Raman Microscopic Analysis of Internal Stress in Boron-doped Diamond Thin Films

Emma M.a. Sundin

University of Texas at El Paso, emsundin@miners.utep.edu

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RAMAN MICROSCOPIC ANALYSIS OF INTERNAL STRESS IN BORON-DOPED DIAMOND THIN FILMS

EMMA MARTA ADELAIDE SUNDIN
Master’s Program in Physics

APPROVED:

______________________________
Felicia S. Manciu, Ph.D., Chair

______________________________
Stephen W. Stafford, Ph.D.

______________________________
Marian Manciu, Ph.D.

______________________________
William G. Durrer, Ph.D.

______________________________
Charles Ambler, Ph.D.
Dean of the Graduate School
Dedication

I dedicate this thesis to my parents, with love.
CHARACTERIZATION OF INTERNAL STRESS IN BORON DOPED DIAMOND THIN FILMS BY RAMAN MICROSCOPY

by

EMMA MARTA ADELAIDE SUNDIN, BSc Physics

THESIS

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Abstract

The correlations between induced stress on undoped and boron-doped diamond (BDD) thin films, sample chemical composition, and fabrication substrate are investigated in this study via confocal Raman microspectroscopic analysis. Stability of BDD films is relevant to fast-scan cyclic voltammetry, as film delamination and dislocation of BDD-coated electrodes that can occur during neurosurgical electrode implantation can negatively impact the biosensing reliability of this technique. Electrodes were fabricated by coating cylindrical tungsten rods using a custom-built chemical vapor deposition reactor. The results of the analysis reveal a direct correlation between regions of pure diamond and enhanced material stress, as well as preferential boron incorporation into the diamond lattice. Higher amounts of boron addition were shown by the Raman mapping to coincide with definite stress release throughout the entire film thickness. Additionally, \( \text{sp}^2 \) type carbon impurities may contribute to high values of compressive stress beyond those predicted by the film—substrate lattice mismatch.
Table of Contents

Acknowledgements ........................................................................................................... v

Abstract .............................................................................................................................. vi

Table of Contents ............................................................................................................... vii

List of Figures ...................................................................................................................... viii

Chapter 1: Introduction .................................................................................................... 1
  1.1 Scope and Motivation ................................................................................................. 2
  1.2 Boron-doped Diamond Thin Films ........................................................................... 3

Chapter 2: Experimental Methods ................................................................................... 5
  2.1 Sample Preparation ................................................................................................. 5
    2.1.1 Fabrication of Samples ..................................................................................... 5
    2.1.2 Preparation for Mapping .................................................................................. 7
  2.2 Raman Microscopy ................................................................................................. 8
    2.2.1 Raman Scattering ............................................................................................. 8
    2.2.2 Confocal Raman Microspectroscopy ..................................................................10
    2.2.3 Stress Analysis .................................................................................................15

Chapter 3: Results and Discussion .................................................................................. 16
  3.1 Boron Incorporation ............................................................................................... 16
  3.2 Carbon Impurities ................................................................................................. 21
  3.3 Internal Stress ........................................................................................................ 24
    3.3.1 Distribution of Internal Stress ......................................................................... 24
    3.3.2 Correlation with Boron Incorporation ............................................................. 25
    3.3.3 Double-layer Sample ...................................................................................... 25

Chapter 4: Conclusion ..................................................................................................... 27

References ......................................................................................................................... 28

Vita 32
List of Figures

Figure 2.1: Chemical vapor deposition reactor, Mayo Clinic ........................................ 7
Figure 2.2: Energy-level diagram of Stokes and anti-Stokes Raman scattering .............. 10
Figure 2.3: WITec alpha 300R system ........................................................................ 11
Figure 2.4: WITec alpha 300R light path diagram ......................................................... 12
Figure 2.5: Diagram of confocal microscope beam path ............................................... 14
Figure 3.1: Undoped diamond thin film, surface mapping ........................................... 18
Figure 3.2: Lightly boron-doped diamond thin film on W substrate, surface mapping .... 19
Figure 3.3: Heavily boron-doped diamond thin film on W substrate, surface view ........ 20
Figure 3.4: Undoped and lightly boron-doped thin films on W substrate, side-wall mappings 22
Figure 3.5: Heavily boron-doped thin films on W substrate, side-wall mappings .......... 23
Chapter 1: Introduction

This thesis presents a study of the effects of boron doping on the internal stress found in fabricated diamond materials, specifically in thin films grown on wire-like cylindrical tungsten substrates.

