

BRILLOUIN LIGHT SCATTERING OF
ION-IMPLANTED AND ANNEALED DIAMOND
SURFACES

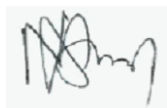
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A thesis submitted to the Faculty of Science, University of the Witwatersrand, Johannesburg, in fulfilment of the requirements for the degree of Doctor of Philosophy.

Johannesburg, July, 2015.

Declaration

I declare that this thesis is my own, unaided work. It is being submitted for the degree of Doctor of Philosophy at the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other university.



(Signature of candidate)

24th day of July 2015

Abstract

The sub-surface region of chemical vapour deposition (CVD) diamond was transformed by C^+ ion implantation followed by isochronal annealing up to 1200 °C. Different implantation regimes and with different energies at different implantation temperatures would give different thicknesses were studied. This enabled a study in the evolution of the stiffness of the damaged layer as a function of annealing. The technique of choice for this study was the non-destructive Brillouin light scattering (BLS) utilizing two scattering geometries; indirectly scattered phonons (Krüger-type geometry) for temperature anneals up to 600 °C, and the conventional surface ripple mechanism up to 1200 °C. It has been argued that surface acoustic waves (SAW) on a transparent medium are enhanced by applying a thin metallic reflective layer on the surface, this study has showed that opacity of the substrate is key. In fact, bulk modes with SAW-like characteristics emanating from indirect photon scattering off phonons after reflection at the smooth reflective back of the sample dominated down to transmission below 5% which was observed after annealing between 500-600 °C (low annealing temperatures). The other complementing techniques employed to understand the changing structure of the ion implanted diamond were Raman spectroscopy, electromagnetic transmission in the visible range, electron energy loss spectroscopy (EELS) and high-resolution transmission electron microscopy (HRTEM) in addition to theoretical techniques: transport of ions in matter (TRIM), finite element modelling (FEM) and elastodynamic Green's functions. Although the electronic techniques showed a structurally changing material at the low annealing temperatures, the optical ones did not show significant changes in the ion-damaged material possibly due to lack of distinct interface between the pristine diamond and the ion irradiated region at these lower annealing temperatures.

SBS has also shown the transition in elastic properties that occur as C⁺ implanted diamond is annealed between 500-600 °C. The transition is from a hard to a softer material, shown by the appearance of slower acoustic modes that do not scale with the sine of angle of incidence. Another important transition occurs after annealing at 1000 °C, when a surface acoustic wave mode for the amorphous region was observed. The velocities of the Rayleigh mode obtained after annealing at 1000 and 1200 °C was within the range of reported Rayleigh velocities of a tetrahedral amorphous carbon (ta-C) ranging from 5100-6700 m/s. Two elastic constants that sufficiently describe the ion implanted and annealed anisotropic layer were C_{11} =250 GPa and C_{44} =110 GPa, obtained by fitting the experimental data with the elastodynamic Green's dispersion functions. The engineering constants obtained from these elastic constants were Young's modulus (E)=244 GPa, bulk modulus (B)=100 GPa, shear modulus (G)=110 GPa and Poisson's ratio (ν)=0.107.

Progress made from this study advocates the creation of a 'mirror' interface at a depth $\geq 0.5 \mu\text{m}$ by ion-implanting diamond with He⁺ ions then rapidly annealing it at 1200 °C. The mirror will be used in reflecting light back into the strained diamond film above. The diamond film can then be implanted (e.g. with C⁺) and the effects of the damage could possibly yield changes in the SBS spectra which can be studied using the Krüger-type geometry. It is then hoped that the puzzle of SBS in an ion-damaged translucent layer in the annealing regime of room temperature to 600 °C will be unlocked. Furthermore, this study pioneers BLS work in amorphous carbons sandwiched between strained diamond (with a differential opacity and density at the top) and pristine diamond below. This combination forms a complex multi-layer, and it therefore opens up opportunities for further academic discourse. Moreover the observation that SAW modes differ depending on differences in fluence, fluence profile and annealing temperature can be applied in making diamond-based microelectromechanical systems (MEMS) with different sound velocities on the same diamond plate.

The precious Khasandi M.T and our lovely nations

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Chapter 1

Introduction

This work studied the properties of near surface modified CVD diamond. The sub-surface modification was done through ion implantation of carbon ions into virgin diamond on the (100) surface. This is in line with the Diamond, Thin Hard Films and Related Materials group (DiHard) focus area hosted by the Centre of Excellence in Strong Materials. DiHard at the University of the Witwatersrand use optical spectroscopy and electron microscopy techniques to study the mechanical and optical properties of hard materials modified by ion beams as well as thin hard films. The thrust and depth of the groups activities is found at their website [1]. In line with the groups goals to extensively study hard materials due to their varied novel applications, this work employed the non-destructive surface Brillouin scattering as the main diagnostic tool to study the elastic properties of ion beam modified CVD diamond; as-implanted and thermally treated. The work sought to complement other works done on ion-modified diamond of almost similar implantation regimes studied using TEM [2] and Raman spectroscopy [3]. A succinct discussion is given below on the material of interest, diamond from its basic building block to its aftermath products as a result of ion implantation and heat treatment.

1.1 Carbon

Carbon is the first of group IV elements in the periodic table, with atomic number $Z=6$ and atomic mass, $A=12.02$, chemically represented by the symbol C. This means that it has 2 electrons in the K-shell and 4 in the unfilled valence L-shell. The four electrons in the outer L-shell are available for chemical reactions. Since an element's properties are determined by its reaction to the local environment, the valence electrons therefore, play a major role in determining the properties of C which shows great diversity than any other group IV elements. The diversity results from the type of chemical bond C atoms form among themselves and/ or with other elements. The diversity is quantified by the wide range of carbon compounds and the many different structures shown by carbon in its elemental state. Generally for carbon allotropes, one of the $2s$ electrons mixes with n electrons from the three $2p$ atomic orbitals to result in sp^n hybridization, where $n=1$ (polymers), 2 (graphite), 3 (diamond) [4]. Two or more combination of atomic orbitals form molecular orbitals of different bond strength. A strong σ molecular orbital is formed by the lateral overlap of two sp hybrid orbitals, while a π molecular orbital is formed by the side by side overlap of the sp hybrid atomic orbitals.

Carbon is among the most abundant elements and available in all the states of matter. It is found in many different compounds; in the food we eat, in the air we breath, in cosmetics, in clothes we wear, gasoline that powers our vehicles and factories and coal that generates our electricity. Generally the role played by carbon in the chemistry of life makes it one of the most important elements in nature. Many industries use carbon either as the sole raw material or as a mixture in other elements for formation of compounds. It is therefore an element worthy of study in whichever form it has found application. The common forms

of solid carbon are diamond, graphite and coal while rare ones like graphene also exist. Diamond, graphite and graphene are crystalline while coal is impure and amorphous. This study focused mainly on the solid state crystalline diamond as a pre-cursor and the product of ion damage when the diamond is bombarded with carbon ions.

1.1.1 Diamond

Diamond's unique properties makes it a worth material for study by material's scientists, engineers and mineralogists. The study of this material has therefore been going on for some time now [5, 6, 7]. For scientists, its ever widening applications drives the desire to know this material better. In particular, thin layer of diamond, the diamond surface and/ or interface continue to attract interest by researchers since the chemistry of the surface under various environments and tunability for materials application needs full understanding for effective application. There has been worldwide effort to exploit diamond as a high performance semiconductor in harsh, high-power, high temperature, high radiation environments. The unique property of colour centres in diamond as a single photon source may have applications in quantum information processing.

Diamond, with an electronic configuration of $1s^2 2s^2 2p^2$, has a half filled valence shell like other group IV elements. The $2p$ orbital can be split into three sub-orbitals, $2p_x$, $2p_y$ and $2p_z$. The $2s$ orbitals hybridize with the $2p$ orbitals giving rise to four unpaired electrons which in turn creates room for strong covalent bonding. To ensure minimum repulsion, the four sp^3 hybrid orbitals arrange themselves in a three dimensional space at bond angle 109.47° which enables them to get as far apart as possible from each other [8]. This leads to a special face centred cubic structure called the diamond lattice.

Diamond which is the cubic modification of crystalline carbon, belongs to the space group $Fd\bar{3}m$ (face centred cubic) with two atoms per primitive cell [9]. The structure can be viewed as two interpenetrating fcc lattices shifted along the body diagonal by $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})a_0$, where $a_0=3.567 \text{ \AA}$ [10, 11] is the lattice parameter of the cubic unit cell as shown in figure 1.1. The basis unit cell consisting of 2 atoms is shown by the dotted lines and like any other FCC structure, it has primitive cell volume of $a_0^3/4$.

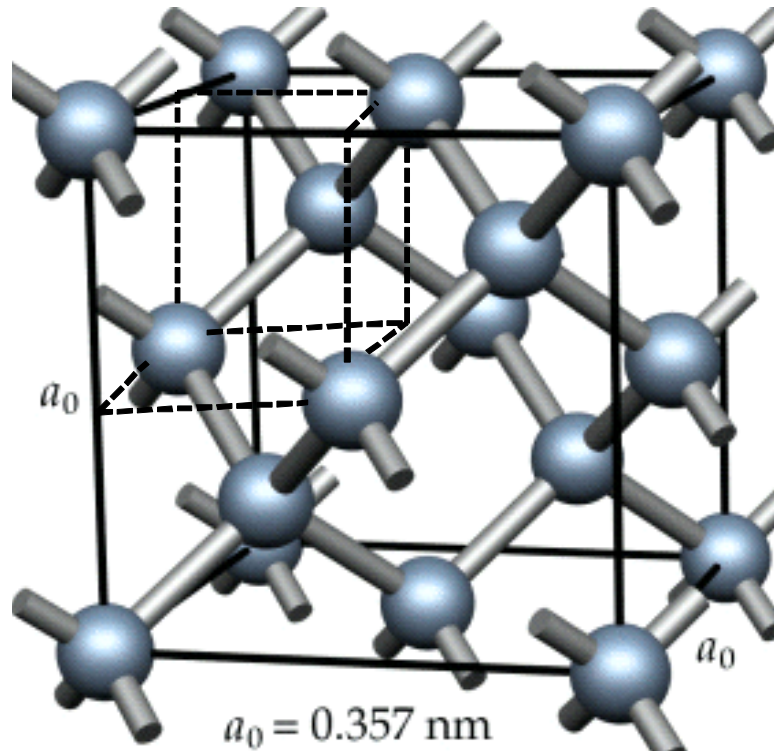


Figure 1.1: The tetrahedral coordination of the diamond structure showing the two interpenetrating fcc Bravais lattices that the carbon atoms occupy [12].

Diamond possesses a high atomic density of $(2 \text{ atoms}) / (\text{volume } a_0^3/4) = 1.76 \times 10^{23} \text{ atoms/cm}^3$ and a high density of strong atomic bonds. This, coupled with the fact that the bonds are strongly directional in nature, makes diamond extraordinarily hard, offering the greatest resistance to plastic flow of any known material [13]. A small lattice constant and high covalent bonding gives diamond excellent mechanical and tribological properties that have been applied in industrial operations

i.e. in cutting, surgical knives, grinding and polishing. Diamond's excellent wear resistance and low coefficient of friction makes it an ideal material for bearings and wire drawing applications. The number of covalent bonds that must be broken determines the shear strength of a material. In diamond, the (111) plane happens to have the least, making it the natural cleavage plane.

Diamond, with a high refractive index of 2.417 when irradiated with electromagnetic radiation of $\lambda=589$ nm [14] has been used traditionally as a gem material due to its sparkling beauty. Applying Snell's law, it is observed that the critical angle for the air-diamond boundary, ($\sin^{-1}(n_{air}/n_{diamond})$ is $\approx 24.4^\circ$), a small angle of incidence. This means that light rays that approach diamond at incident angles $>$ the critical angle experience total internal reflection, and may repeat several times if they hit the other planes at higher angles before finally refracting out with a dazzling brilliance. Moreover, diamond has high dispersive power [14] that ensures high dispersion of light into its component colours giving the cut gem a sparkling radiance. It is also worth noting that diamond has minimal absorption which allows an efficient photon transport. These special properties have made diamond a highly valued aesthetic gem material. Actually, diamond has been fondly referred to as "A woman's best friend" because of its cosmetic beauty.

Diamond has low thermal expansion coefficient, good thermal shock resistance but very high thermal conductivity [15]. Type IIa has a thermal conductivity of ≈ 2000 W/mK while that of silver is only 400 W/mK at 300 K [16]. Thus, in terms of thermal conductivity, diamond is second to none. In the electronics industry, the high thermal conductivity of diamond makes it an ideal heat sink for semiconductor devices while for appliances that apply diamond electronics, it acts as its own heat sink. Fast dissipation of heat from electronic devices is desired, since the devices

become unreliable when they become too hot. Unlike in metals where heat is conducted by electrons, lattice vibrations (phonons) are responsible for the high thermal conductivity in diamond. Diamond's high modulus of elasticity makes it a robust material which adapts excellently to rapid heat release.

Diamond has a wide band gap of 5.47 eV [10]. The wide band gap is responsible for the high breakdown field but with a disadvantage of low intrinsic carrier concentration of $\approx 1e \text{ km}^{-3}$ at room temperature [13]. Dielectric breakdown voltage (DBV) is a measure of an insulators ability to withstand the stress of high voltages placed across it. This property, coupled with the fact that diamond has a high melting point of $\approx 3820 \text{ K}$ makes diamond-based devices ideal for high power high temperature applications. Unlike diamond, silicon-based devices experience crystal damage when operated above room temperature due to increased diffusion of impurities in the crystal. On the other hand the small dielectric constant of diamond of 5.7 [17] leads to low capacitance hence fast switching speeds. In natural diamonds, the common inherent impurities are hydrogen, nitrogen and sometimes boron. These impurities and their levels determine the type of diamond apart from influencing the optical, mechanical and electronic properties of the diamond.

Other characteristics unique to diamond such as phase stability at room temperature, imply that it can not easily transform to the more stable allotrope, graphite. It is chemically inert hence resistant to effects of any acids or other chemicals. This makes it find applications in corrosive and harsh environments. Moreover, this property is an important consideration in post annealing treatment after formation of an amorphous layer which can be attacked by chemicals. Diamond devices are largely immune to radiation damage and can therefore operate at much higher temperatures. This means that they could be used in ultra-high-speed switches,

in low-power applications, sensors in irradiated environments, in space, and in extremely hot and cold locations.

