carried out using three different radioactive sources; $^{22}$Na, $^{60}$Co, and $^{137}$Cs and a detector calibration factor of 6.6396 keV/channel with an offset channel of -25.3177 was obtained.

4.4.2 Results and Discussion

The above paragraph gives a brief outline of the work that was conducted to find the N content in N incorporated UNCD samples. From the initial NRA studies, the NRA spectrum of UNCD film - UNCD/W/Si (10% N$_2$) - deposited with 10% of N$_2$ is shown in Figure 4.4.1. It turns out that the amount of N content incorporated in the UNCD films found by regular NRA was difficult to quantify. However, rough
estimation concludes that N concentration in UNCD is less than 1 at%. In Figure 4.4.1, a close-up section of the NRA spectrum where the $^{14}\text{N} (\text{d},\text{p})^{15}\text{N}$ cross section peaks should appear is shown as well. It was difficult to determine the exact N content in the N incorporated UNCD due to the existence of the $^{28}\text{Si} (\text{d},\text{p})^{29}\text{Si}$ nuclear reaction that almost overlaps with the nitrogen nuclear reaction.

![NRA spectrum](image)

**Figure 4.4.1** NRA of UNCD film deposited with 10% of N$_2$ concentration in the plasma mixture. The inset figure is a close-up of the NRA spectra where $^{14}\text{N} (\text{d},\text{p})^{15}\text{N}$ cross section peaks should appear. The simulated N peak accounts for about 1at.% of N content.

For the RNRA work, nitrogen concentrations and nitrogen depth profiles in the UNCD films- deposited with 20% of $^{15}\text{N}_2$ gas added to their growth plasmas- and
the standard film Si$_3$N$_4$ were obtained by using the 897 keV resonance of the $^{15}$N (p, $\alpha_1\gamma$) $^{12}$C nuclear reaction. Gamma particles as result of this nuclear reaction have a peak at an energy position of 4.43 MeV with narrow resonance width of 1.7 keV. The narrow resonance width allows for accurate depth profiling with a well defined proton beam energy. To avoid the complex calculation of detector efficiency and resolution, a thick Si$_3$N$_4$ on Si was used as standard for the measurements. RBS was carried out to confirm the stoichiometry of the Si$_3$N$_4$ sample. The RBS spectrum, shown in figure 4.2.2, was simulated with 42.8 at% Si and 57.2 at% N which gave us an excellent fit with the experimental data. The natural abundance of $^{15}$N in nitrogen is 0.37 at%; therefore, we expect 0.21 at% of $^{15}$N in Si$_3$N$_4$.

A typical spectrum of 4.43 MeV $\gamma$ rays due to the $^{15}$N (p, $\alpha_1\gamma$) $^{12}$C reaction in the UNCD film when bombarded with protons is shown in Figure 4.4.2. In the region of interest, three peaks were observed. The first two peaks are escape peaks with energies of $E_{\gamma} - 0.511$ MeV and $E_{\gamma} - 1.022$ MeV respectively. These escape peaks originate from the interaction of $\gamma$ rays (photons) with the crystal material of the NaI (TI) detector [145]. The third peak at $E_{\gamma}$ is the peak of interest and its yield is proportional to the $^{15}$N concentration $C_N(x)$ in the probed depth of the sample. By careful fitting and analysis, the measured yield curve $Y(E_p)$ was obtained through an integration of area under the peak in a set range of energy $\Delta E$. In addition, to reduce any other contributions from parasitic reactions below the used reaction, several background measurements were done. These background yields are then subtracted from the yield curve $Y(E_p)$ of gamma rays.
Figures 4.4.3 and 4.4.4 present RNRA raw data obtained for Si$_3$N$_4$, $^{15}$N-UNCD/Si (20% N$_2$), and $^{15}$N-UNCD/Cr/Si (20% N$_2$) samples respectively. These RNRA spectra were extracted at different incident energies ($E_p$) of the proton beam to allow for $^{15}$N depth profiling in each sample. From the RNRA raw results, it is apparent that $^{15}$N content distributions are somewhat uniform in the standard film and in the UNCD/Si (20% N$_2$) film. However, it is not uniform for the $^{15}$N-UNCD/Cr/Si (20% N$_2$) since more $^{15}$N content gradually increases towards the interface region of the Cr
and UNCD layers in the sample. These findings are in agreement with the RBS results summarized in the Table 4.2.2.

**Figure 4.4.3** RNRA results of $^{15}$N (p, $\alpha\gamma$) $^{12}$C reactions in the standard film Si$_3$N$_4$ obtained at varying proton beam energies $E_p$. Inset figure is a close-up of the $\gamma$ spectra regions of interest.
Figure 4.4.4 RNRA spectra of $^{15}$N (p, αγ)$^{12}$C reactions in the UNCD films: I. $^{15}$N-UNCD/Si (20% N$_2$) and II. $^{15}$N-UNCD/Cr/Si (20% N$_2$). Results obtained at different energies $E_p$ of the protons beam. Inset figures are close-ups of the regions of interest in the γ spectra.
The RBS results of the sample $^{15}$N-UNCD/Cr/Si (20% $N_2$) show that there are two intermixing regions in the film. The UNCD/Cr region has a thickness of about $1100 \times 10^{15}$ atoms/cm$^2$ and Cr/Si has a measured thickness of $400 \times 10^{15}$ atoms/cm$^2$. We believe that this diffusion of Cr in UNCD and Si is due to the high temperature deposition of the films. Since Cr is highly reactive with N [146], therefore, the concentration of $^{15}$N with depth in $^{15}$N-UNCD/Cr/Si sample follows the Cr concentration in the sample.