Diamond materials are of interest because of their useful properties such as hardness and chemical inertness in a biological environment [1]. These properties make diamond coatings promising for medical applications.

One such application, and the larger long-term goal of the work presented in this thesis, is the application of diamond coatings to the electrodes used in deep brain stimulation (DBS). The samples studied come from a collaboration with the Mayo Clinic, where they were produced in a custom-built reactor by collaborators.

The work presented here uses the optical imaging technique of Raman confocal microspectroscopic mapping in order to study the boron-doped diamond thin films on these coated electrodes. Raman microspectroscopy is an imaging technique that combines microscopy and spectroscopy [2]. The spectroscopic aspect of this technique permits observation of the vibrational states of a material’s constituent molecular bonds, and therefore to characterization of the molecular composition of a sample; the microscopic element allows very small regions of the sample to be probed at high magnification. Combined into a single technique, Raman microspectroscopy therefore allows an investigator to collect data that may then be used to produce highly magnified images or mappings of a sample with regions of different molecular composition made visible by false color. The data collected may also be analyzed in other ways, including analysis to calculate and visualize internal stress in a material by measuring the
differential shifts of Raman spectral signatures. In regards to the current study, such analysis allows the identification of electrodes with low internal stress; low stress corresponds to more stable diamond material, which is desirable in this application.

Raman microspectroscopy is used in this investigation to probe three main points of interest: first, whether boron is in fact successfully incorporated into the diamond crystal lattice; second, how boron incorporated into diamond affects the material’s internal stress; and third, whether impurities are being incorporated during fabrication, and, if so, their effects on the material’s internal stress.

1.1 Scope and Motivation

This thesis focuses on the analysis of the boron-doped diamond thin film material grown on the substrate. The specifics of the fabrication of these materials by chemical vapor deposition (CVD) is outside the scope of the current work, and was performed by collaborators (K.E. Bennet, K.H. Lee, J. Tomshine, and others). The methods are, however, touched upon briefly at the end of Chapter 2, in Section 2.2.1, Fabrication of Samples. The author directs the interested reader to the referenced sources, especially [1], in which is found a more detailed description of the fabrication process.

The motivation and long-range application of the work here presented is, as stated above, the fabrication of more robust electrodes for use in deep brain stimulation (DBS). DBS is a therapeutic technique in which electrical impulses are delivered to the inner regions of the brain by means of electrodes. The technique, which was developed in the 1980’s, has been used successfully as a therapy for Parkinson’s disease, chronic pain, and major depression [1], [3]. The stability of the electrodes used in DBS can be improved by applying a thin film of diamond to the outside of the electrode [1]. Furthermore, incorporation of boron atoms into the diamond
(“doping”) has been shown to improve this thin film by reducing the internal stress in the diamond lattice, essentially making the coating less fragile. By studying the differences in boron-doped diamond thin-film coated electrodes produced by different methods and with different amounts of boron, superior fabrication techniques can be distinguished and better electrodes produced.

1.2 Boron-doped Diamond Thin Films

The properties of diamond, which include high hardness and high charge carrier mobilities, make it an attractive material for biomedical and electrochemical applications [4].

Pure diamond is naturally an excellent electrical insulator, a semiconductor with a wide band gap of 5.45 eV [4]–[6]. Therefore, some modification of diamond is necessary if it is to be used as a material in electrodes. That is, the diamond material must be made capable of conducting electricity if it is to function as an electrode in aqueous (biological) environments. Such a modification is easily achieved by the use of chemical vapor deposition (CVD) and the introduction of boron into the diamond crystal lattice [6]. This incorporation is known as doping. Boron doping of diamond changes the diamond’s electrical properties, turning it into a p-type semiconductor.