In medical applications, diamond is biocompatible. C particles in living tissues are traditionally regarded as biologically inert and noninflammatory [18], a property that has made diamond find applications as biomedical implant materials and as exteriors of mammography probes, nanorobots and nanorobot aggregates in nanomedicine [19].

Diamond has distinguished itself as a material with a combination of properties that ranks highest among its other competitors documented in many paper articles and reviews. The summary is well documented in citations in the PhD theses of Nicolas Makau [20], Emmanuel Nshingabingwi [21], da Costa [22], in the MSc dissertation of Thuto Makgato [23] and in a publication by Gracio et al [24] which outlines the outstanding properties of diamond. As in this work they all used synthetic diamond for investigation and characterization. The advent of synthetic diamond was not only a great leap forward in advancing technological application of diamond but also a great opportunity for meaningful academic discourses in understanding diamond. Variability of natural diamond had led to the saying that “No two natural diamonds are the same” [25]. However, the discovery of methods and procedures to make diamond in the laboratory did not only make this very expensive material accessible but also ensured production of a material that is of high quality with reproducible properties. Such a material can hence be used for research and other industrial and technological application without possibility of failure. This study is a beneficiary of the processing of synthetic diamond.

However, despite its outstanding properties, diamond fails prematurely when

used in machining ferrous materials. Diamond based tools suffer from thermochemical stability at elevated temperatures above 700 °C. The heat and friction triggers a chemical reaction that causes the carbon in the diamond to diffuse into the iron material. Polycrystalline boron nitride (PCBN) on the other hand is thermally stable at high temperatures up to ≈ 1200 °C and has high resistance to chemical attack. Compared to conventional tool materials such as tungsten carbide and ceramics, PCBN is the best substitute for diamond-based tools in machining work-piece materials that have high affinity for carbon if diffusion wear of the cutting edge is to be avoided at elevated temperatures [26].

1.1.2 Graphite

Unlike in diamond where tetrahedral bonding is exhibited, graphite has a layer structure. The C atoms are arranged in a hexagonal pattern within each layer (graphene sheet). The layers are stacked in the ABAB sequence. In graphite three of the four electrons available for bonding establish strong co-planar bonds of the type sp^2 of length 1.41 Å. The three sp^2 hybrid orbitals arrange themselves in a two dimensional space to get as far apart as they possibly can. The geometry that achieves this is trigonal planar geometry, where the bond angle between the hybrid orbitals is 120°. The unmixed pure p orbital lies perpendicular to this plane. The remaining electron is available for a mixed role of co-planar and inter-planar bonding, weak interactions as well as electrical conduction. Each plane that forms a 2-dimensional graphene sheet is a distance of ≈ 3.35 Å from its nearest neighbour. The layers are therefore held together by weak van der Waals forces. The graphite unit cell can therefore be described as a hexagonal structure with dimensions $a = b = 2.46$ Å $\neq c = 6.708$ Å [27] as seen in figure 1.2. There are four atoms per unit cell. The carbon atoms represented by dark circles in plane

A have direct neighbours in adjacent planes (α atoms) while those represented by open circles have no direct neighbours in adjacent planes (β atoms). The crystal structure corresponds to the space group $P6_3/mmc$, in which the 6_3 screw axis is a consequence of the AB stacking [28].

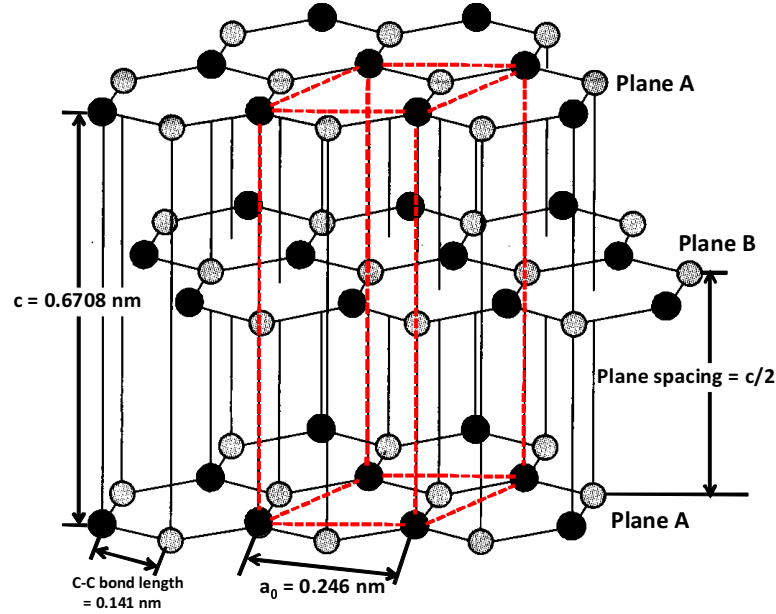


Figure 1.2: Schematic representation of graphite. An outline of the unit cell is represented by the red dotted lines [29].

Graphite, being a good example of a semi-metal has unique electrical properties that are of particular interest to scientists. It is anisotropic, a good electrical and thermal conductor along the layers due to the in-plane sp^2 bonding but a poor one off-layers due to the weak van der Waals forces [28]. The conductivity property has been utilized for instance in making electrodes of an electrical arc lamp and Leclanché cells [30]. The π -orbital electrons delocalized across the hexagonal atomic sheets of carbon contribute to the graphite's conductivity.

Graphite is a soft material with a greasy texture. Its powder is used as a dry lubricant. The low-friction behaviour is associated with the low resistance to shear between neighbouring atomic layers. The slipperiness of graphite, responsible for its excellent lubrication properties has been observed in frictional force microscopy

(FFM) experiments where friction coefficients as low as 0.001 have been recorded [31]. Dienwiebel *et al* [32] in their studies suggest that this is due to an effect called superlubricity.

Graphite is opaque with a steel grey/ black appearance. Though it has a sub-metallic luster, it is quite brittle. It leaves a mark on some surfaces, a property shared with lead and molybdenite [27], a property applied in the manufacture of pencils.

Graphite has a high melting point, in the range of 3700-4000 K for low rate of heating [33]. It is inert to many chemicals, however, it burns completely when heated in oxygen to form carbon dioxide just as diamond does, it also oxidizes to CO₂ when boiled in a mixture of concentrated sulphuric acid and potassium dichromate. This has been applied in etching away graphite from amorphized diamond. This chemical inertness property and stability over wide range of temperatures makes graphite a good refractory material.

Technologically, though originally developed in large quantities for use in electrodes, it has found other applications including that of neutron moderator in nuclear power reactors, where it serves to slow down fast neutrons without absorbing them. It is also important in various components of rockets and spacecraft, where it remains strong at very high temperatures.

Differences between diamond and graphite

Pure diamond and graphite are composed of C atoms only. The differences between them and the unique properties each exhibits are due to the difference in their bonding. Graphite has a sheet like structure where all the atoms lie in a plane and are only weakly bonded to the graphite sheets above and below. Diamond on the other hand has a framework structure where the carbon atoms are bonded to other

carbon atoms in three dimensions as opposed to two as observed in graphite. The C-C bonds in both materials are actually quite strong, but it is their application that makes them distinctly different as expounded by Kalish *et al.* [4];

- Mechanically, diamond is the hardest mineral known (least deformable, 10 on Mohs scale) while graphite is the stiffest material in nature (highest in-plane elastic modulus) and also one of the softest (in the c-axis) (1 - 2 on Mohs scale).
- Tribologically, diamond is abrasive while graphite is a lubricant.
- Electrically, diamond is an insulator while graphite is a conductor.
- Optically, diamond is transparent while graphite is opaque (black).
- Chemically, diamond crystallizes in the isometric system while graphite crystallizes in the hexagonal system. Diamond is chemically inert although it oxidizes in air above 600 °C, graphite readily burns in air and is etchable.

1.1.3 Amorphous carbon

Solid materials may either be crystalline or glass-like. Crystals fill up space with atoms or molecules in specific, fairly rigid patterns. The positions of the atoms are such that if any section of pure crystal is slid up, down, in, out or sideways a given distance, it fits perfectly in the new position. This is called translational symmetry. If the same section of the crystal is spun through certain angles, the atoms will also line up; this is rotational symmetry. An amorphous material (glass-like) is one lacking in long range order and therefore lacks translational or rotation symmetries. In our case we created one by taking a crystalline diamond then removed the order by damaging (introducing vacancies and interstitials) then annealing it. A practical

controllable way of doing this was by firing C ions into the material at high speed so that collisions inside the material knock most atoms from their original positions. This technique called ion implantation works best if most atoms of the target have very little internal energy and so unable to diffuse back to their original positions as the process continues. This is achieved if ion implantation is done at low temperatures. During ion implantation of diamond, many bonds are broken, leading to point defects. At a high enough irradiation dose (greater than 2.5×10^{15} atoms/cm² with damage of 10^{22} vac/cm³, the damage of the crystal is irreversible [34]. Annealing irreversibly damaged diamond gives rise to a material with different bonding states, in general it consists of sp^n bonds, where $n=1, 2$ and 3 . In cases where it is sp^3 bonds rich, it is tetrahedral amorphous carbon denoted as *ta*-C and where sp^2 bonds dominate, the material is graphite-like amorphous carbon denoted as *a*-C, the polymer chains (sp^1 bonds) hold the crystallites of the other disordered structures together [35].

The two structures can be distinguished clearly by their macroscopic and microscopic properties. At the microscopic level, the kind of structure is determined by the ratio of the fourfold, diamond-like bonds to threefold, graphite-like bonds. The sp^3 bonds dominate in *ta*-C while the sp^2 bonds are more in *a*-C materials. The *ta*-C material has higher density, ≈ 3 g/cm³, is a weak *p*-type semiconductor with a wide band gap of 2.5 eV and much harder than the *a*-C type [36, 35]. Amorphous carbon is therefore a disordered phase of carbon lacking long range order [37] as can be seen in figure 1.3 generated by molecular dynamics.

Robertson and O'Reilly [39] argue that for a group IV element at sp^3 site, each of the four valence electrons lie in an sp^3 hybrid which forms a σ bond with its neighbour. At an sp^2 site, only three of these electrons are used in σ bonds, the

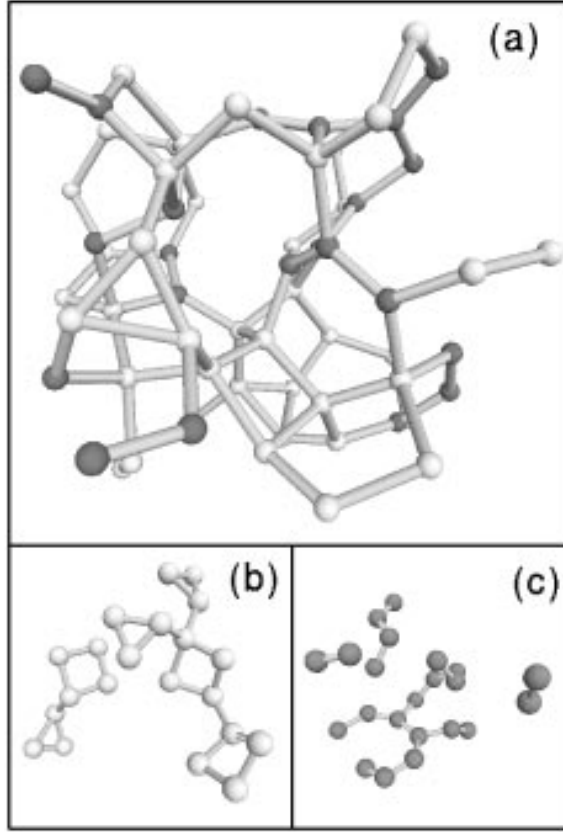


Figure 1.3: (a) A 64 atom *ta*-C network of bonds (lines) and atoms. The dark spheres represent a threefold coordinated atoms while the light spheres are the fourfold coordinated atoms. The three- and four- membered rings showing how they group in clusters in the structure are shown separately in (b) and (c), respectively [38].

fourth enters a π orbital which lies normal to the σ bonding plane. The importance of the π states is that they are weakly bonding so that they usually lie closest to the Fermi level E_F , forming both the valence and conduction band states.

The *ta*-C phase has many properties similar to those of diamond. Drabold *et al* [40] assert that *ta*-C is typically about 80-90% sp^3 bonded carbon and the remainder is sp^2 . Like diamond, *ta*-C therefore finds application in thin film electronics, optical windows and wear resistant coatings for optical, electrical components and magnetic storage devices. It protects these devices against wear and corrosion due to its high hardness, high wear resistance, electrical resistance, high density, atomic smoothness and chemical inertness [41, 42].

Schultrich *et al* [43] point out that quantitative characterization of amorphous

structure is important due their application. For example amorphous carbon films enable structures incompatible in their crystalline states to be combined. In this way, broad structural variability, extending from diamond-like to graphite-like to polymer-like behaviour can be realized. The structural variability of carbon means that they can be used as coatings for different applications, but with enhanced sensitivity to technological conditions. Schneider *et al* [15] also argue that amorphous diamond-like carbon (DLC) films combine the outstanding properties of diamond with those of the amorphous microstructure. The DLCs form from cubic and hexagonal lattices that randomly alternate. This creates no long range order hence there are no fracture planes like in pure diamond (111 plane) along which to break. They are therefore smooth and less brittle while their main properties such as density, hardness and Young's modulus depend on the sp^3/sp^2 ratio. This ratio can be varied within a wide range which enables in the making of films with a desired customizable property for various applications.

Amorphous forms of a material can have advantages over its crystalline form. In diamond for instance, though it is the hardest material known, its crystalline structure contains planes of weakness. Diamond cutters exploit these weak planes to cleave some of the facets. They do not cut it but actually break the gem along weak planes. Though this helps give diamond its dazzle, it is a disadvantage for other applications where the strength of this material is needed. For diamond, the strength is therefore direction dependent. Cleaving along certain planes is not a bad property, necessarily, but it is limiting. However, amorphous diamond may have isotropic properties. Thus a uniform super-hardness, combined with the light weight that is characteristic of all forms of carbon could open up exciting areas of application, such as cutting tools and wear-resistant parts for all kinds of

transportation.

1.2 The Diamond Surface/ Interface

Surfaces and/ or interfaces are boundaries where molecules from the environmental gas/liquid/solid phases come into contact with the material. To control how materials function, to be able to know and understand how to produce better ones and diversify their use, the properties of the surfaces/ interfaces must be understood through both theoretical predictions and experimental data.