To utilize the analysis of RNRA spectra for the depth profiling measurements, equation 4.7 was used. Converting energy step to a depth scale requires a knowledge of the stopping cross sections of the material bombarded with energetic ions beams which were protons in our case. Calculations of the stopping cross sections of the $Si_3N_4$, $^{15}$N-UNCD/Si (20% $N_2$), and $^{15}$N-UNCD/Cr/Si (20% $N_2$) samples were conducted by the use of Ziegler, Biersack and Litmark (ZBL) theory [147][148]. In additions coefficients from tables of Appendix 3 of reference [126] and the SRIM 2008 program are used [149][150]. Table 4.4.3 presents the calculated stopping power cross sections with the respective depth scale at the incident proton energies for the standard film and the UNCD films.
Table 4.2.3 Calculated values of the stopping powers $\varepsilon_N$, $\varepsilon_{\text{UNCD}}$, and $\varepsilon_{\text{Si}_3\text{N}_4}$ along with the depth scales at each step energy of the RNRA samples

<table>
<thead>
<tr>
<th>Energy (keV)</th>
<th>Depth Scale $x(E_p)$[nm] UNCD</th>
<th>Depth Scale $x(E_p)$[nm] Si$_3$N$_4$</th>
<th>$\varepsilon_N$ eV.cm$^2$/10$^{15}$atoms</th>
<th>$\varepsilon_{\text{UNCD}}$ eV.cm$^2$/10$^{15}$atoms</th>
<th>$\varepsilon_{\text{Si}_3\text{N}_4}$ eV.cm$^2$/10$^{15}$atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>898.0</td>
<td>0.0</td>
<td>0.0</td>
<td>5.2</td>
<td>4.5</td>
<td>4.9</td>
</tr>
<tr>
<td>900.0</td>
<td>26.3</td>
<td>28.8</td>
<td>5.2</td>
<td>4.5</td>
<td>4.9</td>
</tr>
<tr>
<td>902.0</td>
<td>52.7</td>
<td>57.7</td>
<td>5.1</td>
<td>4.5</td>
<td>4.9</td>
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<td>904.0</td>
<td>79.1</td>
<td>86.6</td>
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<td>4.9</td>
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<td>4.8</td>
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<td>4.8</td>
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<td>319.5</td>
<td>5.1</td>
<td>4.5</td>
<td>4.8</td>
</tr>
<tr>
<td>922.0</td>
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<td>4.8</td>
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</table>

From the RNRA analysis of the raw data shown in Figures 4.4.3 and 4.4.4, gamma yields are then estimated for $^{15}$N content at each beam energy step for the two UNCD
samples along with their standard film. Figure 4.4.5 displays these yield estimations as functions of the beam energy for the samples UNCD/Si (20% N\textsubscript{2}), \(^{15}\text{N}\)-UNCD/Cr/Si (20% N\textsubscript{2}), and their calibration standard. It can be seen that \(^{15}\text{N}\) contents incorporated in the samples are distributed uniformly for UNCD/Si (20% N\textsubscript{2}) and standard films. Nevertheless, that was not the case of the film \(^{15}\text{N}\)-UNCD/Cr/Si (20% N\textsubscript{2}) because of the reason explained earlier. Moreover, knowing the film thickness from the RBS studies on the samples, regions which host the most of \(^{15}\text{N}\) atoms in the \(^{15}\text{N}\)-UNCD films are seen.

**Figure 4.4.5** RNRA measured \(\gamma\) yields from \(^{15}\text{N}\) (p, \(\alpha\gamma\))\(^{12}\text{C}\) nuclear reaction for \(^{15}\text{N}\)-UNCD films and \(\text{Si}_3\text{N}_4\) standard. Yields \(Y(E_p)\) were obtained as functions of the incident proton energy.
Finally, knowing the calculated values of the stopping cross sections of protons in the sample materials, the measured yields $Y(E_p)$ shown in the figure 4.4.5, and the sample thickness along with the standard N concentration obtained by the RBS studies, nitrogen content at each depth scale in the $^{15}$N-UNCD films can be estimated. For the $^{15}$N content estimation at a certain depth profile $C_N(x)$, equation 4.6 is utilized. Total concentrations of $^{15}$N atoms incorporated in the UNCD films deposited with 20% of $^{15}$N$_2$ gas in the growth plasma are then estimated to be the summations of all measured $C_N(x)$ over the range of the sample thickness,

$$C_{N_{Total}} = \sum_{j=0}^{E_d} C_N(x_j)$$

(4.8)

where $j = E_i, E_{i+2}, \ldots, E_d$ with $E_i$ corresponding to the resonance proton energy of 898 KeV and $E_d$ equals the energy equivalent of the film thickness.

RNRA work on the $^{15}$N incorporated UNCD films concludes that the total concentration of $^{15}$N atoms in the $^{15}$N-UNCD/Si (20% N$_2$) is 0.13 at. %, while the total numbers of $^{15}$N atoms residing in the $^{15}$N-UNCD/Cr/Si (20% N$_2$) film is 4.24 at. %. Summaries of the RNRA findings are given in Table 4.2.4 and in Figure 4.4.6.
Table 4.2.4 Calculated concentrations of $^{15}$N atoms incorporated in the UNCD films at varying depth scale up to the film thicknesses

<table>
<thead>
<tr>
<th>Energy (keV)</th>
<th>Depth Scale $x(E_p)$ [nm] UNCD</th>
<th>$^{15}$N-UNCD/Si (20% N$_2$) $C_N(x_j)$ [at. %]</th>
<th>$^{15}$N-UNCD/Cr/Si (20% N$_2$) $C_N(x_j)$ [at. %]</th>
</tr>
</thead>
<tbody>
<tr>
<td>898.0</td>
<td>0.0</td>
<td>0</td>
<td>0</td>
</tr>
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<tr>
<td>936.0</td>
<td>507.0</td>
<td>0</td>
<td>0.344720927</td>
</tr>
</tbody>
</table>
I. \[ ^{15} \text{N-UNCD/Si (20\% N}_2 \text{)} ; d = 307 \text{ nm} \]

II. \[ ^{15} \text{N-UNCD/Cr/Si (20\% N}_2 \text{)} ; d = 478.3 \text{ nm} \]

**Figure 4.4.6** I. Gamma yields of nuclear reactions $^{15}$N (p, $\alpha \gamma$) $^{12}$C, and II. Depth profile of $^{15}$N in the UNCD films deposited with 20\% of $^{15}$N$_2$ in their growth plasmas.
5.1 Theories

Dielectric phenomena taking place in solids due to their interaction with the light can be quantified by a number of parameters, such as coefficients of reflection, transmission, and absorption. These coefficients can then be utilized to determine the properties of the medium (solid) at the macroscopic level.