The fabrication technique of CVD allows for the production of diamond thin films on a substrate, and, if a dopant is introduced into the reactor, the production of doped diamond films. One important factor regarding electrodes produced in this way, and which effects the durability of the electrodes and their thin-film coatings in the long term, is induced stress, caused either during fabrication or after, perhaps during neurosurgical implantation. The appropriate choice of substrate—ideally one with properties (surface energy, lattice type, structure, and thermal properties) that are closely matched to those of the doped diamond thin film to be applied—can
help to reduce the internal stress in the coating material. Of the possible substrates, the surface energy and lattice constant of tungsten (W) most closely resemble those of diamond: the approximate surface energy of tungsten at melting temperature is 3111 ergs/cm², while the surface energy of diamond is approximately 330 ergs/cm². Tungsten has a lattice constant of 3.16 Å, while diamond’s lattice constant is 3.75 Å [7], [8]. Tungsten differs significantly from diamond in a couple of ways. First, tungsten and diamond have different coefficients of thermal expansion: tungsten has a larger coefficient of $4.3 \times 10^{-6}$/K, while diamond has a coefficient of only $1.18 \times 10^{-6}$/K. Furthermore, tungsten and diamond are structurally dissimilar: the lattice structure of tungsten is body-centered cubic (BCC), while that of diamond is face-centered cubic (FCC) [7], [9].

The internal stress in the diamond thin film material is also affected by the temperature used in the CVD reactor during growth of the films, by the substrate shape, and by the pressures of the gasses used in the reactor [1], [7], [8], [10]–[14].
Chapter 2: Experimental Methods

The samples in this study were fabricated by collaborating investigators at the Mayo Clinic using a custom-built chemical vapor deposition (CVD) reactor. Varying concentrations of feed gases were introduced into this reactor to form doped diamond thin films on cylindrical tungsten metal substrates. Raman confocal microscopy was then used to map incorporation of boron dopant into the crystal lattice of the diamond thin-film samples. In addition, the Raman microscopic data collected were also analyzed to map internal stress present in these samples.

2.1 Sample Preparation

The samples were prepared by collaborators at the Mayo Clinic in a custom-built CVD reactor. Before mapping, samples were dry-mounted using glass slides and clamps. After surface mapping as performed, samples were cut using shears to allow for cross-sectional mapping of thin films.

2.1.1 Fabrication of Samples

The samples consist of boron-doped diamond thin films grown on cylindrical tungsten substrates. Before CVD was performed, the tungsten substrates were etched electrochemically by immersing in 1 M NaOH. After this they were abraded using sonication and a slurry of diamond powder grit and isopropyl alcohol for 30 minutes. As a final step, the substrate rods were rinsed with deionized water.

After etching of the substrates, the BDD films were grown on them using a custom-built hot-filament CVD reactor (Figure 2.5) located at the Mayo Clinic [1], [15]. The gases present in the reactor were nominally 99% H₂ and 1% CH₄. The reactor chamber pressure was held at 20 Torr during film production. In order to more uniformly distribute the films, the reactor included a feature that allowed rotating of the electrodes during deposition, parallel to the filament coil central axis. To achieve filament and substrate temperatures of 2300 °C and 800 °C respectively,
a proportional integral derivative (PID) software control loop was employed to ramp the power up to 450 W. Stability of filament temperature was monitored using a Spectrodyne DFP 200 optical pyrometer; stability of substrate temperature was monitored using an Omega Engineering type K thermocouple.

To obtain thin films with different amounts of boron doping, different amounts of trimethylborane (TMB) flow gas were released into the chamber (1000 ppm in H gas, Voltaix Products, Branchburg, NJ, USA). To obtain lightly doped films, 10 ppm TMB (2 sccm TMB/hydrogen, 2 sccm methane, 196 sccm hydrogen) chamber concentrations were used. To obtain heavily doped films, the chamber concentration was increased by a factor of ten to 100 ppm (20 sccm TMB/hydrogen, 2 sccm methane, 178 sccm hydrogen). Undoped films were produced under identical temperatures but with no TMB (2 sccm methane, 198 sccm hydrogen).[15]
2.1.2 Preparation for Mapping

All samples were dry mounted for the mappings and spectra presented (Figures 3.1-5). For surface mappings (Figures 3.1, 3.2, 3.3), the samples were affixed to glass slides using adhesive tape; no further preparation was performed for these mappings. For side-wall mappings (Figures 3.4, 3.5), the samples were first cross-sectioned transversely using shears. The cuts were made approximately 1 cm from the tapered end of the sample. These short segments were then mounted upright in a small rubber-cushioned clamp, which was then positioned on the microscope stage. In the case of Figure 3.5a-c, a second cut was made ~200 µm from the tapered end to expose only the extreme tip of the cylindrical tungsten substrate, which appears in these mappings as a dark central disk.
2.2 Raman Microscopy

Raman microspectroscopy is a spectroscopic technique that can be used to characterize samples at the molecular level and at microscopic scales. It is based on the theory of Raman scattering, an inelastic photon scattering phenomenon first described by C.V. Raman in 1928 [16].