An ideal surface is an abstraction created by passing a plane through an infinite crystal and separating the two parts to infinity. Such a surface forbids any changes in the system rather than the establishment of a different set of boundary conditions. The position of atoms and electron density inside the semi-infinite crystal remain the same as the original infinite crystal. However, in a real surface, the three dimensional symmetry of the crystal is destroyed in the direction perpendicular to the surface plane, i.e. the surface may reconstruct. Consequently, the wave functions of the electrons are modified in the vicinity of the surface. The resulting relaxation of the electron charge density creates a new self-consistent potential in the surface region of which the principal component is a surface dipole. Electrons possessing a large kinetic energy can tunnel into the potential barrier created at the surface. The excess electron density outside and the uncompensated positive charge inside the surface creates a surface dipole layer [44].

If atoms other than the substrate's are added to the surface plane, either from vapour phase or by segregation of the bulk impurities onto the surface, other surface structures arise. These structures may be due to ordered adsorption of up to a monolayer of atoms, epitaxial growth or mixing of adatoms with surface atoms to form ordered/ disordered surface alloys.

Ion implantation with C^+ as done in this study prevents any possible chemical doping effects. Upon implantation, a thin layer of damaged diamond was buried behind a very thin nearly pristine diamond that remains at the surface. The damage in the buried layer is predominantly towards the end of the range for a single energy implant while it can be uniformly distributed using multiple energies. The damage falls abruptly towards end of range leading to a sharp boundary between the damaged layer and the pristine diamond. Derry *et al* [45] have observed that for implantation above the critical damage density, the damaged layer graphitizes upon annealing and forms sharp boundaries with and within the diamond.

If the implanted sample is annealed beyond 600 °C and boiled in etching acid then a thin ‘skin’ of diamond can be easily lifted off exposing the damaged layer [46]. This damaged region composed of a mixture of sp^2 and sp^3 is a better electrical conductor than virgin diamond and easily forms carbides when in contact with carbide forming metals [47]. This is the layer where metals that form ohmic contacts attach. In essence therefore, this layer forms the metal-diamond interface. It is at the core in application of diamond in device fabrication, hence the need to study and understand its stiffness. Some transition metals are adsorbed on boron doped diamond to form Schottky junctions [48]. These junctions form a depletion layer which is responsible for charge carrier exchange between the metal and the semiconductor. Annealing a metallized diamond may lead to formation of a carbide at the interface with carbide forming metals. The carbide is responsible for not only a strong metal-carbon bond [49] but also for the formation of ohmic contacts [50]. While the formation of a carbide is good for strong metal-semiconductor interfaces, it leads to bond strains especially where the lattice constants of the participating materials differ greatly.

Determination of elastic constants is an important step in the study of a material since they also give information about the binding forces in the material. Their values are decisive in engineering design to avoid material failure. They, to a great extent affect a material's thermodynamic properties due to a low lying branch of acoustic vibrations, the bending modes as predicted by Lifshitz [51]. These properties may be directly important in themselves if the material's mechanical properties are of primary concern in its application. Elastic properties are also important since they relate to or reflect other material properties such as structural changes and electronic effects [52]. Nakamura *et al* [53] say that elastic constants are a central issue in both scientific and practical study of diamond, they provide crystallographic information on atomic bondlength, atomic potential and Debye temperature. They also indicate changes in stiffness and presence of defects through softening.

Elastic constants are related to the sound waves inherent in the acoustic vibrations in the material. This concept is used in this work using surface Brillouin scattering on ion-modified diamond. This work therefore sought to find the elastic properties of the ion damaged region formed differently i.e. single and multiple energy implantation regimes and a dose difference. The measurements examine changes in elastic properties of the samples from the as-implanted to annealed conditions by probing their elastic waves. Elastic wave phenomena have been successfully applied in signal processing (telecommunications), echography (medicine) and as a non-destructive testing technique (in metallurgy).

There has been substantial progress to harness the full potential of CVD diamond in wide band gap semiconductor electronics. Diamond has been known to surpass the other materials i.e. SiC, ZnO and GaN in this class since it has a direct

band gap of 7.5 eV and indirect band gap of 5.47 eV and a room temperature conductivity in excess of 2000 W/mK [54]. Diamond's unique properties such as no native oxide, though with the same crystal structure as Si, a small dielectric constant, fully covalent yet a wide band gap semiconductor makes it an ideal candidate for production of such devices.

1.3 Thesis outline

Chapter 1 has provided the reader with a picture of the material of interest, diamond. A general review of material properties and structure of diamond and other carbon allotropes that result from annealing damaged diamond i.e. graphite and amorphous carbon has been presented. These two, as will be shown, emerge after permanent modification through annealing of diamond that was ion implanted beyond the critical limit. They form important surfaces/ interfaces for diamond application. In this way a validation for this study has been presented.

Chapter 2 is devoted to the theory of elasticity and vibration of particles in a crystal. These phenomena form the basis of discussions in the different analytical techniques used in this work. Propagation of elastic and electromagnetic (EM) waves in matter is also discussed. In this discussion special attention is given to transparent materials like diamond which this work focusses on.

In chapter 3, samples, sample preparation including ion implantation and annealing are discussed. Detailed preparatory procedure is elucidated. Finally explanation of the functioning of major instruments used in this study is explained.

Chapter 4; The theory that guides ion implantation which was the main diamond modification technique is explained. The theory behind thermal treatment of the implanted diamond and the subsequent Brillouin scattering measurements done on the implanted diamond is explained. It also delves into the analytical techniques

applied in this study. The main technique, surface Brillouin scattering (SBS) is discussed. The other supporting techniques, Raman spectroscopy and Transmission Electron Microscopy (TEM) among other techniques that were necessary in complementing and filling up gaps will be discussed briefly.

Chapter 5 is a results chapter dedicated to ion-implanted and un-annealed diamond. This lays the basis for selection of certain procedures that were discovered to be important to the achievement of the main results given in chapter 7 after diamond is annealed.

In chapter 6, a “mirror” created at the interface of diamond and damaged layer forms the basis of the discussions. It is a result of failure to find the Rayleigh mode in pristine and as-implanted diamond discussed in chapter 5. The work done on a smaller scattering geometry created by He^+ implantation and annealing to create a mirror-like interface buried beneath the diamond surface is discussed. It is a futuristic chapter, where the findings therein are proposed for studying ion implanted diamond at lower annealing temperatures (200-500 °C).

Chapter 7 is dedicated to observations and discussions of higher annealing temperatures (600-1200 °C). The regimes are segmented based on observations from the principal technique, SBS. Old peaks disappear while new ones appear after annealing at 600 °C. The new peaks result from the ion implanted and annealed region hence need to treat them differently. The vast information obtained by studying annealed diamond and the results obtained are discussed. Recommendations for future work based on deductions from the results of chapters 5-7 are finally outlined in chapter A.

Appendices are included and are devoted to figures, calculations and explanations that were too detailed to be included in the main text.

Chapter 2

Elasticity and wave motion in crystals

2.1 Theory of elastic crystal

In this chapter the theory of elasticity and the dynamic properties of solids that in effect determine measurements of elastic properties of solids such as travelling elastic waves in isotropic medium is discussed. Anisotropic cubic diamond and the isotropic case when the material becomes amorphous upon annealing of ion implanted diamond will also be discussed. Any deformation which is reversible is called elastic deformation. It is characterized by lack of residual deformation after removal of the deforming load. Elasticity is essentially discussed in terms of stress and strain (deformation) tensors. These are concerned respectively with the forces and with the continuous and periodic displacements of atoms from their equilibrium positions which gives rise to vibrations and waves that are important in the main analytical technique used in this study.

2.1.1 Strain

A force applied to a solid changes its shape or size, the solid is said to be strained, and the deformation is called strain. When a solid deforms, the distance between

any two adjacent points changes. The displacement vector $\mathbf{u}$ that shifts a point $P(\mathbf{r})$ to a new location $P'(\mathbf{r}')$ in a material can be found by following the vectors $\mathbf{r}$ and $\mathbf{r}'$ from the origin of the coordinate system such that:

$$\mathbf{u} = \mathbf{r}' - \mathbf{r} \quad (2.1.1)$$

If the displacement vector $\mathbf{u}$ is not a pure translation or rotation, then the solid is said to undergo an elastic distortion. The distortion may be caused by an applied force on the material or motion of a longitudinal wave through it. The deformation is accompanied by displacement of particles from their mean positions. The distance between any two adjacent points (atoms), dl is given by

$$dl = \sqrt{dx_1^2 + dx_2^2 + dx_3^2}$$

$$dl = \sqrt{dx_i^2}, \quad (2.1.2)$$

where $i = 1, 2, 3$, and in a Cartesian system $x_1 = x$, $x_2 = y$ and $x_3 = z$. After deformation the distance between the same set of points becomes dl'

$$dl' = \sqrt{dx_1'^2 + dx_2'^2 + dx_3'^2}$$

$$dl' = \sqrt{dx_i'^2}, \quad (2.1.3)$$

relating dl' and dl with an infinitesimal displacement vector du , we have

$$dl'^2 = dx_i'^2 = (dx_i + du_i)^2$$

$$dl'^2 = dl^2 + 2 \frac{\partial u_i}{\partial x_k} dx_i dx_k + \frac{\partial u_i}{\partial x_k} \frac{\partial u_i}{\partial x_l} dx_k dx_l, \quad (2.1.4)$$

substituting $du_i = \frac{\partial u_i}{\partial x_k} dx_k$ in the last step of equation (2.1.4). With $\frac{\partial u_i}{\partial x_k} dx_i dx_k = \frac{\partial u_k}{\partial x_i} dx_i dx_k$ and swap of i and l in the last term, finally we have

$$dl'^2 = dl^2 + 2\eta_{ik} dx_i dx_k, \quad (2.1.5)$$

where η_{ik} is called the Lagrangian strain, defined as

$$\eta_{ik} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i} - \delta_{ik} \right), \quad (2.1.6)$$

and δ_{ik} is the Kronecker delta. By expressing the strain in terms of the displacement field gradient, we have

$$\eta_{ik} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i} + \frac{\partial u_i}{\partial x_k} \cdot \frac{\partial u_k}{\partial x_i} \right) \quad (2.1.7)$$

For most solids the deformations are small i.e. the relative variation of distances inside the solid is small. For such infinitesimal displacements, the product term in equation (2.1.7) can be dropped, giving an infinitesimal strain

$$\epsilon_{ik} \approx \frac{1}{2} \left(\frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i} \right) \quad (2.1.8)$$

Equation (2.1.8) gives a strain tensor which has nine strains ϵ_{ik} ; $i, j = 1, 2, 3$. It can be seen from equation (2.1.8) that $\epsilon_{ik} = \epsilon_{ki}$, there is symmetry with respect to interchange of indices implying that the strain tensor has only six independent components. The three components for which $i = k$ i.e. u_{11} , u_{22} and u_{33} define normal strain (extension per unit length) in the three cartesian axes directions. The other components for which $i \neq k$, define shear strain (change in shape of the solid).

With the diagonal elements $u^{(1)}$, $u^{(2)}$, $u^{(3)}$ the strain in any point can be written as the sum of three independent terms, giving strain in three orthogonal main directions.

$$dl'^2 = (1 + 2u^{(1)}) dx_1^2 + (1 + 2u^{(2)}) dx_2^2 + (1 + 2u^{(3)}) dx_3^2 \quad (2.1.9)$$

For $u^{(1)} \ll 1$ and neglecting higher order terms, the relative change of elongation becomes

$$\frac{dx'_i - dx_i}{dx_i} = \sqrt{1 + 2u^{(i)}} - 1 \approx u^{(i)}. \quad (2.1.10)$$

Writing the relative volume change of an infinitesimal small volume element $dV \rightarrow dV'$ as the sum of the diagonal elements of the strain tensor,

$$\frac{dV' - dV}{dV} = u_{ii}. \quad (2.1.11)$$

2.1.2 Stress

The resultant force $\mathbf{F}$ on any partial volume of an elastic body is an integral over the forces on any element of the volume $\int \mathbf{F} dV$. By Newton's third law, the action and reaction for all forces between any two points within the volume can be written as the sum over the integrals of the three components F_i , $\int F_i dV$, which can be translated into an integral over the surface:

$$\int F_i dV = \int \frac{\partial \sigma_{ik}}{\partial x_k} dV = \oint \sigma_{ik} df_k \quad (2.1.12)$$

where df_k are the components of a vector that is always oriented in the direction normal to the surfaces, F_i is expressed as divergence of the second rank tensor called the stress tensor σ_{ik}

$$F_i dV = \frac{\partial \sigma_{ik}}{\partial x_k} \quad (2.1.13)$$

For a solid in a static mechanical equilibrium state, the net force on any given infinitesimal volume must be zero. If the solid is deformed, the static mechanical equilibrium breaks down, the net force on a given volume is no longer equal to zero. Removal of this force tends to restore the solid back to its equilibrium state. Stress is defined as force exerted per unit surface area. Like strain, stress is a field factor, varying from point to point in a body.

Visualize an infinitesimal cube centred at X and placed in the principal plane of the coordinate system (xy , xz and yz). The stress in the medium at point X is characterized by the forces acting across the face of the cube (see figure 2.1).

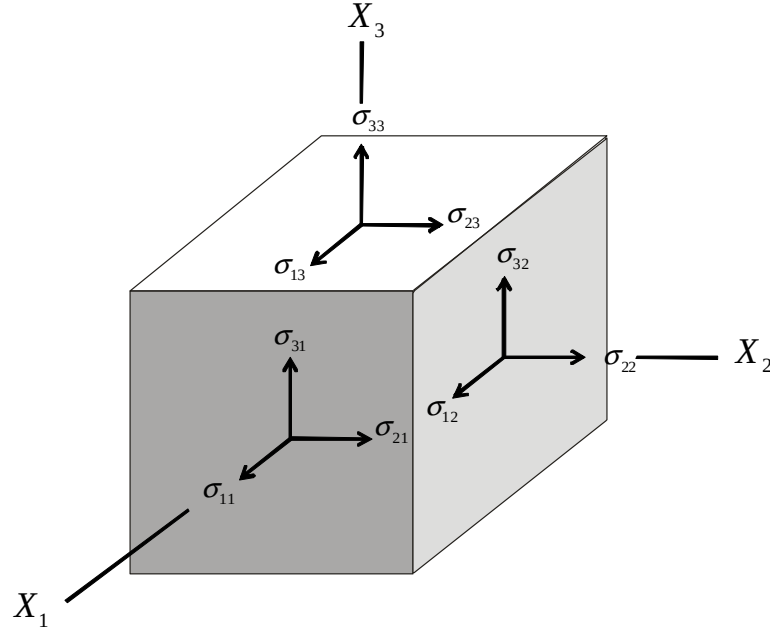


Figure 2.1: Stresses σ_{ik} as the force per unit area transmitted across the faces of an infinitesimal cube by the surrounding material [55].