From the Maxwell equations, some important relationships can be obtained for dielectric functions, optical constants, and for the propagation of electromagnetic (EM) waves in a homogeneous medium. Thus, use of the wave equation (5.1) for a non-conducting and non-magnetic medium in one dimension,

\[
\frac{\partial^2 E(x,t)}{\partial x^2} = \frac{\varepsilon}{c_0^2} \frac{\partial^2 E}{\partial t^2} \quad (5.1)
\]

where \(E(x,t)\) is given by a plane wave of the form

\[
E = E_0 e^{i(kx-\omega t)} \quad (5.2)
\]
the dispersion relation for the propagation of the EM wave can be obtained in the following form,

$$
\kappa^2 = \frac{\omega^2}{c_0^2} \varepsilon(\omega) \quad (5.3)
$$

where $\varepsilon(\omega)$ is the complex dielectric constant which determines the dispersion of the light wave as it is interacting with a material. The propagation constant $\kappa$ can be expressed by the index of refraction ($N$) as well.

$$
k = \frac{N\omega}{c_0} \quad \text{with} \quad N = \sqrt{\varepsilon(\omega)} \quad (5.4).
$$

Using the real and complex values of refractive index and the dielectric function

$$
N(\omega) = n(\omega) + i\kappa(\omega), \quad \text{and} \quad \varepsilon(\omega) = \varepsilon_r(\omega) + i\varepsilon_i(\omega). \quad (5.5)
$$

where the imaginary parts may be chosen as positive or negative [151], the imaginary parts lead immediately to EM damping in space, formulated by

$$
E(x, t) = E_0 e^{i\left(\frac{N\omega}{c_0}x - \omega t\right)} = E_0 e^{-\left(\frac{2\pi\kappa}{\lambda}\right) x} e^{i(k\times - \omega t)} \quad (5.6)
$$

The expression, $\frac{2\pi\kappa}{\lambda}$, describes the attenuation of the electrical field, which is related to the absorption coefficient $\alpha$ defining by Lambert’s law [151],

$$
I(x) = EE^* = I_0 e^{-\alpha x}.
$$

Comparing Lambert’s law and the light plane wave equation, the absorption coefficient is then given by
\[ \alpha = \frac{4\pi \kappa}{\lambda} \]  

(5.7)

Now, from the Maxwell’s driven equations (5.4), (5.5), and (5.7), the real and the imaginary parts of the two functions \( N(\omega) \) and \( \varepsilon(\omega) \) are correlated via

\[ \varepsilon_r = n^2 - \kappa^2, \quad \text{and} \quad \varepsilon_i = 2n\kappa \]  

(5.8).

In practice, if the real or imaginary part of the \( N(\omega) \) and \( \varepsilon(\omega) \) functions is experimentally measured then the other part in the respective function may be calculated; assuming the strength of the light electrical field is weak enough not to cause a nonlinear response when interacting with the media; using the well-known Kramers-Kronig relations (KKR)[152],

\[ f_r(\omega) - 1 = \frac{2}{\pi} \mathcal{P} \int_0^{\infty} \frac{\omega' f_i(\omega')d\omega'}{\omega'^2 - \omega^2} \]  

(5.9)

\[ f_i(\omega) = -\frac{2\omega}{\pi} \mathcal{P} \int_0^{\infty} \frac{f_r(\omega')d\omega'}{\omega'^2 - \omega^2} \]  

(5.10)

where \( f_r(\omega) \) and \( f_i(\omega) \) are the real and imaginary parts of a function \( f(\omega) \). \( \mathcal{P} \) is the principle value of the integrals.

For the UNCD films subjected to this work, spectroscopic ellipsometry is one of the main tools used to obtain the dielectric qualities of the films materials. Therefore, it is of interest to look at the physics of the interaction of polarized light with a film surface. When a polarized monochromatic light beam is incident upon an interface separating two isotropic media, as shown in Figure 5.1.1,
The subscripts \(i\), \(r\), and \(t\) represent the incident, reflected, and transmitted waves respectively. The \(s\)-axis is out of the page plane and the \(p\)-axis is in the plane of the page. The angle of incidence and reflection is \(\theta_0\), while the angle of refraction is \(\theta_1\).

The polarization states of the reflected and refracted light are modified in general. The reflected complex electric field components, \(E_{rp}\) and \(E_{rs}\), projected along the two orthogonal directions, parallel (\(p\)) and perpendicular (\(s\)) to the plane of incidence respectively, are related to the incident complex electric field components, \(E_{ip}\) and \(E_{is}\), by [153]

\[
\frac{E_{rp}}{E_{ip}} = r_p = |r_p|e^{i\delta_{rp}} \quad \text{and} \quad \frac{E_{rs}}{E_{is}} = r_s = |r_s|e^{i\delta_{rs}} \tag{5.11}
\]

while the refracted complex electric field components, \(E_{tp}\) and \(E_{ts}\), are related to the incident complex electric field components by

\[
\frac{E_{tp}}{E_p} = t_p = |t_p|e^{i\delta_{tp}} \quad \text{and} \quad \frac{E_{ts}}{E_{is}} = t_s = |t_s|e^{i\delta_{ts}} \tag{5.12}
\]
where $\delta_{rp}$, $\delta_{rs}$, $\delta_{tp}$, and $\delta_{ts}$ are the phase shifts of the field components upon reflection and refraction respectively. The plane of incidence is defined so as to contain the wave vectors of the incident, reflected, and refracted beams. In the equations (5.11 and 5.12), $r_p$, $r_s$, $t_p$, and $t_s$ are the complex amplitude reflection and refraction coefficients for the $p$- and $s$- directions respectively, determined by the boundary conditions on Maxwell's equations. They are given by

$$r_p = \frac{N_1 \cos \theta_0 - N_0 \cos \theta_1}{N_1 \cos \theta_0 + N_0 \cos \theta_1} \quad (5.13)$$

$$r_s = \frac{N_0 \cos \theta_0 - N_1 \cos \theta_1}{N_0 \cos \theta_0 + N_1 \cos \theta_1} \quad (5.14)$$

$$t_p = \frac{2N_0 \cos \theta_0}{N_1 \cos \theta_0 + N_0 \cos \theta_1} \quad (5.15)$$