The specific technique used to collect the results presented in this thesis was confocal Raman microspectroscopy. This technique combines the techniques of Raman spectroscopy with those of confocal microscopy. The combination of these techniques allows for mapping of small regions of a material’s surface: for each point in the resulting image, a Raman spectrum is recorded; these spectra are then analyzed and combined to create a false-color 2D image of the microscopic region under study, with different false-colors indicating different molecular signatures of interest. The spectra may also be analyzed to provide insight into the internal stress of the material.

2.2.1 Raman Scattering

Raman scattering is an inelastic photon scattering phenomenon first described by C.V. Raman in 1928 [16]. Among the different kinds of scattering events possible, Raman scattering is statistically very rare, occurring in only about one in $10^7$ photon collisions. The vast remainder of scattering events in photon—matter collisions is predominantly composed of forms of elastic scattering, such as Raleigh scattering.

Because the cross section for Raman scattering is so low, in order to detect the Raman effect, it is necessary to use a light source that is both very strong and of very consistent
wavelength. In modern Raman spectroscopy, this source is a laser. In early experiments performed by C.V. Raman, heavily filtered and concentrated sunlight was used as the excitation source.[16]

When a photon is scattered by the Raman effect, its energy, and thus frequency, is changed (Fig. 2.1). Usually this change is observed as a decrease in energy (and therefore a decrease in frequency). This phenomenon, where the incident photon loses energy to the molecule, is known as Stokes-Raman scattering. However, in some cases an increase in energy can also occur. This Raman scattering phenomenon is conversely referred to as Anti-Stokes Raman scattering. In either case, the wavelength of the scattered photon is given by the equation

$$\nu = \nu_0 - \frac{\Delta E}{h}$$

The precise wavelength shifts caused by Raman scattering (and the aggregate numbers of photons experiencing shifts---the measured intensity of a shift) differ distinctively depending on the particular mix of bonds present in a molecular sample. Spectroscopic techniques based on Raman scattering are therefore able to probe the vibrational and rotational properties of the bonds in a molecule, and can identify different species of closely related molecules to a high degree of precision and with great sensitivity.

Furthermore, Raman spectroscopy has the advantage of being unimpeded by the presence of water. In contrast, infrared spectroscopic techniques cannot be used on such aqueous samples. This is because water absorbs the infrared (IR) light used as the excitation source for IR-based spectroscopy. As Raman uses, instead, as the excitation source, laser light in the visible wavelengths, this technique is minimally affected by the presence of water in the sample.
An alpha 300R WITec system in the Optical Spectroscopy and Microscopy Laboratory at The University of Texas at El Paso, pictured in Figure 2.2, was used for acquisition of the data presented in Chapter 3. The main components of this system comprise a confocal microscope, a white-light illumination source, a laser excitation source, a diffraction grating, control electronics, and a computer software interface. The software interface consists of two main components: the *WITec Control* software, which is used for control of the system, including maneuvering of the microscope stage, control of illumination, and image and spectral acquisition; and the *WITec Project Plus Advanced Fitting Tool*, which is used for analysis of the collected Raman spectroscopic data.
The WITec alpha 300R system allows observation of the sample through two main beam paths. Each beam path uses a separate illumination source of either white-light or laser, chosen appropriate to its application.

The first beam path, using the white-light lamp illumination source, is used for visual orientation and image acquisition of the sample. The beam from the white-light illumination source (marked “09” in Fig. 2.3) enters the confocal optics and is directed down by the
beamsplitter. The white-light beam is then focused onto the sample from above (direct illumination). An image of the sample is then focused by the objective lens (of power 20x, 50x, or 100x, interchangeably) up through the optics and ultimately onto a small CCD camera mounted on the eyepiece. This camera is connected to the computer system, and allows real-time observation of the sample surface, positioning of the sample, and acquisition of white-light illuminated images.