For uniform stress, only forces on three visible faces are necessary since the forces on the opposite sides are equal and opposite.

$$\sigma_{ik} = \lim_{\delta A \rightarrow 0} \frac{\delta F_i^k}{\delta A}, \quad i, k = 1, 2, 3 \quad (2.1.14)$$

where δF_i^k is the i th component of the force acting across the surface facing outwards along the x_k direction and δA is the area of that face, constituting the Cauchy stress tensor $\{\sigma_{ik}\}$ [55]. The first suffix in σ_{ik} denotes the direction in which the force acts while the second shows the direction of the outward normal to the surface on which the force acts. Like strain, the diagonal components (ones for which $i = k$) are the normal components of stress while the off-diagonal ($i \neq k$) are the shear components. The stress tensor also must be symmetric (i.e. $\sigma_{ik} = \sigma_{ki}$) in order for the moment of force acting on the cube to tend to zero, hence the torques of pairs of forces $\delta F_i^k = \delta F_k^i$ cancel. This again leaves us with only six independent stress components.

If a perfectly elastic solid is lightly stressed, a temporary deformation, presumably permitted by an elastic displacement of the atoms in the space lattice, takes place. Removal of the stress results in a return of the solid to its original shape and dimensions. The equation relating the applied stress and resultant deformation is termed a constitutive relation, since it is dependent on the characteristics of the material for which the mathematical representation is sought [56]. Hooke's law can thus be generalized to state that each component of the stress tensor is linearly related to each component of the strain tensor. The materials relationship can be written in two ways;

$$\sigma_{ik} = C_{ikjl} \epsilon_{jl} \quad (2.1.15)$$

and its inverse (inverted Hooke's law),

$$\epsilon_{ik} = S_{ikjl}\sigma_{jl}. \quad (2.1.16)$$

Here, C_{ikjl} is the fourth rank tensor with $3^4=81$ coefficients known as the elastic stiffness tensor of a material which are a measure of the material's resistance to elastic deformation. The other 81 coefficients of S_{ikjl} are called the elastic compliance and are a measure of the ease with which a material deforms [55]. These two constants (stiffness and compliance) are material-specific properties. Taking into consideration the symmetry of the stress and strain tensors, for instance,

$$C_{iklm} = C_{ikml} = C_{kiml} = C_{kilm}, \quad (2.1.17)$$

and similarly for their inverse, the number of coefficients (stiffness and compliance) reduces to $6^2=36$.

2.1.3 Work done due to strain of a crystal

Suppose $\Phi(0)$ is the internal energy of a unit mass of a material in the state in which strain is measured, then for small strain, we have

$$\Phi = \Phi(0) + \left[\frac{\partial \Phi}{\partial \epsilon_{ik}} \right]_0 \epsilon_{ik} + \frac{1}{2} \left[\frac{\partial^2 \Phi}{\partial \epsilon_{ik} \partial \epsilon_{jl}} \right]_0 \partial \epsilon_{ik} \partial \epsilon_{jl} \dots \quad (2.1.18)$$

Since $\Phi(0)$ corresponds to the relative minimum, the first derivative equals zero;

$$\left[\frac{\partial \Phi}{\partial \epsilon_{ik}} \right]_0 = 0, \quad (2.1.19)$$

and hence energy of deformation is given by,

$$\Delta\Phi = \Phi - \Phi(0) = \frac{1}{2} \left[\frac{\partial^2 \Phi}{\partial \epsilon_{ik} \partial \epsilon_{jl}} \right]_0 \partial \epsilon_{ik} \partial \epsilon_{jl} + O(\epsilon_{ik}^3). \quad (2.1.20)$$

Work must be done to create a state of strain, hence $\Delta\Phi$ must always be positive. Neglecting third- and higher order terms, the right hand side of equation (2.1.20) must therefore be positive

$$\left[\frac{\partial^2 \Phi}{\partial \epsilon_{ik} \partial \epsilon_{jl}} \right]_0 = \left[\frac{\partial^2 \Phi}{\partial \epsilon_{jl} \partial \epsilon_{ik}} \right]_0 \quad (2.1.21)$$

The work done ΔW when an applied stress, σ_{ik} causes a strain ϵ_{ik} is,

$$\Delta W = \sigma_{ik} \epsilon_{ik}, \quad (2.1.22)$$

Identifying ΔW with $\Delta\Phi$, we have

$$\sigma_{ik} = \left[\frac{\partial^2 \Phi}{\partial \epsilon_{ik} \partial \epsilon_{jl}} \right]_0 \epsilon_{jl}, \quad (2.1.23)$$

so that equations (2.1.15) and (2.1.21) can be written as,

$$C_{ikjl} = \left[\frac{\partial^2 \Phi}{\partial \epsilon_{ik} \partial \epsilon_{jl}} \right]_0 = C_{jlik}. \quad (2.1.24)$$

This implies that the coefficients defined by equation (2.1.15) have a further symmetry involving 15 equalities in order to fulfil the positive energy function requirement, if the energy is negative the crystal will be unstable [57]. Consequently, the maximum number of independent elements of the fourth rank tensor (2.1.17) is reduced to 21. In an anisotropic body there are at most 21 independent components [55]. The 21 components are usually a simplification exploited in the Voigt

contracted notation [57]. This is done in matrix notation using itemized identities to abbreviate the tensor notation and to replace the tensor by a 6×6 matrix of two indices per pair ik with a single index $\alpha=1,2,3,\dots,6$ as follows,

Tensor notation	11	22	33	23, 32	13, 31	12, 21
Matrix notation	1	2	3	4	5	6

With this notation we can rewrite equation (2.1.15) as,

$$\begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46} \\ C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56} \\ C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66} \end{bmatrix} \begin{bmatrix} \epsilon_1 \\ \epsilon_2 \\ \epsilon_3 \\ \epsilon_4 \\ \epsilon_5 \\ \epsilon_6 \end{bmatrix}. \quad (2.1.25)$$

For a cubic crystal, which can be taken as a good approximation for many cases, equation (2.1.25) reduces to (2.1.26) due to further symmetry considerations [58],

$$\begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{bmatrix} \begin{bmatrix} \epsilon_1 \\ \epsilon_2 \\ \epsilon_3 \\ \epsilon_4 \\ \epsilon_5 \\ \epsilon_6 \end{bmatrix}. \quad (2.1.26)$$

For a cubic isotropic crystal, the remaining constants take the following relations,

$$C_{11} = C_{12} + 2C_{44}, \quad (2.1.27)$$

showing that there are only two independent constants. This are identified with the Lamé coefficients,

$$\lambda = C_{12}, \mu = C_{44}, 2\mu + \lambda = C_{11}. \quad (2.1.28)$$

On evaluating the inverse of equation (2.1.26), the stiffness and compliance constants of a cubic crystal are found to be related by the following equations [58],

$$\begin{aligned} C_{14} &= 1/S_{44}; \\ C_{11} - C_{12} &= (S_{11} - S_{12})^{-1}; \\ C_{11} + 2C_{12} &= (S_{11} + 2S_{12})^{-1}. \end{aligned} \quad (2.1.29)$$

2.1.4 Engineering constants

The matrix of the elastic constants C_{ij} of an isotropic medium is fully determined by two independent quantities; C_{11} and C_{44} . For thermodynamic stability, $C_{44} < (3/4)C_{11}$, and the isotropy condition is met by equation (2.1.27). Engineering constants; Young's modulus (E) which describes the change in length of a crystal in response to a pull, bulk modulus (B), the ratio of the infinitesimal increase in pressure to the relative decrease in volume, and Poisson's ratio (ν), the relative contraction perpendicular to the direction of pull, are then derived from these constants [59]

$$E = \frac{C_{44}(3C_{12} + 2C_{44})}{C_{12} + C_{44}} = C_{44} \frac{3C_{11} - 4C_{44}}{C_{11} - C_{44}} : \quad (2.1.30)$$

$$B = \frac{C_{11} + 2C_{12}}{3} = C_{11} - \frac{4}{3}C_{44} : \quad (2.1.31)$$

$$\nu = \frac{C_{12}}{C_{11} + C_{12}} = \frac{C_{11} - 2C_{44}}{2(C_{11} - C_{44})} = \frac{C_{11}/C_{44} - 2}{2(C_{11}/C_{44} - 1)} : \quad (2.1.32)$$

while the the ratio of shear stress to the shear strain i.e. shear modulus/ modulus of rigidity (G) coincides with C_{44} , i.e. $G=C_{44}$.

Applying the wave velocities (transverse, v_T and longitudinal v_L) obtained from experiments and corroborated by theoretical calculations, the engineering constants of any given material can be calculated [60]:

$$E = \rho v_T^2 \frac{3v_L^2 - 4v_T^2}{v_L^2 - v_T^2}, \quad (2.1.33)$$

$$B = \frac{1}{3}\rho(3v_L^2 - 4v_T^2), \quad (2.1.34)$$

$$\nu = \frac{v_L^2 - 2v_T^2}{2(v_L^2 - v_T^2)}. \quad (2.1.35)$$

The inverted Hooke's law (2.1.15) in section 2.1.2 shows that stress-strain relationship leads to some important physical quantities. By writing the equations of strain components in terms of the stress components and comparing them with equations that define elasticity we can use them also to determine the engineering constants [57],

$$\begin{bmatrix} \epsilon_1 = s_{11}\sigma_1 + s_{12}\sigma_2 + s_{13}\sigma_3 \\ \epsilon_2 = s_{12}\sigma_1 + s_{11}\sigma_2 + s_{12}\sigma_3 \\ \epsilon_3 = s_{12}\sigma_1 + s_{12}\sigma_2 + s_{11}\sigma_3 \\ \epsilon_4 = 2(s_{11} - s_{12})\sigma_4 \\ \epsilon_5 = 2(s_{11} - s_{12})\sigma_5 \\ \epsilon_6 = 2(s_{11} - s_{12})\sigma_6 \end{bmatrix}, \begin{bmatrix} \epsilon_1 = \frac{1}{E}\{\sigma_1 - \nu(\sigma_2 + \sigma_3)\} \\ \epsilon_2 = \frac{1}{E}\{\sigma_2 - \nu(\sigma_3 + \sigma_1)\} \\ \epsilon_3 = \frac{1}{E}\{\sigma_3 - \nu(\sigma_1 + \sigma_2)\} \\ \epsilon_4 = \frac{1}{G}\{\sigma_4\} \\ \epsilon_5 = \frac{1}{G}\{\sigma_5\} \\ \epsilon_6 = \frac{1}{G}\{\sigma_6\} \end{bmatrix}. \quad (2.1.36)$$

Comparing the coefficients we have,

$$s_{11} = \frac{1}{E}, \quad s_{12} = -\frac{\nu}{E}, \quad 2(s_{11} - s_{12}) = \frac{1}{G}, \quad (2.1.37)$$

from which follows a relationship that combines these engineering constants,

$$G = \frac{E}{2(1 + \nu)}. \quad (2.1.38)$$

For normal stress σ_x and the corresponding strain ϵ_x in the x -direction, Hooke's law gives,

$$\epsilon_x = \frac{1}{E}\sigma_x. \quad (2.1.39)$$

The form of Hooke's law that relates a shear stress, τ , and shear strain, γ , is given by,

$$\gamma_x = \frac{1}{G}\tau_x. \quad (2.1.40)$$

Chanda and Roy [61] observed that an elongation/ compression in one direction, due to axial force, produces a contraction/ expansion in the lateral direction, i.e. at right angles to the direction of force (see figure 2.2). Thus, a tensile stress, σ_x , which produces a tensile strain, ϵ_x in the x -direction will also produce a contractive strain, ϵ_y , in the y -direction, the two being related by,

$$\nu = -\frac{\epsilon_y}{\epsilon_x}, \quad (2.1.41)$$

which on combination with equation (2.1.39) yields

$$\epsilon_y = -\frac{\nu}{E}\sigma_x. \quad (2.1.42)$$

Equation (2.1.42) defines the contribution of stress σ_x in the x -direction to the total strain in the y -direction.

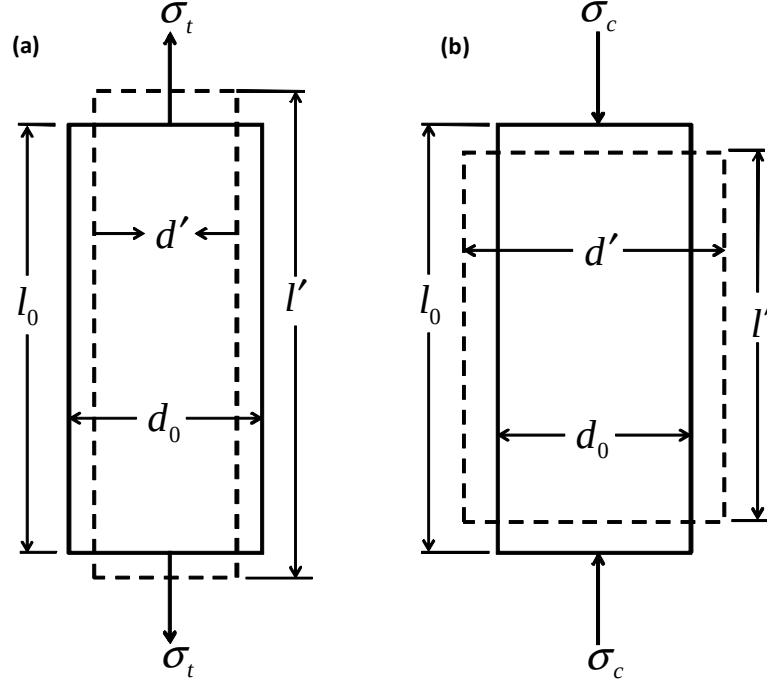


Figure 2.2: (a) Tensile strain, showing how elongation due to axial stress causes contraction of a material in the lateral direction, (b) Compressive strain [62].