$$t_s = \frac{2N_0 \cos \theta_0}{N_0 \cos \theta_0 + N_1 \cos \theta_1} \quad (5.16)$$

and known as the Fresnel complex amplitude reflection ($r$) and transmission ($t$) coefficients for the $p$ and $s$ polarized light [153]. $N_0$ and $N_1$ are the complex indices refractive of the incident medium (0) and the reflecting medium (1). $\theta_0$ and $\theta_1$ are the angles of incidence and transmission, respectively. Changes in the magnitudes $|r_p|$ and $|r_s|$ and in the phases $\delta_p$ and $\delta_s$ lead to changes in the polarization states of light upon reflection. Measurements of these changes form the basis of ellipsometry. In ellipsometry spectroscopy, the change in the polarization state upon reflection is measured as the ratio of the reflected to the incident polarization states, and
is given by [153]

\[ \rho = \frac{|r_p|}{|r_s|} e^{i(\delta_{rp} - \delta_{rs})} = \tan \psi e^{i\Delta} \quad (5.18) \]

where \( \psi \) and \( \Delta \) are the two ellipsometrical angles defined by

\[ \psi = \tan^{-1} \frac{|r_p|}{|r_s|}, \quad \text{and} \quad \Delta = (\delta_{rp} - \delta_{rs}) \quad (5.19). \]

In the case of a stratified structure that consists of a stack of substrate-supported parallel layers with ideal interfaces, which is common for film structures [154], as shown in Figure 5.1.2,

**Figure 5.1.2** Reflection and transmission of an incident plane wave by an m-layers structure (films: 1 to m) sandwiched between the semi-infinite ambient (0) and substrate (m+1) media. \( \theta_0 \) is the angle of incidence at the first layer; \( \theta_j \) is the angle of incidence at the \( j+1 \) layer of thickness \( d_{j+1} \) and complex index of reflection \( N_{j+1} \). \( \theta_m+1 \) is the angle of refraction into the substrate.
the reflected beam contains information from each layer depending on the photon energy, angle of incidence, layer thickness, and dielectric function of the layer. This can be described formally as [154]

\[ \psi = F\{h\nu, \theta_0, N_0, N_j(j = 1, \ldots, m), N_{m+1}, d_j(j = 1 \ldots m)\} \] (5.20)

\[ \Delta = G\{h\nu, \theta_0, N_0, N_j(j = 1, \ldots, m), N_{m+1}, d_j(j = 1 \ldots m)\} \] (5.21)

The reflection coefficients for the film structures as a whole can be calculated from the scattering matrix \( S \), which represents the combined properties of the stratified structure [155][156].

Relative to the latter theoretical description, the energy band gap of the UNCD film or a film material in general can be determined by the reflection spectra. According to the empirical Tauc Model [157], the spectra of the optical absorption coefficient can be analyzed by using the following equations

\[ a\nu = B(h\nu - E_g)^m \quad ; \text{for } h\nu > E_g \] (5.22)

\[ a\nu = 0 \quad ; \text{for } h\nu < E_g \] (5.23)

where \( B \) is a constant that depends on details of the band structure, \( h\nu \) is the photon energy, \( E_g \) is the energy band gap. Values of \( m \) are related to the allowed band transitions in which \( m = 0.5 \) responds to the direct transitions while \( m = 2 \) corresponds to the indirect transitions. Thus, the optical band gap \( E_g \) then can be determined from the plot of \((a\nu)^{1/m}\) vs. photon energy \( E = h\nu \), as the intercept of the extrapolated linear fit with the abscissa axis [158-161].
5.2 Ellipsometrical Studies on UNCD Films

5.2.1 Instrumentation and Data Analysis

The spectroscopic ellipsometrical studies on the UNCD films for this research have been obtained using a Horiba Jobin Yvon UVISEL ex-situ spectroscopic ellipsometer located at the clean room of the CNM at ANL. This spectroscopic ellipsometer has a wide spectral range span from UV to NIR (142 to 2100 nm). Measurements on the UNCD films were taken in the energy range of 1.4 to 6 eV at a variable angle of incidence of 55°-85° degrees. The light source used consists of a 20 W halogen lamp and near UV LED combined, a single grating monochromator, collimating optics, and a filter wheel. The filter wheel is used to insert a long pass filter (transparent in the higher range of ~ 475 nm) into the beam path at the long wavelength (λ ≥ 473 nm) in order to eliminate the second order reflection from the grating in the monochromator. Optical fiber connected the input head to the source. The input head consisted of a polarizer and liquid crystal modulator. Light, upon reflection from the sample, passed through the output head and was thereupon collected by the CCD (charge-coupled device) detector. The sample was mounted between the two elements leading to the polarization-sample-analyzing routine ellipsometer configuration (see Figure 5.2.1). A shutter is provided so that a dark cycle measurement can be made in the absence of the incident beam. Finally, a photomultiplier tube (PMT) is used to measure the intensity of the reflected polarized light transmitted by the rotating analyzer versus time.
Figure 5.2.1 Common configuration of the Spectroscopic Ellipsometer (SE).

A computer is used to control the operation of the ellipsometer. Three stepping motors are used to set the monochromator, filter wheel, and fixed polarizer. The angular frequency of the rotating analyzer is stabilized at 64 Hz. DeltaPsi2 software was used as a means for the data acquisition and analysis.

Data analysis of an ellipsometrical experiment is the most important step to be able to obtain useful results. Although spectroscopic ellipsometry (SE) techniques are very powerful [153][162], the direct information obtained from SE is not meaningful.
by itself. Thus, in order to evaluate dielectric constants and the thickness of a sample from spectroscopic ellipsometry, it is necessary to perform a data analysis that consists of intensive modeling, calculations, and fitting of the measured \((\psi, \Delta)\), the two ellipsometrical angles mentioned in section 5.1. Then the quantitative information can only be obtained through numerical inversion, i.e., a mathematical computation of the scattering matrix associated with a simulated sample structure that can best describe the measured \((\psi, \Delta)\) spectra [163-165]. Therefore, ellipsometry is an indirect optical technique, and requires a model of the sample for calculating the scattering matrix to provide data that fits the measured ones. The choice of the proper model requires the sample specifications, such as the material of the substrate and of the film, the number of layers in the stratified multilayered structure and the presence of oxides or surface roughness. Major parts of data analysis are dielectric function modeling, use of effective medium approximations (EMA) [166-168], construction of an optical model, and fitting of calculated data to the measured spectra.