![Figure 2.4: WITec alpha 300R light path diagram](image)

Diagram showing the light path of the WITec alpha 300R Raman microscope setup used, with components labeled: 1) Excitation laser (532 nm Nd:YAG, in this case), 2) Optical fiber, 3) Objective lenses, 4) Scan table, 5) Filter set, 6) Optical fiber, 7) Lens-based spectroscopy system (diffraction grating setup), 8) CCD detector, 9) White-light illumination, 10) Z-stage for focusing [29]

The second beam path uses a green excitation laser and diffraction grating, in combination with the confocal optics, to collect spectroscopic data on the sample. The excitation
source used for this thesis was a 532 nm Nd:YAG laser (neodymium-doped yttrium aluminum garnet). In this light path, the beam proceeds from the excitation laser via an optical fiber into the confocal microscope optics (Fig. 2.4). From this point, as in the white-light path, the laser light is directed to the sample by the beamsplitter, which directs a portion of the beam down towards the sample. The beam is then focused by the objective lens onto the plane of focus (for measurement made level with the sample depth). The laser light, now focused onto a very small area of the sample, scatters off the sample. As described earlier in this chapter, a small portion of the 532 nm photons interact with the sample’s molecular bonds and are scattered in accordance with the Raman effect, and consequently change wavelength (i.e., these photons gain or lose energy). The far greater part of the scattered photons that do not experience Raman scattering are instead scattered by Rayleigh scattering, and thus retain their original 532 nm wavelength. These Rayleigh-scattered photons are absorbed by the filter set (marked “05” in Fig. 2.3), essentially removing them from the beam. This filtered beam, which is composed only of the Raman-scattered photons (within the efficiency limits of the filter), is then directed to the diffraction grating (marked “07” in Fig. 2.3) via another optical fiber. Here, the beam is spread out into its component wavelengths, which are recorded by the CCD and relayed to the computer system for analysis.
As explained earlier in this chapter, the amount of energy lost by the incident photons during Raman scattering determines shifts in photon wavelength from that of the excitation laser. In Raman spectroscopy, these shifts in wavelength are customarily expressed in terms of wavenumber (cm$^{-1}$). These shifts correspond to different magnitudes of energy loss by the excitation photons, and correspond to different vibrational interactions. When viewed in aggregate over many photons, these shifts correspond to specific molecular signatures. The number of photons measured by the CCD detector at each of the various energies corresponds to the intensity of each of the respective Raman spectroscopic peaks found at different shifts.

Figure 2.5: Diagram of confocal microscope beam path
This diagram shows a simplified view of the light-path of a standard confocal microscope. The light enters from the left, at the point labeled “Point light source” (through another pinhole, not shown), is redirected towards the focus plane. The light scattered off the sample/focus plane is directed through another pinhole (shown at top, here) before entering the detector. [30]
The mechanism behind the inelastic interaction between photons and crystalline or molecular bonds observed with Raman scattering is the photons’ interaction with vibrations within the lattice or the molecule. These bond vibrations are present in discrete (quantized) excited states, or modes, and are known as phonons (the term chosen for its parallel to the use of the word “photons” to refer to discrete quanta of electromagnetic energy) in crystalline structures such as that of diamond.

In addition to single-spectrum acquisition at a small point on a sample, the system also allows 2D mapping of samples. These mappings are achieved by the recording of point spectrographic measurements at each of many progressive points in a 2D region. This is achieved by moving the motorized microscope stage, which is under software control. Once a 2D spectroscopic dataset of the region is built up, the spectra may then be filtered by the analysis software to allow the creation of false-color images based on Raman signatures corresponding to specific molecular compositions.

2.2.3 Stress Analysis

The WITec Project Plus Advanced Fitting Tool software is capable of performing analysis to probe the internal stress of a material. This analysis technique was used to produce the stress mappings shown in Figures 3.1-3c, and 3.4-5 c and f. The mechanism for this analysis is based on measuring the magnitude of the wavelength shift of characteristic Raman peaks. For example, the magnitude of the diamond peak shifts proportionally with the magnitude of internal stress in the material [14], [15], [17]–[19]. When the material is under stress, the characteristic Raman line for pure diamond, at 1332 cm\(^{-1}\), has been shown to shift \(~3\) cm\(^{-1}\)/1 GPa [20]–[23]. These shifts may therefore be analyzed at each point in the Raman mapping to produce a heatmap showing the amounts of internal stress in the materials.
Chapter 3: Results and Discussion

This chapter presents the results of the measurements performed on the samples. Samples with three different levels of boron doping were measured: undoped (Figures 3.1a-d and 3.4a-c), lightly doped (Figures 3.2a-d and 3.4d-f), and heavily doped (Figures 3.3a-d and 3.5a-f). For individual samples with each of these levels of doping, both surface mappings and side-wall mappings were taken. False-coloring in the mappings is used to show regions of different molecular composition. Mappings of internal stress were also produced for both surface and side-wall mappings. Lastly, integrated single-spectra were also acquired for samples at each level of doping.