Diamond and ta-C have a unique low ν compared to other covalent bonded materials. This may be attributed to a high bond angle rigidity of sp^3 carbon bonds. Hydrogenated a-C on the other hand has been found to have high values of $\nu \approx 0.3$ or more implying that the hydrogen in ta-C:H reduces the network's rigidity [63].

2.2 Elastic waves propagation

Materials are composed of atoms which undergo vibrational motion about their equilibrium positions. The particles of the material are displaced from their equilibrium positions but restored by electrostatic forces. These elastic restoring forces together with the inertia of the particles lead to the oscillatory motion in the material. Time-varying vibrations in materials are called acoustics. This occurs in a medium that contain a large number atoms that vibrate uniformly to produce a mechanical wave. In space, waves are characterized by oscillatory patterns that maintain their shape while propagating in a stable manner.

Sound refers to vibrations travelling in the form of pressure waves in an elastic medium. In air, sound travels longitudinally by the rarefaction and compression of air molecules in the direction of propagation. In solids, a number of different types of sound waves are possible since particles can support vibrations in other directions as well. The propagation of waves is often described by what are called “wave modes”. Four sound modes based on particle’s oscillations are possible: longitudinal waves and shear (transverse) waves which propagate in the bulk of materials, surface waves, and plate waves in thin materials. At solid surfaces and interfaces not very far from the surface other modes due to complex vibrations arise: Rayleigh (elliptical orbit), Stoneley (wave guided along interface) Plate wave (symmetrical mode), Love (parallel to plane layer and perpendicular to wave direction), Lamb (component perpendicular to surface), and Sezawa (antisymmetric mode) waves.

In optical spectroscopic techniques, a laser beam spot of the order of $10^3 \mu m^2$ [64] is incident on the sample. The medium under such laser beam illumination contains about 10^9 atoms. For dimensions of this order, the solid being probed is a continuum compared to the light spot size. A light propagating through such

a medium produces an oscillating dipole moment per unit volume. The oscillating moments in turn radiate electromagnetic energy in all directions [65]. In the continuum model the equations of motion for each elemental volume of a solid are written in terms of the displacement field $\mathbf{u} = \mathbf{u}(\mathbf{r}, t)$ representing the displacement of each point from its position $\mathbf{r}$ in the undeformed state. For a linear elastic medium, these are elastodynamic equations which for a homogeneous and isotropic medium can be written in the form [66],

$$\frac{\partial^2 \mathbf{u}}{\partial t^2} = v_t^2 \nabla \times \nabla \times \mathbf{u} + v_l^2 \nabla (\nabla \cdot \mathbf{u}), \quad (2.2.1)$$

where velocities $v_l = \sqrt{(\lambda + 2\mu)/\rho} = \sqrt{(B + \frac{4}{3}\mu)/\rho}$ and $v_t = \sqrt{\mu/\rho}$, are written in terms of the mass density ρ , the bulk modulus B , and the shear modulus, G (μ) or the Lamé constants λ and μ (as implemented in equation (2.1.28)). By the Stokes-Helmholtz decomposition of the vector field $\mathbf{u}$ into an irrotational and solenoidal component, $\mathbf{u} = \mathbf{u}_l + \mathbf{u}_t$ with $\nabla \times \mathbf{u}_l = 0$ and $\nabla \cdot \mathbf{u}_t = 0$, equation (2.2.1) splits into decoupled equations;

$$\begin{aligned} \frac{\partial^2 \mathbf{u}_l}{\partial t^2} &= v_l^2 \nabla^2 \mathbf{u}_l, \\ \frac{\partial^2 \mathbf{u}_t}{\partial t^2} &= v_t^2 \nabla^2 \mathbf{u}_t, \end{aligned} \quad (2.2.2)$$

showing that v_l and v_t are velocities of longitudinal and transverse waves, respectively. Equation (2.2.1) is therefore a superposition of three plane waves, one longitudinal (LA or l) and two mutually perpendicular transverse (TA₁, TA₂ or t_1, t_2) waves of the type:

$$\mathbf{u}_\alpha = \text{Re}\{Q_{\mathbf{q}\alpha} \mathbf{e}_{\mathbf{q}\alpha} e^{i[\mathbf{q} \cdot \mathbf{r} - \omega_\alpha(\mathbf{q})t]}\}, \quad (2.2.3)$$

where $\mathbf{q}$ is the acoustic wavevector, α is a branch index ($\alpha = l, t_1, t_2$), $Q_{\mathbf{q}\alpha}$ is the complex amplitude of the normal coordinate $\xi_\alpha(\mathbf{q}) = Q_{\mathbf{q}\alpha}e^{-i\omega t}$, $\mathbf{e}_{\mathbf{q}\alpha}$ is a polarization unit vector ($\mathbf{e}_{\mathbf{q}l} \parallel \mathbf{q}$; $\mathbf{e}_{\mathbf{q}t} \perp \mathbf{q}$) and ω is the the acoustical angular frequency. As shown earlier, the elastic properties are described by a fourth rank stiffness (compliance) tensor (equations 2.1.14 and 2.1.15), within every crystallite there are three acoustic wave modes for every propagation direction (trirefringence) [67]. The dispersion relations of these vectors are $\omega_l(\mathbf{q}) = v_l|\mathbf{q}|$ and $\omega_{t_1, t_2}(\mathbf{q}) = v_t|\mathbf{q}|$ [66].

2.2.1 Green's function

The elastodynamic Green's function provides the fundamental solution for the anisotropic elastic theory for an anisotropic material. Ven-Gen Lee [68], has argued that all materials generally have elastic anisotropic properties, which means the mechanical behaviour of an engineering material is characterized by the direction dependence. It is assumed that the medium is subjected to a time- and position-dependent distribution of body force $\mathbf{F}(x, t)$, defined per unit mass and having a harmonic time dependence [69].

$$\mathbf{F}(x, t) = \mathbf{F}(x)\exp(-i\omega t), \quad (2.2.4)$$

The equation of motion for the components of the elastic displacement field $u(x, \omega)\exp(-i\omega t)$ in the medium is given by [70]

$$C_{ijkl}\frac{\partial^2 u_l}{\partial^2 x_j \partial x_k} + \rho\omega^2 u_i = -F(x), x_3 > 0, \quad (2.2.5)$$

summing over all indices, the particular integral of equation 2.2.5 is given as

$$u_i(x, \omega) = - \int_{-\infty}^{\infty} d^3x' g_{ij}(x, x', \omega) F_j(x'), \quad (2.2.6)$$

where $g_{ij}(x, \omega)$ is the elastodynamic Green's tensor.

Green's function $G_{km}(\mathbf{x} - \mathbf{x}')$ of an infinite elastic medium is defined as the displacement component in the x_k -direction at point $\mathbf{x}$ when a unit body force in the x_m -direction is applied at point $\mathbf{x}'$ in the infinitely extended medium [68]. The displacement tensor $\mathbf{G}$ in a three dimensional anisotropic elastic material satisfies the equation of equilibrium;

$$C_{ijks} \frac{\partial^2 G_{km}}{\partial x_j \partial x_s} + \delta_{im} \delta(\mathbf{x} - \mathbf{x}') = 0, \quad (2.2.7)$$

where $\delta(\mathbf{x} - \mathbf{x}')$ is the Dirac delta function, δ_{im} is the Kronecker delta, C_{ijks} are the elastic constants, and the repeated indices imply summation.

Considering the response of the system to an external force $\mathbf{F}$ normal to the surface ($\mathbf{F}=(0,0,F)$) applied at the layer's upper surface,

$$\sigma_{l3}^-(\mathbf{x}_{\parallel}, x_3 = -h, \omega) = -F \delta(\mathbf{x}_{\parallel}) \delta_{l3}, \quad l = 1, 2, 3. \quad (2.2.8)$$

where $\delta(\mathbf{x}_{\parallel}) = \delta(x_1) \delta(x_2)$ is the 2D δ -function. The negative sign has to do with the fact that the surface traction $\sigma_{j3}(\mathbf{x}_1, x_3 = -h, \omega)$ are in response to the applied force, which is expressed in terms of its inverse Fourier transform [69]

$$\sigma_{l3}^-(\mathbf{x}_{\parallel}, x_3 = -h, \omega) = -\frac{\delta_{l3}}{(2\pi)^2} \int_{-\infty}^{\infty} d^2 k_{\parallel} F_l \exp(i\mathbf{k}_{\parallel} \mathbf{x}_{\parallel}), \quad l = 1, 2, 3. \quad (2.2.9)$$

The response of the system to the force F , gives the solution of the equations of motion in the form of a superposition of outgoing plane waves whose amplitudes are proportional to F [71]. With reference to figure 2.3 (the general representation of a thin film on some substrate separated by a very thin layer of oxide or carbide/

nitride, in the case of this study, thin graphitic carbon (see chapter §6)), in the top layer (+) the solution is given by:

$$u_i^+(\mathbf{x}, \omega) = \frac{F}{(2\pi)^2} \int_{-\infty}^{\infty} d^2 k_{\parallel} \sum_{n=1}^6 A^{(n)} U_i^n \times \exp[i(\mathbf{k}_{\parallel} \mathbf{x}_{\parallel} + k_3^{(n)} x_3)], \quad (2.2.10)$$

in the intermediate layer, the solution has the form

$$u_i^-(\mathbf{x}, \omega) = \frac{F}{(2\pi)^2} \int_{-\infty}^{\infty} d^2 k_{\parallel} \sum_{n=7}^{12} A^{(n)} U_i^n \times \exp[i(\mathbf{k}_{\parallel} \mathbf{x}_{\parallel} + k_3^{(n)} x_3)], \quad (2.2.11)$$

and finally, in the substrate,

$$u_i(\mathbf{x}, \omega) = \frac{F}{(2\pi)^2} \int_{-\infty}^{\infty} d^2 k_{\parallel} \sum_{n=13}^{15} A^{(n)} U_i^n \times \exp[i(\mathbf{k}_{\parallel} \mathbf{x}_{\parallel} + k_3^{(n)} x_3)], \quad (2.2.12)$$

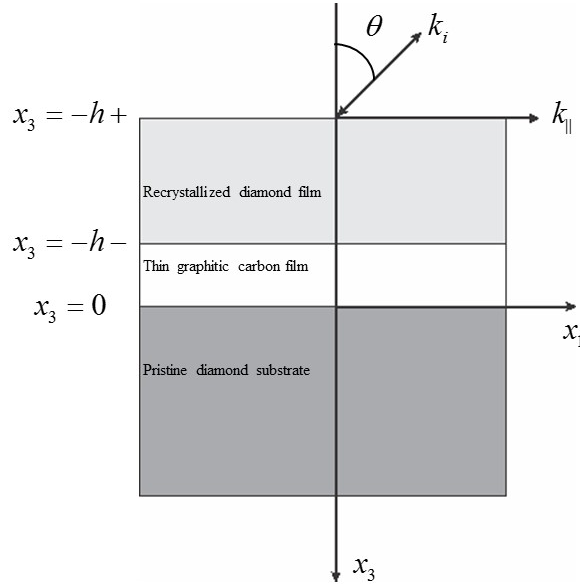


Figure 2.3: SBS geometry of thin damaged diamond film on diamond, the intermediate graphitic layer is a very thin carbon material created by ion-implantation of diamond by He ions then annealed at 1200°C (adapted from [71]).

For each of the $\mathbf{k}_{\parallel}$ and ω , coefficients A^n in equations (2.2.10)-(2.2.12) are fifteen unknown constants for plane wave decomposition. The third component k_3 of

wavevector $\mathbf{k}$ and the polarization vector U_i are related by a set of three linear Christoffel equations

$$(C_{ijkl}k_jk_l - \rho\omega^2\delta_{ik})U_k = 0, \quad (2.2.13)$$

where $k_3^{(n)}$ are the roots of the characteristic sextic equation, and δ_{ik} is the Kronecker delta symbol. The Christoffel equations together with their secular equations 2.2.14 represent the bulk wave dispersion relation for anisotropic medium, thus,

$$\Omega(\mathbf{k}, \omega) = |C_{ijkl}k_jk_l - \rho\omega^2\delta_{ik}| = 0. \quad (2.2.14)$$

The determinant in equation (2.2.14) describes a sixth order polynomial with k_3 and ω as parameters, which generally yields six solutions. In the top layer, all the six equations must be taken into account [71]. Every [72] says that in calculating the Green's function $G_{33}(k_{\parallel}, \omega)$, all six solutions of this equation are retained for the layer (top thin film), and only the three outgoing ones for the substrate. The three partial waves (labelled as $n = 7, 8, 9$) retained in the diamond film correspond to the outgoing waves on the basis that they are either homogeneous (bulk) waves (k_e^n real) with ray or group velocity vectors, $\mathbf{V}_g = \nabla_k \omega(k)$, directed into the interior, or inhomogeneous (evanescent) waves ($\mathbf{k}_3^n$ complex or pure imaginary) which decay into the interior ($\text{Im } k_3^n > 0$). Those with ($\text{Im } k_3^n < 0$), grow exponentially, and for the substrate are discarded as unphysical. The displacement field in the layer is a linear superposition of the six waves, and in the half space it is a superposition of three outgoing waves.

The surface dynamical response is the Fourier domain surface dynamic Green's function $G_{33}(k_{\parallel}, \omega)$, it represents the x_3 - component of the displacement response

of the surface to a periodic force acting on the surface in the x_3 -direction with temporal and spatial frequencies ω and $k_{\parallel} = (k_1, k_2)$, respectively [73]. A surface acoustic wave shows up as a pole of the Green's function in the imaginary (dissipative) part providing information on interpretation of the surface Brillouin spectra. The surface response is determined by the amplitudes of the six waves in the layer and their displacements at the surface, and is given by [72];

$$G_{33}(k_{\parallel}, \omega) = \frac{i}{\omega} \sum_{n=1}^6 \frac{\text{adj}(\mathbf{B}_3^{(n)}) U_3^{(n)}}{\det|\mathbf{B}|} \exp\{-k_3^{(n)} h\} \quad (2.2.15)$$

where adj and det are adjoint and determinant of the matrix, respectively.