Figure 5.2.2 presents a flowchart of the experimental procedure for the ellipsometrical study conducted on the UNCD films investigated in this work. In this procedure, to take actual measurements on UNCD samples first we choose a desirable incident angle either through a standard sample or by using a Brewster angle relation defined as \((\tan \theta_B = \frac{n_2}{n_1})\). Then we scan the sample surface using the SE source of light to obtain the experiential result. Second, an optical model corresponding to the sample is constructed, and then dielectric functions of each layer are selected.
Figure 5.2.2 Flowchart of the experimental procedure in the ellipsometrical analysis.
If the dielectric functions are not known then dielectric function modeling is used. For dielectric function modeling in the transparent region ($\varepsilon_2 \sim 0$), the Cauchy model [168] is used. When there is free-carrier absorption, the data analysis is generally performed using the Drude model [168]. In our work, we are dealing with dielectric functions of group-IV semiconductor crystals which show complicated structures where the bandgap of these crystals (indirect transition) increases with the order of Ge $<$ Si $<$ C (diamond), and the dielectric functions also shift toward higher energies with this order [169]. In the SE experiment, the range of spectral wavelengths is generally of 1-5 eV, so the Sellmeier or Cauchy model [169] have been applied which tend to work well for diamond. The dielectric function of the substrate can be obtained from the pseudo-dielectric function (equation 5.25) if there are no overlayers and surface roughness is negligible [170]. Most of the dialectic function models and values for different materials are included in the software of the equipment and can be applied easily during the building of the optical model. Using analytical parameters such as $d_b$ (bulk thickness) and $d_s$ (substrate thickness), calculated ($\psi$, $\Delta$) are fitted to the experimental spectra. In the next step, the fitting error $\chi^2$ is evaluated through the following equation, which has been widely used for various functions [171-172]:

$$
\chi = \frac{1}{\sqrt{M-P-1}} \{ \sum_{j=1}^{M} \left( \frac{\psi_{ex}(h\nu_j) - \psi_{ca}(h\nu_j)}{\delta\psi(h\nu_j)} \right)^2 + \left( \frac{\Delta_{ex}(h\nu_j) - \Delta_{ca}(h\nu_j)}{\delta\Delta(h\nu_j)} \right)^2 \}^{1/2}
$$

(5.24)
where $M$ is the number of data points and $P$ is the number of parameters ($\delta\psi, \delta\Delta$) showing measurement errors in $(\psi, \Delta)$. The smaller the value of $\chi^2$, the better. In this work we usually aim to have $\chi^2 \sim 1$. When the fitting error is large, the optical model or dielectric functions are revised. At the minimum reached $\chi^2$, the optical/dielectric constants and film thicknesses of the sample are finally determined. Nevertheless, it is important to notice that an optical model used in ellipsometrical analysis merely represents an approximated sample structure, and obtained results are not necessarily correct even when the fit is sufficient. Accordingly, when the optical constants or film structures of a sample are not well known, the ellipsometry results must be justified using other measurement methods. This is the greatest disadvantage of the ellipsometry technique. Once an analytical method is established, however, it becomes possible to perform a high-precision characterization in a short time using spectroscopic ellipsometry. In this work, all UNCD samples used for the ellipsometry analysis have been exposed to various characterization techniques mentioned in the previous chapters to insure the quality of results obtained on the UNCD films by the spectroscopic ellipsometry (SE). Moreover, all SE results on the UNCD films will be confirmed by other spectroscopic techniques such as UV-Vis spectroscopy and reflectance spectroscopy, as will be shown in the rest of this chapter.
5.2.2 Results and Discussion

The three UNCD films deposited with varying concentrations of N\textsubscript{2} gas in their growth plasma on W coated Si wafers have known thicknesses, surface roughness and microstructure. The basic characterizations and IBA explained in the previous chapters were used to obtain these properties and are used to analyze the SE data as well. Although variable angle SE (VASE) analyses have been carried out, the best angle of incidence is found to be 70\textdegree, which corresponds to the Brewster angle estimated for the incident polarized light on the UNCD film. All measurements were conducted at room temperature and data were taken at several locations on the samples.

The optical models constructed to extract dielectric properties of the UNCD films along with their fitting results of the SE observables quantities $I_s$ and $I_c$ are shown in Figure 5.2.3. $I_s$ and $I_c$ are the observed intensities of the polarized light that are related to the two measured ellipsometrical angles ($\psi, \Delta$). To achieve a good (i.e., best fit) agreement between the measured and the calculated SE optical data on the UNCD film, an optical model of a five phase multilayer structure was used. These phases represent the substrate, W interlayer, the interface region between W and UNCD, UNCD layer, and roughness of the film surface. Optical models with multilayer systems are commonly used and fit well for the polycrystalline materials [173-176]. To assign a dielectric function for each phase in the sample constructed optical model, several SE measurements have been conducted on the pre-deposition
wafers, Si and Si coated wafer. Such measurements provide an accurate means to
assign the suitable dielectric function of the first two phases (from the bottom) in the
UNCD model. The substrate and W layer phases were considered homogenous and
their assigned dielectric functions are the Tauc-Lorentz model [177-178] and Drude
free carrier dispersion [179-181]. The dielectric function profiles in the UNCD films
were divided into three phases: the homogenous phase presented by the UNCD layer
in the optical model, the inhomogeneous phase assigned as PNL (pre-nucleation
layer) to take account for the interface region in the film, and finally, the surface
roughness phase (the top layer in the optical model). These three phases are not
considered as separate parts in the physical film; however, such an arrangement was
necessary when building the optical model for the UNCD film to fully describe the
different dielectric responses due to the film structures. The boundary roughness
phase described by the Rayleigh-Rice theory [182-183] has an effective dielectric
function obtained through the effective medium approximation mentioned in the data
analysis section of this chapter. The dispersion function of the PNL layer described
by parameterized joint density of the states (PJDOS) model tends to relate well to the
dielectric response in disordered solid materials [184-185]. Finally, a classical-
oscillator model of the complex dielectric function has been utilized for the UNCD
layer phase in the built optical model of the UNCD film.
\[ I_s = \sin 2\psi \sin \Delta \]
\[ I_C = \sin 2\psi \cos \Delta \]

\[ \chi^2 = 0.98 \]

\[ \chi^2 = 1.9 \]

\[ \chi^2 = 3.2 \]

Figure 5.2.3 Fitting of \( I_s \) and \( I_C \) observables along with the optical models (OPs) used for the SE measured data simulations. At each OP model, fitting result of the layers thicknesses of the UNCD film is also shown. Values of \( I_s \) and \( I_C \) depend on the configuration of the ellipsometer. Solid lines represent measured data while symbols correspond to the calculated values.
The classical-oscillator models of the dielectric function are fundamentally related to the damping effect of harmonic oscillators. The selected dielectric functions which represent the dielectric responses of the best fitted optical model of the UNCD film are Kramers–Kronig consistent in the complete spectral range.