3.1 Boron Incorporation

Figures 3.1-3a,b and 3.4,5a,b,d,e present Raman morphological mapping of the samples. The following Raman vibrational line values were used for the coloration of the figures [4], [15], [24]–[26]: The characteristic Raman vibrational line at 1332 ± 2 cm\(^{-1}\) was chosen for diamond. Diamond is represented by red false color in Figures 3.1-3a,b and 3.4,5a,b,d,e. For boron incorporation, the line at 1200 cm\(^{-1}\) was used; for paired boron atoms (accumulation in the diamond lattice), the line at 500 cm\(^{-1}\) was used. Both types of boron are represented by blue false color in Figures 3.1-3a,b and in 3.4-5a,b,d,e. For sp\(^2\) carbon impurities the band centered at 1500 cm\(^{-1}\) was used. Carbon impurities are represented by green false color in Figures 3.1-3a and in 3.4-5a.

In the false-colored mappings, the simultaneous presence of two or more of the analyzed materials (pure diamond, boron, and sp\(^2\) carbon) is visible as a new color due to additive mixing of the false colors used. Specifically, regions that appear yellow (in the morphological mappings,
not in the stress mappings) contain a combination of coincident boron and carbon impurities, because yellow is the additive result of mixing red and green. Regions that appear magenta mark those regions that possess coincident boron and diamond, because magenta is the additive result of mixing blue and red. White regions (as in, e.g., Figure 3.2a) mark areas that possess all three colors/materials: diamond, boron, and sp$_2$ carbon.

Boron is observed to incorporate non-uniformly throughout the material, as seen in Figures 3.2b and 3.3b. In these figures, in order to better view boron incorporation, only pure diamond (red) and boron (blue) are visualized by false color, and sp$_2$ carbon is not visualized. In both Figures 3.2b and 3.3b, regions of pure diamond are still present. These regions are visualized by red color in the figures, and represent regions of the film where no boron has been incorporated into the diamond lattice. This uneven incorporation is caused by the known phenomenon of boron’s preferential incorporation into the diamond lattice [1], [10], [25]–[28]. The boron incorporation is seen to be more uniform in the lightly doped sample than in the heavily doped sample. This greater uniformity is seen in the uniform magenta color in Figure 3.2b, which represents an even distribution of diamond (red color) and boron (blue color). The less uniform incorporation in the heavily doped sample can be explained by boron’s tendency to incorporate interstitially (i.e., at crystal boundaries) after it has first substituted for carbon. In some cases, for higher doping amounts, it may aggregate as molecular boron. The methods of incorporation for boron concentrations >10$^{20}$ atoms/cm$^3$ (the levels that confer conductive properties to diamond) are incompletely understood at present [8], [15]. The presence of this interstitial boron has been reported to be the cause of the much higher thermal expansion coefficient in heavily boron-doped diamond films, when compared to undoped diamond films [8].
Figure 3.1: Undoped diamond thin film, surface mapping
Raman mappings showing a surface view of undoped diamond thin film on tungsten substrate. Mapping (a) shows regions of pure diamond as red and carbon impurities as green. In this sample, the distribution of diamond and carbon impurities is such that the false coloring combines to display yellow (red and green). Mapping (b) shows only the diamond component (as red), while impurities are not colored; (c) shows a stress mapping, with regions of higher stress indicated by bright yellow, and of lower stress by darker yellow/brown; (d) presents an integrated single spectrum for this sample, showing the characteristic peaks for diamond and carbon impurities. [15]
Figure 3.2: Lightly boron-doped diamond thin film on W substrate, surface mapping
Raman mappings showing a surface view of a lightly doped diamond thin film on tungsten substrate. Mapping (a) shows regions of pure diamond as red, paired boron atoms as blue, and carbon impurities as green. Mapping (b) shows only the diamond component (as red) and the boron component (as blue); impurities are not colored; (c) shows a stress mapping of the same sample, with regions of higher stress indicated by bright yellow, and of lower stress by darker yellow/brown; (d) presents an integrated single spectrum for this sample, showing the characteristic peaks for paired boron, pure diamond, and carbon impurities. [15]
Figure 3.3: Heavily boron-doped diamond thin film on W substrate, surface view
Raman mappings showing a surface view of a heavily boron-doped diamond thin film on tungsten substrate. Mapping (a) shows regions of pure diamond as red, paired boron atoms as blue, and carbon impurities as green. Mapping (b) shows only the diamond component (as red) and the boron component (as blue); impurities are not colored; (c) shows a stress mapping of the same sample, with regions of higher stress indicated by bright yellow, and of lower stress by darker yellow/brown; (d) presents an integrated single spectrum for this sample, showing the characteristic peaks for paired boron, diamond, and carbon impurities. [15]
3.2 Carbon Impurities