A schematic section of a constant-frequency surface for an anisotropic solid for acoustic slowness (inverse phase velocity, $\mathbf{s}_{\parallel} = \mathbf{k}_{\parallel}/\omega$) is shown in figure 2.4. Real solutions are depicted by solid curves, they correspond to bulk homogeneous plane waves (bold for outgoing waves which have energy ray vectors pointing into the solid, and faint for incoming waves with energy ray vectors pointing towards the surface). Complex solutions which correspond to inhomogeneous waves, occur in complex conjugate pairs and are depicted by dashed curves [72]. Points a, b and c are $\mathbf{k}_{\parallel}$ thresholds where solutions change from complex to real. The limiting bulk waves (surface skimming or lateral waves) at these $k_{\parallel}$ values have vectors $\mathbf{V}_g$ which are parallel to the surface of the solid.

The region between 0 and c is known as the *supersonic* region, point c is the *transonic* state and beyond c is the *subsonic* region. Rayleigh wave (RW) solution for the free-standing surface of a solid is found in the subsonic region not far from c. For $k_{\parallel}$ between 0 and c, there are one to three bulk waves with real values of $k_{\perp}$, that are coupled to and which carry energy away from the surface. In this region, Im G displays three kinks labelled L (longitudinal), FT (fast transverse) and ST

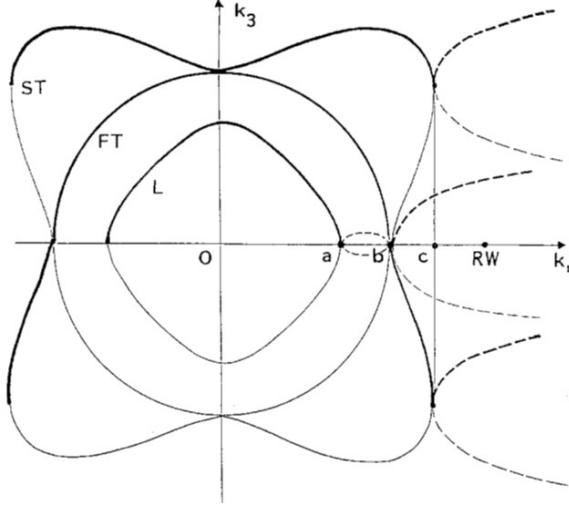


Figure 2.4: A plane section of a constant-frequency surface of an anisotropic solid [72, 73].

(slow transverse) corresponding to slowness a , b , and c , respectively.

2.3 Propagation of Electromagnetic waves

Electromagnetic waves have their highest velocity when travelling in vacuum. The presence of matter affects their speed due to interaction between them. Spectroscopic analytical techniques rely on interaction of matter with EM waves. In the main and some supporting techniques used in this work, laser light was used to study the properties of the material. A brief explanation is hereby given on propagation of light in transparent materials following the treatment of Amici *et al* [74]. To limit complexity of the problem for EM waves travelling through different matter, it is assumed that the density of each separate material is constant. There is also a finite discontinuity of dielectric susceptibility at the interface.

When an EM wave having an electric field $\mathbf{E}(\mathbf{x}, t)$ impinges on a material, it induces a polarization vector $\mathbf{P}(\mathbf{x}, t) = \chi \epsilon_0 \mathbf{E}(\mathbf{x}, t)$, where χ and ϵ_0 are the dielectric susceptibility and vacuum permittivity, respectively. In the absence of strain, the susceptibility, $\chi \rightarrow \chi_0$ a tensor constant in media of symmetry lower than cubic,

however in the presence of a strain tensor, the susceptibility is modulated and becomes

$$\chi_{\alpha\beta} = \chi_0 + K_{\alpha\beta\gamma\delta} \epsilon_{\gamma\delta}, \quad (2.3.1)$$

where $K_{\alpha\beta\gamma\delta}$ is the tensor of the elasto-optic coefficients [75]. The electric displacement $\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P}$ is therefore the sum of the linear term $(1 + \chi_0) \epsilon_0 \mathbf{E}(\mathbf{x}, t)$, that relates to the refractive index, and the modulated part of the polarization vector

$$P_\alpha(x_1, x_3, t) = \epsilon_0 \sum_{\beta\gamma\delta} \frac{1}{2} K_{\alpha\beta\gamma\delta} \left(\frac{\partial u_\gamma}{\partial x_\delta} + \frac{\partial u_\delta}{\partial x_\gamma} \right) E_\beta(x_1, x_3, t), \quad (2.3.2)$$

which accounts for Brillouin scattering by elasto-optic interactions.

At the interface χ_0 has a finite discontinuity, represented by a step function, occurring at position which is modulated by the displacement $u_3(x_1, x_3 = h_l, t)$, $l = 1, 2, 3, \dots, L$ number of layers. Expansion of the linear term in series of x_3 around $x_3 = h_l$ leads to a term proportional to $\mathbf{E}(\mathbf{x}, t)$, which accounts for elastic reflection from the static surface, to a term

$$P_\alpha(x_1, x_3, t) = \epsilon_0 \left(\chi_0^{l+1} - \chi_0^l \right) E_\beta(x_1, x_3, t) \times \delta(x_3 - h_l) u_3(x_1, x_3, t) \quad (2.3.3)$$

which accounts for Brillouin scattering at the l th interface by a ripple mechanism. The total field $\mathbf{E}(\mathbf{x}, t)$ in equations (2.3.2) and (2.3.3) can be replaced by the zeroth order electric field $\mathbf{E}^0(\mathbf{x}, t)$ that can be taken in the form

$$E_\beta^0(\mathbf{x}, t) = E_\beta^0(x_3 | k_{1,0}, \Omega_0) \exp(i(k_{1,0}x_1 - \Omega_0 t)), \quad (2.3.4)$$

where Ω is the angular frequency of the EM wave. In the presence of displacements in $(x_1$ and $x_3)$, both polarizations have the form

$$P_\beta(\mathbf{x}, t) = P_\beta(x_3|k_1, \Omega)\exp(i(k_1x_1 - \Omega t)), \quad (2.3.5)$$

with $\Omega = \Omega_0 \pm \omega$ and $k_1 = k_{1,0} \pm q$, and irradiate a scattered field of the form;

$$E(\mathbf{x}, t) = E(x_3|k_1, \Omega_0)\exp(i(k_1x_1 - \Omega t)), \quad (2.3.6)$$

ω is the angular frequency of the scattering phonon and $\mathbf{k}$ and $\mathbf{q}$ are the wavevectors of the EM wave and the scattering phonon, respectively. The two mechanisms of Brillouin scattering are therefore given a unified treatment and any possible interference among them automatically considered.

2.4 Acoustic propagation

The convention of figure 2.3 for multiple layered sample applies in this section following the works of Amici *et al* [74]. In the presence of a field of force per unit volume $f(\mathbf{x}, t)$, where $\mathbf{x}(x_1, x_2, x_3)$, the equations of motion for the displacement vector $u(\mathbf{x}, t)$ within each layer

$$\rho \frac{\partial^2 u_\alpha}{\partial t^2} = \sum_{\beta\gamma\delta} C_{\alpha\beta\gamma\delta} \frac{\partial^2 u_\gamma}{\partial x_\beta \partial x_\delta} + f_\alpha, \quad \alpha = 1, 2, 3 \quad (2.4.1)$$

the fields u^l satisfy the null stress boundary condition at the external surface, and continuity conditions for both displacements and stresses at the interface. Adopting a symmetry where the equation for u_2 , describes waves with shear horizontal polarization that decouples from the other two, which describe waves with

sagittal polarization. The structure of the sample is assumed to be homogeneous along the propagation direction x_1 , when $f_\alpha = 0$, Equation 2.4.1 have solutions proportional to $\exp(i(q_1 x_1 - wt))$ where q_1 is the parallel wavevector and w is the circular frequency; these solutions can be analyzed by the fluctuation-dissipation theorem by considering force fields of the form:

$$f_\alpha(x, t) = F_\alpha(x'_3|q_1, w) \times \exp(i(q_1 x_1 - wt)) \delta(x_3 - x'_3), \quad \alpha = 1, 3 \quad (2.4.2)$$

the complex amplitude $F_\alpha(x'_3|q_1, w)$ being forces per unit area. This force field acts at depth x'_3 , is homogeneous along x_2 and causes, in the whole structure, a wave of the form:

$$u_\beta(x_1, x_3, t) = u_\beta(x_3|q_1, w) \times \exp(i(q_1 x_1 - wt)), \quad \beta = 1, 3 \quad (2.4.3)$$

the real fields $u_\alpha(x_1, x_3, t)$ becoming complex amplitudes $u_\alpha(x_3|q_1, w)$ by Fourier transformation. With these force and displacement fields the interaction energy is:

$$H' = - \sum_{\alpha} u_{\alpha}^*(x'_3|q_1, w) F_{\alpha}(x'_3|q_1, w) e^{-iwt}, \quad (2.4.4)$$

and the solution of equation 2.4.1 can be expressed as:

$$u_\beta(x_3|q_1, w) = 2\pi G_{\beta\alpha}(x_3, x'_3|q_1, w) F_{\alpha}(x'_3|q_1, w), \quad (2.4.5)$$

where $G_{\beta\alpha}(x_3, x'_3|q_1, w)$ is the acoustic Green's tensor. Due to the form of Eqs. 2.4.4 and 2.4.5, thermal averages are given by the fluctuation-dissipation theorem as:

$$\langle u_\beta(x_3)u_\alpha^*(x_3') \rangle_{q_1,w} = i \frac{kT}{2\pi w} (G_{\alpha\beta}^*(x_3', x_3|q_1, w) - G_{\beta\alpha}(x_3, x_3'|q_1, w)). \quad (2.4.6)$$

Equation 2.4.6 motivates the Green's function calculations of displacement components.

2.5 Conclusion

In this chapter the general consideration of interaction of EM waves and matter and propagation of elastic waves in an elastic continuum has been considered. The equations governing these interactions given. The solutions to some of the said equations is the gist of this study as they are explanations of observed phenomena.

Chapter 3

Sample preparation and experimental equipment

3.1 Introduction

This chapter describes the major experimental apparatus employed in this research. A few items are explained in detail, without downplaying the many other techniques that played a supporting role in ascertaining requisite facts, however, detailed descriptions can be found in the appropriate literature. Such apparatus may be briefly mentioned in the chapter on results and discussion. However, a description of samples and how they were prepared before experimentation is first given.

3.2 Samples and sample preparation

The CVD single crystal diamond plates used in this study were obtained as-ready for use from Element Six [76]. The diamonds measured $3.0 \times 3.0 \times 0.5 \text{ mm}^3$ with $3.0 \times 3.0 \text{ mm}^2$ polished faces oriented in a $\langle 100 \rangle$ direction. The as-purchased diamonds were already polished on both sides or on one side to optical grade. The surface roughness of the polished faces was $< 30 \text{ nm}$ as specified by the supplier. Many other such samples have been purchased from the same vendor before for research in the diamond and hard materials group, so there was no compelling

need to do preliminary studies to ascertain the quality of the samples. Therefore, techniques such as Laue diffraction and XRD to determine the crystal orientation and atomic force microscopy (AFM) to determine the surface roughness were not performed. SBS results confirm that the polished surfaces were (100).

Before any ion implantation was done, a mechanical groove was made near one of the vertices of the diamond as shown in figure 3.1. The picture was taken by an AxioCam ERc 5s camera on a SteREO Discovery.V8 optical microscope with a magnification of $\times 10$. The groove was cut using a Nd-Yag laser, at iThemba LABS, Gauteng, South Africa. After grooving, the diamond was then boiled in the oxidizing acid mixture to remove glue used to secure the sample on the holder, and etch away the graphite in the groove as well as any oxides and other impurities on the surface. The oxidizing acid was a 3:4:1 perchloric (HClO_4), sulphuric (H_2SO_4) and nitric (HNO_3) acid mixture. After the hot oxidizing acid treatment, the samples were then rinsed in distilled water in an ultrasonic bath for 20 minutes. The sample surfaces were observed under an electron microscope of magnification $\times 10$ to ensure that they were clean for ion implantation. Ion irradiation was done on the sample side opposite the grooved side. This was done in anticipation of the black colouration the damaged face acquires after high temperature annealing. The groove was very useful in locating the ion implanted side during Raman and SBS measurements. The groove also aided in orientating the sample in-plane in certain desired directions to ensure that the same wave vector was probed during SBS measurements.

All the ion implantations were performed using a Varian 200-20A2F ion implanter located at iThemba LABS (Gauteng). Some implantations were performed at room temperature while others were done at liquid nitrogen temperature. The

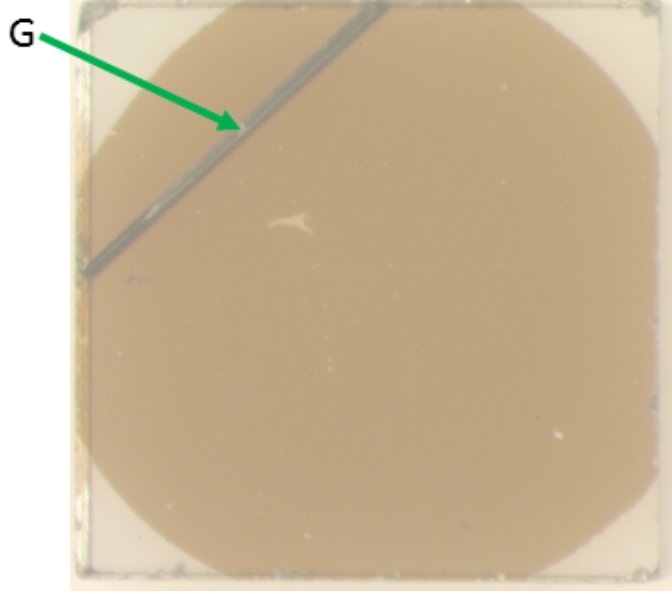


Figure 3.1: (a) Figure of multiple energy as-implanted diamond, the groove labelled G on the un-implanted side helped not only in identifying the implanted from the un-implanted side but also in directional measurements, the vertex near the groove was used as reference point.

ion beam was uniformly scanned over the sample surface using a beam current of $\approx 1.0 \mu\text{A}/\text{cm}^2$. The samples used are described in table 3.1,

Table 3.1: Samples used in this study.