Fitting results of the SE data for the UNCD films are shown in Figure 5.2.3, which clearly show good agreements with the measured data. Deviations (error parameters $\chi^2$) of the fitting estimated by the expression (5.24) indicate an increasing difference between the measured and the calculated data as more of N content is incorporated in the film. This behavior is in agreement with the results of the basic characterizations of the UNCD films which imply changes in the film structures as N$_2$ gas is added to the film’s growth plasma. Raman spectroscopy, AFM, and SEM results pointed out that grains and grain boundaries of the UNCD films were increasing in size as N$_2$ gas is increased in the growth plasma of the film. Thus, scattering of light from the N-incorporated UNCD film was expected to increase with the increase of the grain and grain boundaries sizes. Nevertheless, the SE estimations of the overall thicknesses of the UNCD films were still accurate and did agree with the thicknesses obtained by RBS measurements.

Figures 5.2.4 and 5.2.5 display optical constants and dielectric coefficients respectively as functions of the light wavelength and the N-content incorporated in the films. The dielectric properties of the films were deduced directly from the results shown in Figure 5.2.3. The ellipsometer observables $I_S$ and $I_C$ can be converted readily
to the two ellipsometer measured angles ($\psi, \Delta$), using equations given in Figure 5.2.3. Then by utilizing the theory shown in section 5.1 (i.e., equation (5.18) and complex Fresnel functions), the important complex dielectric $\varepsilon(\omega)$ function of a material can be related to the ellipsometrical measured angles using [186];

$$
\varepsilon(\omega) = N_1^2(\omega) = N_0^2(\omega) \sin^2 \theta_0 [1 + \left(\frac{1-\rho}{1+\rho}\right)^2 \tan^2 \theta_0] \tag{5.25}.
$$

The optical and dielectric coefficients of the UNCD films show clear trends of decreasing as the wavelength of light is increased toward the IR region. That can be explained on the basis of the fact that light with larger wavelengths will be less sensitive to the nanostructures of the film. Moreover, imaginary parts of the dielectric coefficients, which are related to the absorption function in the UNCD films through equations (5.4) and (5.7), display an increasing trend for the samples prepared with $N_2$ gas added to the growth plasma. $k$ and $\varepsilon_i$ values of the UNCD films deposited with 20% $N_2$ gas are much higher when compared to the UNCD film with 0% $N_2$ gas. The relation between the N concentrations in the film and its absorption properties can be explained in terms of the effects of nitrogen content on the nanostructure of the film; i.e., changes in the grain and grain boundaries sizes. In general, optical and electric properties are mainly influenced by the grain sizes and grains distributions of the sample [187-189].
Figure 5.2.4 Optical constants of the UNCD films as a function of wavelength ($\lambda$) and N content incorporated in the films.
Figure 5.2.5 Dielectric coefficients of the UNCD films as a function of wavelength (λ) and N concentration incorporated in the films.
Furthermore by utilizing the obtained values of the extinction coefficients $k$ of the UNCD films, absorption coefficients can be calculated. It is possible then to find the optical band gaps of the films using an empirical model, i.e., the Tauc model stated earlier in this chapter.

The results in Figure 5.2.6 are presented to explore the effects of N content in the UNCDs on the energy band gaps of the films. From the results, it is obvious that the indirect band gap energies of the UNCD films decrease as functions of the increasing $N_2$ gas content in the films growth plasmas. Similar conclusions have been drawn from earlier studies on nitrogenated nanocrystalline diamond films [190-191].

![Figure 5.2.6 Tauc plots to obtain the indirect band gap energies of UNCD samples deposited with different % of $N_2$ gas.](image-url)
5.3 UV/Vis Spectroscopy of UNCD Films

5.3.1 Background and Experimental Setup

UV/VIS spectroscopy is the measurement of light absorption by a sample material in the near-ultraviolet to visible range; the spectrum ranges from 200 nm to 800 nm. A UV/VIS spectrophotometer uses ultraviolet and visible electromagnetic radiation to energetically promote valence electrons in a molecule to an excited energy state. Then it measures the absorption of energy to promote the electron by the molecule at a specific wavelength or over a range of wavelengths. Different molecules absorb radiation of different wavelengths. An absorption spectrum will show a number of absorption bands corresponding to structural groups within the molecule. In particular, the absorption of UV or VIS radiation corresponds to the excitations of the outer electrons of the molecule. There are many types of electronic transitions which can be obtained through the UV/VIS spectroscopy measurements, however, the most important three transitions are transitions involving $\pi$, $\sigma$, and $n$ electrons. In Figure 5.3.1, a $\pi$ transition corresponds to sp$^2$ and $\sigma$ to sp$^3$ bonds, and these are signatures of graphite and crystalline carbon, respectively [192]. These are the transitions of interest in this work since they give an insight into the optical absorption edges of the UNCD films.
For the UV/VIS spectroscopy measurements, specially prepared samples of UNCD film have been used. These UNCD films were deposited on quartz substrates to enhance light transmission through the samples. To correlate UV/VIS spectroscopy results with the N content incorporated in the UNCD film, three UNCD/quartz films (Table 2.3.1) were deposited with 0%, 10%, and 20% of N\textsubscript{2} gas diluted to their growth plasmas. All UV/VIS measurements on these UNCD films have been obtained by a Varian Cary-50 UV/VIS spectrophotometer in a scanning range of 190-1100 nm at room temperature.