Greater levels of boron accompany a decrease in sp\(^2\) carbon, as seen by a comparison of figures 3.1a, 3.2a, and 3.3a. The undoped sample, Figure 3.1a, displays high levels of sp\(^2\) carbon: there is an abundance of both pure diamond (red) and carbon (green), resulting in the even yellow false color seen (yellow being the additive result of mixing red and green). The lightly doped sample, Figure 3.2a, displays reduced levels of sp\(^2\) carbon compared to the undoped sample. The heavily doped sample, Figure 3.3a, also displays little sp\(^2\) carbon. These observations from the mappings can be confirmed by inspection of the single-spectrum integrations presented in Figures 3.1-3d: the peak around 1500 cm\(^{-1}\) has much larger amplitude in the undoped sample (Figure 3.1) when compared to the lightly and heavily doped samples (Figures 3.2 and 3.3). Therefore, we may conclude that the addition of boron improves the quality of the deposited diamond material by reducing the amount of carbon impurities present and increasing the speed of crystallization [15].

In the side wall morphological mappings, high concentrations of sp\(^2\) carbon impurities were observed at the interface between the tungsten substrate and the film (Figures 3.4a,d and 3.5a,d).
Figure 3.4: Undoped and lightly boron-doped thin films on W substrate, side-wall mappings

Raman mappings showing side-wall (cross sectional) views of (left) an undoped diamond thin film and (right) a lightly boron-doped diamond thin film, both on tungsten substrates. Mappings (a) and (d) show regions of pure diamond as red, paired boron atoms as blue (d only), and carbon impurities as green. Mappings (b) and (e) show the same two samples (undoped on left, lightly doped on right), but only coloring the diamond component (as red) and the boron component (as blue), and not showing carbon impurities, for clarity. Finally, mappings (c) and (f) shows stress mapping of these same two samples, with regions of higher stress indicated by bright yellow, and of lower stress by darker yellow/brown. [15]
Figure 3.5: Heavily boron-doped thin films on W substrate, side-wall mappings
Raman mappings showing cross-sectional views of two different samples of heavily boron-doped diamond thin film on tungsten substrates, sectioned transversely. Mappings on left (a-c) are of a sample that has been sectioned near the tapered end (note small diameter). Mappings on right (d-f) show another sample that has been sectioned nearer the middle, presenting a side-wall view. Mappings (a) and (d) show regions of pure diamond as red, paired boron atoms as blue, and carbon impurities as green. Mappings (b) and (e) show the same two samples, but only coloring the diamond component (as red) and the boron component (as blue), and for clarity not coloring carbon impurities. Finally, mappings (c) and (f) shows stress mapping of these same two samples, with regions of higher stress indicated by bright yellow, and of lower stress by darker yellow/brown. [15]
3.3 Internal Stress

Stress mappings produced by surface confocal Raman microspectroscopy are presented in Figures 3.1c, 3.2c, and 3.3c, 3.4c,f, and 3.5c,f. The mappings have been colored to indicate the relative computed magnitudes of internal stress in different regions of the mappings. Regions with high internal stress appear as a bright yellow color, while regions of low internal stress appear dark brown in color. The following sections present the results of the stress mapping and provide accompanying discussion.

In terms of quantification of stress, internal stresses in the materials are seen as shifts from established Raman characterization lines by positive shifts of $4.5 \pm 2$ to $12 \pm 2 \text{ cm}^{-1}$. This corresponds to internal stresses of 1.5 to 4 GPa [15]. (For further details on the analysis method used, refer to Section 2.1.3, Stress Analysis.) The higher stresses were found in the undoped diamond films, while the lower stresses were found in the boron-doped films.