Sample	Implant species	Implant energy (keV)	Polish Description	Fluence ($\times 10^{16}$ ions/ cm^2)
1	-	-	Both sides	-
2	^{12}C	Multiple [Table 3.2]	Both sides	1.0
3	^{12}C	Single (150)	Both sides	1.5
4	-	-	One side	-
5	^{12}C	Single (150)	One side	1.5
6	^{12}C	Multiple [Table 3.3]	Both sides	1.0
7	He^+	Single [CIRA routine]	One side	6
	He^+	Single [Room temperature]	Both sides	1.0

Raman spectroscopy, visible light transmittance and SBS measurements were conducted on the diamond samples from pristine state to annealed state. To study the effect of heat treatment on the ion-irradiated region, isochronal annealing was done on the same sample for 30 minutes at temperatures 200 °C, 400 °C, 500 °C,

Table 3.2: Implantation energies of ^{12}C ions and doses giving a total fluence of 1.0×10^{16} ions/cm 2 in sample 2. This follows the routine worked in [77] that produces an almost uniform damage in the implanted region.

Energy (keV)	Fluence ($\times 10^{16}$ ions/cm 2)
50	0.1200
80	0.2192
120	0.2608
150	0.4000
Total	1.0

Table 3.3: Implantation energies of ^{12}C ions and doses giving a total fluence of 1.0×10^{16} ions/cm 2 in sample 6

Energy (keV)	Fluence ($\times 10^{16}$ ions/cm 2)
37	0.0625
51	0.0625
64	0.0625
77	0.0625
90	0.0625
103	0.0625
116	0.0625
128	0.0625
140	0.125
170	0.375
Total	1.0

600 °C, 800 °C, 1000 °C and 1200 °C. A continuous Ar gas flow ensured an oxygen free environment during annealing. However, the 1 hour anneal was done on sample 7 after He ions implantation. Before and after each measurement cycle or whenever it was necessary, the sample was cleaned with acetone followed by methanol then rinsing with distilled water in ultrasonic bath for 20 minutes each.

3.3 Ion implanter

The ion implanter used in this work was a pre-analysis type. In this type of implanter, the ions are first selected (analyzed) before being accelerated. The sequence of events therefore includes ionizing atoms (projectiles), selecting the

species of interest, accelerating them to the desired energies then directing the beam towards the wafer/ target. Depending on the final energy which the ions can finally attain, we have medium current implanters (MCI) and high current ion implanters (HCI). The one used in this work was a MCI (delivering ions in the keV range), a detailed schematic diagram of such an implanter is shown in figure 3.2. The generation, acceleration and actual implantation of ions must be done in vacuum environments, though the vacuum levels in the different sections of the implanter may be different. Vacuum pumps that can guarantee low pressure, therefore, form an integral part of the ion implanter. Furthermore, the pumps must efficiently handle some highly reactive, toxic gases and products in the implanter such as Arsine (AsH_3), Phosphine (PH_3), Chlorine (Cl), Boron Trifluoride (BF_3) etc. In addition, contamination-free environment should be generated and maintained, mainly achieved using liquid nitrogen to condense oil vapors far from the beamline.

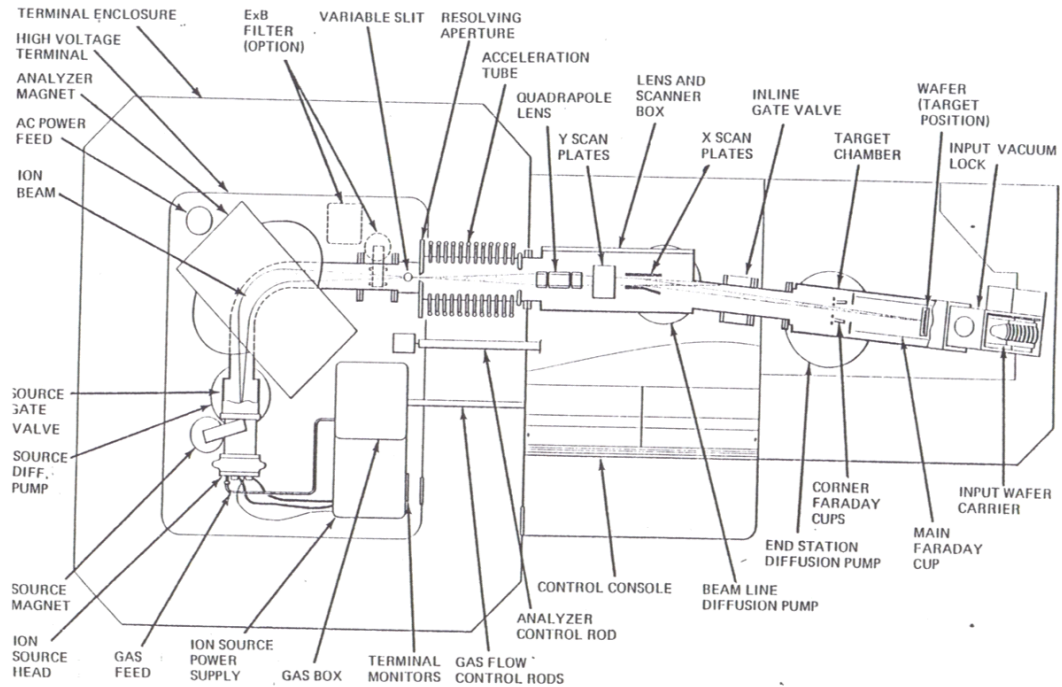


Figure 3.2: Schematic diagram of the Varian 200-20A2F ion implanter used in this work.

A brief explanation of the different parts of the ion implanter and how they

function is given below. The figures used in clarifying facts are heavily borrowed from [78, 79, 80, 81]. Basically, the ion implanter consists of the following major parts:

3.3.1 Ion source

The production of ions, mostly with a single positive charge at the required current for the required species is done in the ion source. The ion source consists of the cathode, the anode, extraction aperture, magnetic field, plasma and source feed system. The cathode is directly heated by passing current through the cathode filament. Tungsten is usually the preferred material but corrosion, surface poisoning and ductility leads to use of alternatives in some implanters: tantalum, molybdenum and rhenium [82]. The heated cathode produces electrons through thermionic emission. The ideal maximum current per cm^2 of the electrons produced is given by the relation:

$$J_e = AT^2 \exp \left[\frac{-e\phi}{kT} \right], \quad (3.3.1)$$

where A and k are constants, ϕ work function of the metal heated at temperature T . The electrons (hot cathode arc discharge) collide with the carrier gas molecules within the ion source chamber causing the gas to split into several different species of positively charged ions, which leads to a plasma. An electromagnet positioned near the ion source chamber provides a weak axial magnetic field that causes the emitted electrons from the filament and those released by ionization to move in helical paths. This not only lengthens the path of the electron but also confines the plasma to a small volume hence improving the ionization efficiency. The chamber body where the cathode is located forms the anode. It is therefore, a large-area

electrode since it also determines the distribution of the plasma as shown in figure 3.3. The material(s) that make it should to a large extent be able to withstand corrosion, erosion, outgassing and flake formation.

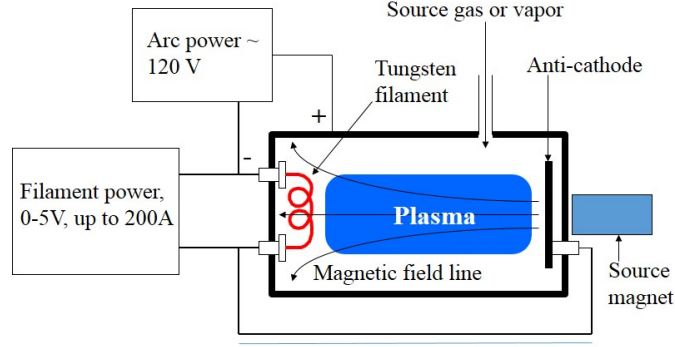


Figure 3.3: Schematic diagram of the ion source. Positive ions are attracted to the exit side of the source chamber, outside which is an extraction electrode biased at a large negative potential with respect to the filament, then travel towards the magnetic analyzer.

The positive ions are then extracted from the chamber by an electric field due to a potential difference between the source exit and the the extraction electrode placed just outside the chamber. The ions gain energy as they accelerate through the potential difference and leave the source as an ion beam. A particular ion will have energy $E=qV$ (where q is charge on the ion and V is the potential difference between ion source and extraction electrode) and for doubly charged ions, the extraction energy will be twice the source voltage. The amount of ion current available from a plasma surface is approximately the product of the positive charge density and their mean velocity component normal to the plasma surface and is given by [82]:

$$\begin{aligned}
 J &\simeq n \left(\frac{kT_e}{m} \right)^{1/2} (\text{ions}/\text{cm}^2 \text{ s}) \\
 &\simeq 3.5 \times 10^{-13} n \left(\frac{T_e}{m} \right)^{1/2} \text{ mA}/\text{cm}^2,
 \end{aligned} \tag{3.3.2}$$

where n is the positive ion density, T_e is the electron temperature and m is the average mass of the positive ions.

3.3.2 Analyzing magnet

The extracted ion beam is a mixture of different fractions of molecules and isotopes of the source feed material. In addition, there exists a certain amount of ions which are created by sputtering from the walls of the source or by ionization of residual gases. The selection of the required ions is done by an analyzing magnet. This is a mass analyzer that separates the ion beam according to their mass and charge. When the magnetic field is of proper strength, only ions of the desired species are deflected through 90° matching the curvature of the magnet chamber and focused by the magnet at the resolving aperture. The unwanted ions are deflected at angles $< / > 90^\circ$ and are collected on the chamber walls or the resolving aperture plate as shown in figure 3.4.

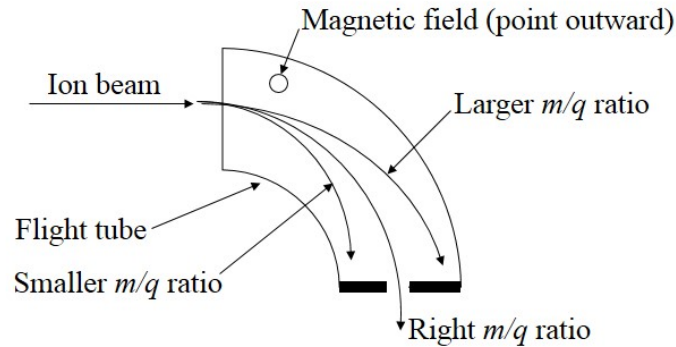


Figure 3.4: Schematic diagram of the ions selection process in the analyzing magnet region where focusing of the desired ions is done.

This implies that the analyzer magnet does not only select the required beam species, but also enables the beam to be focused into the variable slit where it is accepted into the acceleration tube. Moreover, beam purity is important in ion implantation hence the need for magnetic analysis. The implanter resolution

should be so high that it is able to sufficiently separate two neighbouring masses over the required mass range.

When a charged particle with velocity v passes through the magnetic field $\mathbf{B}$ extended by length l set up of the analyzing magnet, it is deflected through an angle φ given by [83];

$$\sin\varphi = \frac{e\mathbf{B}l}{mv}, \quad (3.3.3)$$

into a circular trajectory, whose radius is given by [82]:

$$r = \frac{143.95 \mu_o}{\mathbf{B}} \sqrt{\frac{mV}{n}}, \quad (3.3.4)$$

where e is the charge unit, r is the radius (cm), m is the mass (a.m.u), V is the accelerating voltage (volts) and n is the charge state of the ion.

Similarly, from electromagnetism, the work done on charged a particle, q moving with velocity v due to external potential is equal to the kinetic energy of the particle,

$$K.E = \frac{1}{2}mv^2 = qV_{ext}, \quad (3.3.5)$$

therefore,

$$v = \sqrt{\frac{2qV}{m}}. \quad (3.3.6)$$

Such a particle entering a region with a magnetic field $\mathbf{B}$, experiences a force which causes it to move in a circular trajectory of a radius of curvature r .

$$\frac{mv^2}{r} = qv\mathbf{B}, \quad (3.3.7)$$

therefore,

$$r = \frac{mv}{q\mathbf{B}} = \frac{1}{\mathbf{B}} \sqrt{\frac{2mV}{q}}, \quad (3.3.8)$$

From equation (3.3.8), the mass to charge ratio of the required ions is given by;

$$\frac{m}{q} = \frac{r^2 \mathbf{B}^2}{2V_{ext}}, \quad (3.3.9)$$

and those not required undergo a displacement as shown in figure 3.5. The displacement from the required trajectory is given by:

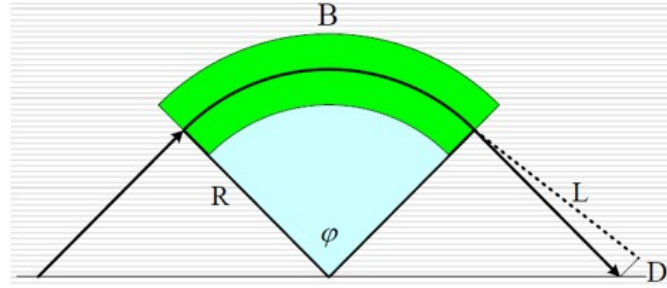


Figure 3.5: Displacement of unwanted ions.

$$D = \frac{2}{R} \frac{\delta M}{M} \left[1 - \cos\varphi + \frac{L}{R} \sin\varphi \right], \quad (3.3.10)$$

Equations (3.3.4) and (3.3.9) show that by varying the magnetic field strength of the analyzer magnet, we can precisely select those ions required for implantation.

3.3.3 Acceleration tube

Upon completion of pre-analysis, the ion beam is extracted from the terminal and accelerated toward the target. The acceleration occurs in an evacuated high voltage multi-gap graded tube. The acceleration tube is an eleven gap, ten electrode device employing 8 resistors to form a series divider network, part of which is shown in figure 3.6. By shorting different lengths of the tube to the terminal, using a piston driven shorting bar it is possible to vary beam currents over a wider energy range.

The exit tube is biased at -2 kV, for suppression of secondary electrons. This negative voltage prevents electrons from backstreaming up the acceleration tube, creating X-rays as they strike surfaces in the vacuum chamber. A failure of this voltage would increase the production of X-rays drastically [82]. In the acceleration tube the ion beam is focused and accelerated to attain the required energy for implantation.

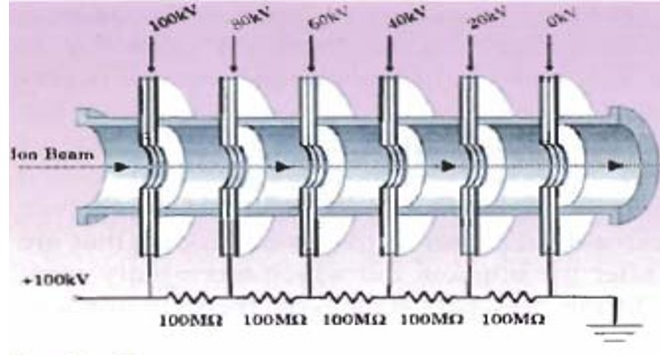


Figure 3.6: Picture of part of the accelerating tube, the ions enter at more negatively biased end [80].