**Figure 5.3.1** Various kinds of electronic excitation that may occur in molecules.
5.3.2 Results and Discussion

Figure 5.3.2 shows the transmittance (T %) of light through that sample which clearly reveals that the T % rate of the UNCD films goes down as the N₂ concentration goes up in the film plasma. That means an increase in the optical absorption activities in the films as more nitrogen is added to their growth plasma (see Figure 5.5.3 for band gap energies as a support to the statement). Similar results have been reported in the literature for nanocrystalline diamond thin films [193]. From Raman and AFM studies on the UNCD films, it was concluded that an increase of N₂ gas concentrations in the film growth plasma promotes structural changes in the films. In particular, the number of sp³ bonded carbon atoms increased with the addition of N₂ gas. Thus, it would possible to attribute the enhancement of the optical absorption in the UNCD film to electronic transitions of π to π*band [194] within the band gap. In addition, it was seen from the basic characterizations that grains and grain boundaries do increase in size when N₂ content in the film plasma increases. Hence, decrease in the values of transmittance for the samples deposited with higher N₂ content could be related to the size increases of the grains and grain boundaries as well. It is well established that transmittance coefficients are mainly influenced by the grain sizes of the sample [195].
Figure 5.3.2 Transmittance rates of UNCD films/quartz deposited with varying concentrations of N₂ gas.

Band gap energies can be estimated from the UV/VIS spectroscopy studies on the UNCD films by utilizing the Tauc model as was the case in the SE studies. The Tauc model is widely used as the appropriate tool to extract information about the band gap of nanocrystalline and amorphous carbon materials [196]. Figure 5.5.3 displays the UV/VIS results on the band gap $E_g$ of the UNCD films, which show similar trends to the results drawn from the SE work on the UNCD films. $E_g$ decreases as a function of increasing N₂ content in the UNCD film plasma. Such results also could be explained in terms of increasing $sp^2$ atomic clusters in the film.
nanostructures due to higher N$_2$ concentration in the film plasma. In Figure 5.3.3 estimations of the UNCD films indirect band gap energies were carried out by linear extrapolation of $(\alpha h\nu)^{1/2}$ curves in range spans between 200 and 300 eV.cm$^{-1/2}$ as was the case in the SE studies. Such a range of $E_g$ estimations has been used frequently for nitride and hydrogenated carbon films [197-198]. As is common practice, the Tauc model was considered applicable over a wide spectral range especially toward the IR region by making an assumption that the tail of localized states in the band gap is negligible relative to the parabolic part of the band gap [157].

![Tauc plots](image)

**Figure 5.3.3** Tauc plots obtained from UV/VIS spectroscopy for the indirect band gap energies of the UNCD/quartz samples deposited with different % of N$_2$ gas.
One more result from UV/VIS spectroscopy investigation on the UNCD film is shown in Figure 5.3.4. Imaginary parts of the dielectric coefficients for the UNCD/quartz films show increasing trends as more N$_2$ gas is added to the film plasma, especially in the visible range. This was expected since these coefficients are closely related to the absorption characteristics in the material. Although UV/VIS spectroscopy is more sensitive to the material structures (direct measurements technique) when compared to spectroscopic ellipsometry, there is still a good agreement between both techniques on the values of the dielectric coefficients obtained for the UNCD films.

**Figure 5.3.4** Dielectric coefficients of the UNCD/quartz films as a function of wavelength (λ) and N concentration incorporated in the films.
5.4 Reflectance Measurements on UNCD Films

Reflection-absorption spectroscopy is a method for finding the optical properties of solid materials [199]. It is nondestructive technique and is typically used to directly measure the amplitude of reflection from a material. Then, dielectric and optical coefficients of the material can be obtained by the use of the Kramers-Kronig (KK) transformation [200-201]. Although such a technique has been used since 1959 [202], it is still a subject of ongoing research. More information about its validity and recent activities on the subject can be found elsewhere [203][204].

Relevant to this ongoing effort to establish an understanding of the UNCD film dielectric properties as a function of the concentration of N₂ gas used in the growth process of the film, reflectance measurements were used to confirm results already obtained, specifically the SE investigations. The reflectance measurements were conducted on the three UNCD samples used in the SE studies. Normal incident light has been directed on the films surfaces and reflection amplitudes were measured by the Filmetrics instrument available at the clean room of CNM at ANL. This instrument was also utilized to find thicknesses of all the UNCD samples subjected to this research. That served as a good way to double check the sample thicknesses obtained by other means as well.

Figure 5.4.1 presents the refractive indices as obtained from the reflectance spectroscopy of the UNCD/W/Si films deposited with different concentrations of N₂ in their growth plasma. These results are in good agreement with the earlier data.
(Figure 5.2.4) obtained by the spectroscopic ellipsometry. This finding and the results extracted from the UV/VIS spectroscopy confirm the validity of the optical models built for the data analysis in the spectroscopic ellipsometry studies. Moreover, the thickness results obtained by the reflectance measurements have good agreements with the data on the UNCD films thicknesses found by the RBS and SE investigations. Table 5.1 lists thicknesses of the UNCD films as depicted from the reflectance spectroscopy.

![Graph of refractive indices](image)

**Figure 5.4.1** Refractive indices measured by the reflectance spectroscopy on the UNCD films. From the data, the $n$ coefficient behaves as a function of wavelength ($\lambda$) and $N_2$ gas content mixed with the film growth plasma.
Table 5.1 Thickness of the UNCD samples on different substrates deposited with different $^{14}$N$_2$ and $^{15}$N$_2$ concentrations. Thickness estimations carried out by the use of reflectance spectroscopy.