3.3.1 Distribution of Internal Stress

The lattice mismatch between tungsten and diamond is one source of induced stress in films. Induced stress from this cause is expected to be greater nearer the tungsten–diamond interface. This is in fact observed in Figures 3.4c,f and 3.5c,f, which present stress mappings of film side walls: the films exhibit greater internal stress (seen as a brighter yellow color) along the inner surfaces, which are in contact with the tungsten substrate.

Carbon impurities are seen to accumulate near the film–substrate interface (Figures 4a,d and 5a,d). This region is correlated with higher internal stress in the stress mappings. However, no tungsten carbide was observed in the samples.
Also seen is that stress is much less nearer the surface of the material (i.e., further away from the substrate). This could be caused by relaxation of the grain boundaries occurring at the surface of the film.

3.3.2 Correlation with Boron Incorporation

The side-wall morphological mappings again show more uniform incorporation of boron into the diamond lattice for the lightly doped sample than for the heavily doped sample: Figure 3.4e is seen to be a uniform magenta color, which indicates the uniform simultaneous presence of diamond (red) and boron (blue) throughout the material. Figure 3.5b, in contrast, which presents a heavily doped sample, exhibits discrete regions of boron and pure diamond. The pattern in these heavily doped samples furthermore exhibit a radial, columnar growth. Comparison between the morphological mappings and the corresponding stress mappings again shows a strong correlation of regions of high sp³ carbon impurities (green color) and high concentration of pure diamond (red color) with regions of high internal stress (brighter yellow color in the stress maps). Conversely, higher concentrations of boron (blue color) can be seen to correlate with regions of lower stress (darker yellow and brown colors in the stress maps).

3.3.3 Double-layer Sample

The assumption was made earlier that the release of internal stress in the material is primarily caused by the enhancement of the thermal expansion parameter that occurs when boron is incorporated. To test this, Raman analysis was performed on the side-wall of the sample that contained two layers on the same substrate (Figure 3.5d-f). The inner layer had been lightly doped with boron while the outer layer had been heavily doped.
Of particular interest in this mapping is the fact that, unlike in other samples, the highest stress region is not coincident with the most \( \text{sp}^2 \) carbon impurity-rich region. Therefore, it appears that the lattice mismatch between the diamond and tungsten still has a greater effect on internal material stress than does the presence of carbon impurities.

Also of note is that the more-heavily doped layer corresponds very precisely to a region of lower stress, and the less-doped layer to a region of higher stress. This makes it clear that the boron doping is a very important factor in the stress release seen here.
Chapter 4: Conclusion

In this study, we investigated the boron incorporation in doped diamond thin films on cylindrical tungsten substrates, and the effects of this boron doping on the internal stress in the diamond material. The mappings of boron incorporation and analysis of internal material stress were performed by means of confocal Raman microspectroscopy. We found that the regions in which boron had been incorporated were correlated with lower-stress regions of the material, while regions of pure diamond exhibited higher internal stress. This result strongly suggests that boron doping of diamond materials improves the durability of these materials.

We also observed sp² carbon impurities present in the samples. Regions rich in sp² carbon were found to be coincident with higher stress. This increased internal stress exceeded that which is expected from the lattice mismatch between film and substrate. These results therefore suggest that the presence of sp² carbon impurities may have a deleterious effect on diamond thin film durability.

Both this decrease in internal stress and concomitant increase in diamond material durability with boron doping, as well as a reduction of sp² carbon impurities, may help to reduce the occurrence of delamination events (separation of film from substrate) when diamond-coated electrodes are introduced to biological environments in the neurosurgical applications that form the motivation for this work.
References


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Vita

Emma M.A. Sundin obtained her Bachelor of Science in Physics in 2015 from The University of Texas at El Paso. As an undergraduate student, Ms. Sundin participated in research and coauthored her first publication, “Raman Microscopic Analysis of Internal Stress in Boron-Doped Diamond” [15], and has since appeared as a coauthor on two other articles. Ms. Sundin was a member of UTEP’s chapter of the Society of Physics Students, in which she served as an officer for three years. She has also worked as an undergraduate and graduate teaching assistant.

Contact Information: emsundin@miners.utep.edu

This thesis was typed by the author.