<table>
<thead>
<tr>
<th>Film ID</th>
<th>$d$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{15}$N-UNCD/Si</td>
<td>294.14</td>
</tr>
<tr>
<td>$^{15}$N-UNCD/W/Si</td>
<td>401.55</td>
</tr>
<tr>
<td>UNCD/W/Si (0% N$_2$)</td>
<td>142.69</td>
</tr>
<tr>
<td>$^{14}$N-UNCD/W/Si (10% N$_2$)</td>
<td>139.31</td>
</tr>
<tr>
<td>$^{14}$N-UNCD/W/Si (20% N$_2$)</td>
<td>150.29</td>
</tr>
<tr>
<td>UNCD/SiO$_2$ (0% N$_2$)</td>
<td>71.1</td>
</tr>
<tr>
<td>$^{14}$N-UNCD/SiO$_2$ (10% N$_2$)</td>
<td>350.0</td>
</tr>
<tr>
<td>$^{14}$N-UNCD/SiO$_2$ (20% N$_2$)</td>
<td>522.6</td>
</tr>
</tbody>
</table>
CHAPTER 6

CONCLUSION

The detailed studies given in the previous chapters of this dissertation are an attempt to understand a complex material. Ultrananocrystalline diamond (UNCD) film is a material that has inspired a substantial number of researchers and technologists around the globe in recent years. It is a promising material with many superlative properties, as that of diamond. Ever since the discoveries of methods to deposit films of diamond, the interest in these materials has increased several fold and to this date diamond and diamond thin films are under intense investigations. Material investigations using thin films have many advantages such as utilizing state of the art spectroscopy techniques which can precisely measure the properties and accurately determine the differences brought upon by the changing of the deposition parameters. UNCD is a special class of nanodiamond thin films that are getting increasing attention because of the smooth surface and phase purity. Moreover, by manipulating its nanostructure the conductivity of the material can be increased and is being considered for device applications. The making of the UNCD films is relatively easy and commonly done using chemical vapor deposition techniques; however, characterizing them is a cumbersome task. The studies presented in this dissertation
show a great deal of effort that went into the characterization of the nitrogen-incorporated UNCD films. The theme of the work presented was to study properties; in particular, the structural, optical, and vibrational properties of the UNCD film with respect to the growth conditions. This leads us toward a greater understanding of the dielectric properties of the film. One of the variables, which was the main topic of this work, is the effect on the properties of the UNCD film when different N₂ gas concentrations are added to the growth plasma. After the deposition of the UNCD films, a set of basic characterizing techniques such as scanning electron microscopy (SEM), atomic force microscopy (AFM), and Raman spectroscopy have been systemically used.

Raman spectroscopy of the UNCD films have shown an increase of the sp² bonds in the film matrix as N₂ gas content in the growth plasma is increased. In addition, by comparative analysis of the Raman spectra, it was concluded that the nanostructures have been modified by the addition of N₂ gas into the growth plasma. In particular, increased grains and grain boundary sizes have been seen due to nitrogen addition to the growth plasma. AFM and SEM investigation on films lead to the same conclusions as well. In addition, AFM studies revealed an increase of the film roughness as a function of increasing N₂ content in the growth plasma.

The understanding of the effects of the changes in the nanostructure of the UNCD film due to N incorporation in the film is important, not only from the fundamental point of view but also for the possible applications of UNCDs in MEMS
and NEMs devices. In general the correlation of the UNCD film properties with its nanostructure depends upon the elemental concentrations of the film. Therefore, it is important to quantitatively determine the amount of nitrogen, hydrogen, and other impurities incorporated in the film during film growth. For that, ion beam analysis techniques have been utilized as a powerful means to probe the elemental composition and thicknesses of the UNCD films. RBS and ERDA analysis on the UNCD films have shown that the deposited films have 90-93 at. % of C and 8-9 at. % of H. From the RBS results it can be seen that there is some intermixing between the W interlayer the and the UNCD film. NRA was used to estimate N content in the UNCD films. These films were deposited with varying N2 gas percentages in their growth plasma. Estimations of N2 content incorporated in the UNCD film by the use of regular NRA techniques were inconclusive. Therefore, RNRA, in particular particle-induced gamma emission (PIGE) analysis was used. Depth-profiling analysis of 15N atoms in the 15N incorporated UNCD films was carried out by collecting gamma particles resulting from 15N (p, αγ) 12C nuclear reactions. UNCD films deposited with 20% of 15N2 gas in their growth plasma were prepared especially for the RNRA studies in order to take advantage of the high sensitivity and narrow resonance of the 15N (p, α1γ) 12C nuclear reaction. The results of the RNRA analysis showed that about 0.13 at. % of N atoms is incorporated in the UNCD film deposited with 20% of N2 content in its growth plasma. This total amount of N atoms was found to be uniformly distributed throughout the depth of the UNCD layer in the film. We have not found any evidence that the measurements of this kind have been done on
UNCD materials. Therefore, we believe that we are the first to report the reliable values of N content trapped in the UNCD films.

A main tool used for the optical measurements is the spectroscopic ellipsometry (SE), which is a powerful technique to obtain optical/dielectric constants of a film. Optical models were constructed and used to analyze the SE data; therefore, solid state theories were used to obtain the dielectric properties of the UNCD films. The real and imaginary optical/dielectric coefficients of the UNCD films were shown to vary with the N\textsubscript{2} content presented into the growth plasma. The dielectric functions of the UNCD film were seen to decrease with increasing N\textsubscript{2} gas concentration in the film growth plasma. As a consequence, absorption and transmission properties of the film were altered. The optical band gaps of the UNCD samples were found to be 2.1 eV, 1.2 eV, and 0.8 eV for N\textsubscript{2} gas concentrations in the plasma 0, 10, and 20\%. The UV/VIS spectroscopy was used to investigate the UNCD film vibrational properties which served to confirm the results from the SE studies. The UNCD film deposited with 0\% of N\textsubscript{2} was found to have an excellent transmittance in visible and IR regions. The transmission of the light in the UNCD films deposited with 10\% and 20\% of N\textsubscript{2} decreased in the visible region but stayed high in the IR region. In general, transmission was found to decrease as nitrogen gas content increased in the plasma mixture of the film.

Dielectric coefficients and energy gap values of the UNCD films obtained by the UV/VIS technique had excellent agreement with the results of the SE work on the films. The agreement established the authenticity of the optical models built to
analyze the measured SE data. Furthermore, reflectance spectroscopy was used as an additional confirmational technique for the findings from the SE and UV/VIS studies. Reflectance data have also agreed with the results extracted from the UV/VIS and SE investigations. More important, reflectance measurements were a valuable technique for the thickness estimation of the UNCD films, which were used as another way to find the film thicknesses in addition to IBA and SEM techniques.

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