3.3.4 Beam manipulating system

An ion beam diverges as it gains energy through the acceleration tube. Therefore a quadrupole doublet lens is positioned immediately following the acceleration tube to focus the beam. The lens which consists of two sets of four poles each, uses high voltages to focus the beam into a small, symmetrical spot on the target. The converged beam is scanned by a set of electrostatic deflection plates so that ions are evenly distributed across the entire target area. The electrostatic scanning is done by two pairs of deflection plates, including a neutral trap. Neutral atoms are highly undesirable since they give an erroneous value of the actual dose implanted if not eliminated along the path. They have the disadvantage that they can not be deflected in electrostatic mechanisms. This problem is solved in most systems

by equipping them with parallel plates of an electrostatic deflection system that bends the charged ions but neutrals move on straight and strike a beam trap. The positive ions are then focussed by the x- and y-scanner plates biased with a varying high voltage to the target as shown in figure 3.7. This ensures that the focused ion beam is scanned over the sample (diamond in this study) in a highly controlled manner in order to achieve uniform implantation by keeping the sample stationary while the beam scans vertically and horizontally as shown in figure 3.8. When properly aligned the scanning motion produces a rectangular scan pattern, producing rolling Lissajous patterns on a connected oscilloscope.

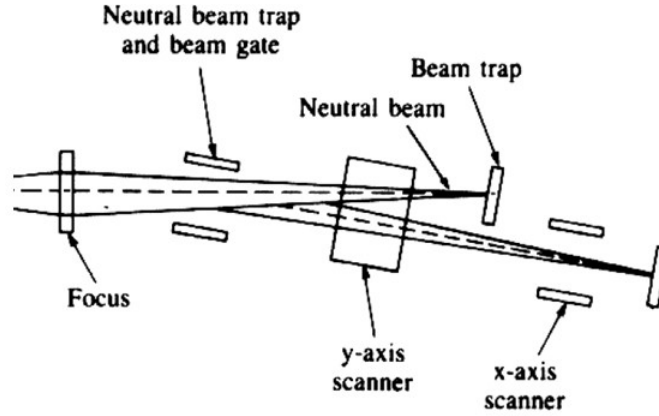


Figure 3.7: Schematic diagram of the manipulating system showing how neutral atoms are isolated from the desired ions.

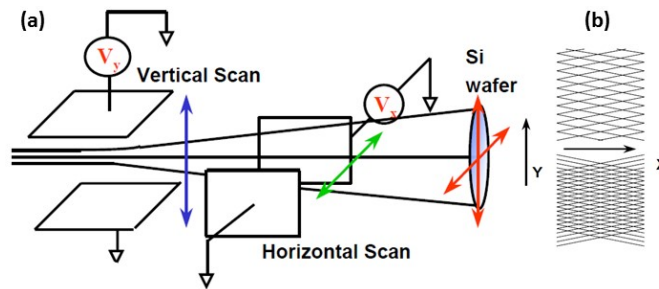


Figure 3.8: (a) Implantation mechanism where the ions are scanned vertically and horizontally to produce (b) uniform damage.

3.3.5 The end station

A sample was firmly inserted implantation cassettes mounted in the end station load/unload carriage for each session. The carriage was then lowered into the implant chamber in such a way that the sample was tilted at angle of 7° . This is standard practice on the Varian 200-20A2F ion implanter used for implantation in this study. The tilt angle is determined by aligning a notch on the carriage with a circular Vernier as shown in figure 3.9. The ion beam reaches the implant chamber where the ions are implanted into the sample. Negative bias is applied to a ring in front of the Faraday cup to collect all secondary electrons, hence cup current = ion current and charge collected by integrating cup current/cup area = dose. A failure in the supply voltage is indicated by the rise of measured beam current and this automatically leads to high dose errors.

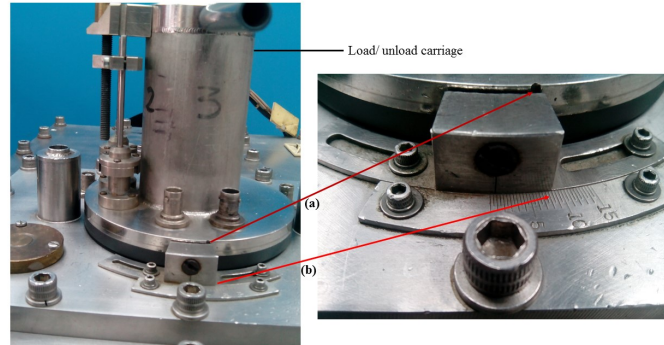


Figure 3.9: (a) External positioning of the load/ unload carriage on the end station of the Varian 200-20A2F ion implanter. When the notch (a) is aligned as shown on the Vernier scale (b), the ions strike the sample surface at an incidence angle of 7° with respect to the normal.

The vacuum system on the source side is equipped with diffusion pumps because of the large quantity of doping gases, whereas the beamline and target chamber are either supplied with fast diffusion pumps or with cryo-pumps. The set-up and control over the entire vacuum system are automatic. However, the tuning of the source, the selection of the ion species and the beam focusing adjustments were done

manually. The implanter used in this study has a single position for implantations. The sample holder is removable for loading and unloading purposes.

During implantation, the samples were inclined at an angle of 7° to the the projectile path to ensure that the ions do not enter the samples along crystal planes. This reduces the effect of channelling [84]. In channelling, the energetic ions travel relatively long distances with minimal collision. This reduces the number of displaced atoms in a cascade, causing an undesired dopant profile. Figures 3.10(a), (b) and (c) illustrate how channelling would easily occur along the principal diamond index planes. Figures 3.10d and 3.11, however, shows the high probability of collisions if (100) plane is tilted at an angle to the direction of incoming ions.

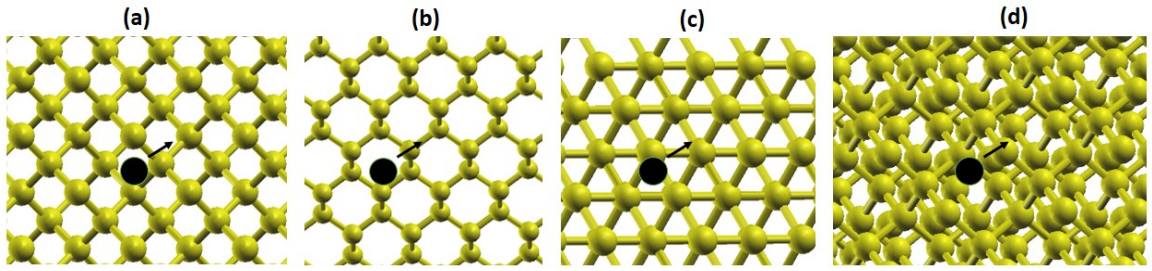


Figure 3.10: Schematic view of the different low index surfaces of diamond (a)-(100), (b)-(110), (c)-(111) while (d) is a slightly displaced (100) corresponding to inclined angle of implantation. The dark atom is an implanted ion into the diamond matrix shown by the arrow. The displaced crystal will experience more collisions and cascades.

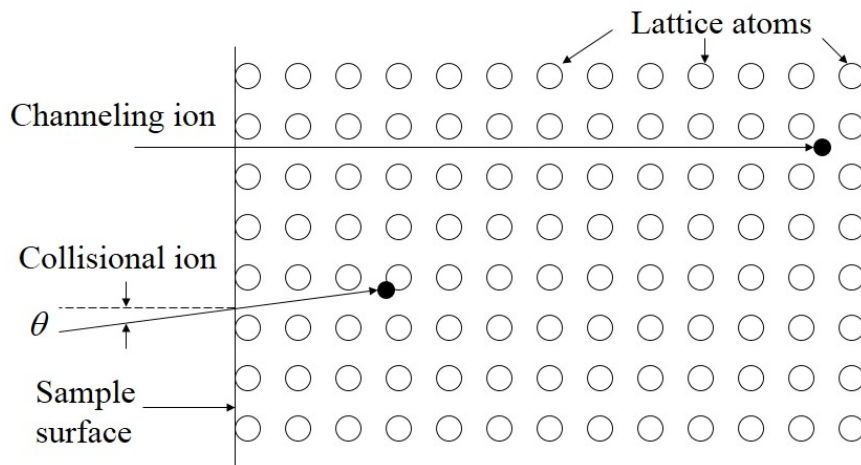


Figure 3.11: A schematic 2-D representation of channelling effect in (100) diamond sub-surface.

When thermal vibrations are ignored, the critical channelling angle ψ_1 (maximum angle between ion and channel for glancing collision to occur) is given by [85]:

$$\psi_1 = 9.73 \sqrt{\frac{Z_1 Z_2}{Ed}} \quad (3.3.11)$$

where Z_1 and Z_2 are the ion and target atom's atomic numbers, E in keV is the ion energy (say 150 keV, for the single energy used in this work), d in Å is the atomic spacing of the target material (1.54 Å, the diamond's atomic spacing). Therefore, ψ_1 for C into diamond is $\approx 4^\circ$, therefore there was no channelling during the ion implantation process in this work.

3.4 The thermal evaporator

It has been suggested by Andrews *et al* [86] that a thin Al layer of ≈ 40 nm thickness improves reflectivity on a transparent sample for SBS measurements. There was need to put a thin layer of Al on the sample surface and impinge light on it. Al metal having a low melting point of 933 K could easily be melted and evaporated in a high vacuum thermal evaporator. An Al strip was coiled out of plain Al foil and placed on a solenoid made from tungsten wire which has a high melting point of 3673 K. Passing high current through the tungsten solenoid causes heating which melts the Al. The evaporated Al atoms move in straight lines in all directions from the source, form a vapour cloud inside the chamber and condenses on all available surfaces in the chamber as a coating/ film. In the process some find their way to the sample's surface. This process is called physical vapour deposition (PVD). It was important that the thickness of the layer be thin, but since a quartz crystal was not installed in the instrument to monitor the thickness of the film, the thickness

of Al was post-deposit determined by Profilometry (at CSIR, Pretoria) and/or X-ray reflectivity (XRR) (Chemistry department, Wits). The variables in this PVD process were sample-source distance, vacuum level for deposition, power through the solenoid and the time for deposition. Calibration of the equipment with the aim of obtaining an approximate thickness of deposited Al was therefore done.

The main additional components required for evaporation were the pumps (rotary (mechanical) and diffusion), the valves, the evaporation chamber, the pressure gauge and a.c power provided through the variac. Figure 3.12 is a schematic diagram showing the main components of a thermal deposition evaporator adapted from [87].

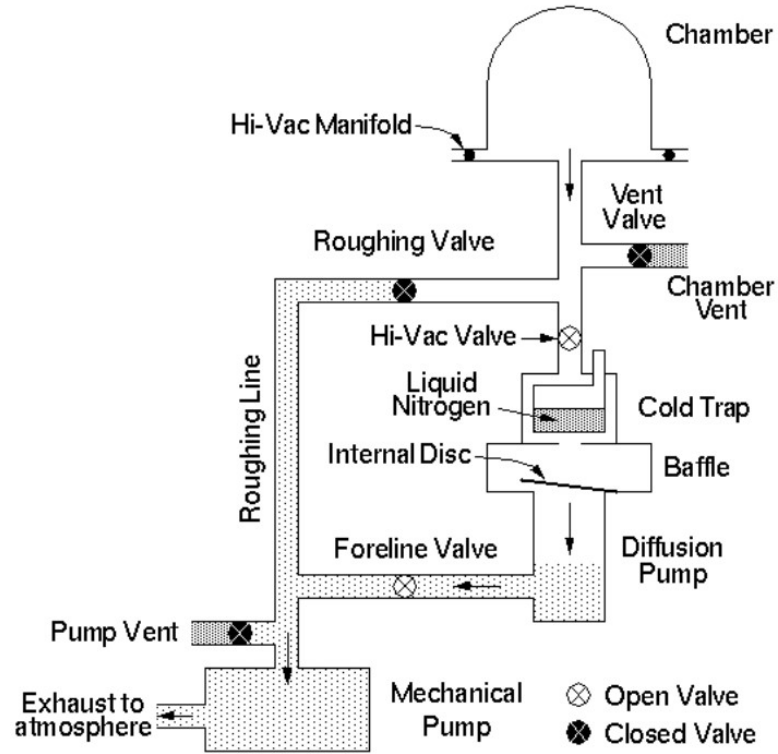


Figure 3.12: Thermal evaporator used in PVD of Al on diamond. This is the configuration when the two pumps are working simultaneously to pump down the chamber to a pressure better than 10^{-5} mbar.

Below is a brief discussion of the functions of the different parts of the system.

Operation procedure is discussed in appendix §A

- The pumps: The rotary pump removes bulk of the air from the system which was initially at atm pressure to $\approx 10^{-2}$ mbar. This is the tolerable forepressure for diffusion pump to function. It then acts as back-up for the diffusion pump. The diffusion pump on the other hand evacuates from $\approx 10^{-2}$ mbar to better than 10^{-7} mbar. A vacuum of between 10^{-5} - 10^{-7} mbar is good enough for deposition.
- The valves: There are five valves that control the flow of fluids hence determining the pressure at different parts in the system.
- The chamber: This is where physical vapour deposition on samples is done.
- The baffle: It is a water cooled region that helps to trap and condense any oil vapour trying to escape into the Hi-Vac area. Oil should not reach the chamber since it poisons the samples and chamber walls.
- The cold trap: Normally filled with liquid nitrogen. The very low temperature (≈ 77 k) in the region just above the diffusion reduces pressure by condensing on its cold surfaces any condensable vapours in the system. By doing this it prevents oil vapour from the diffusion pump from backstreaming into the system. It therefore acts as a third ‘pump’ after the rotary and diffusion [87].

3.5 SBS experimental apparatus

Brillouin scattering being a state of the art technique for non-destructive materials testing has very many independent systems. Each of these complementing systems must be in good working condition for experiments to continue un-interrupted. The systems are power supply, laser system, water cooling systems, external optics (figure 3.13) firmly held on the optical bench, internal optics (figures 3.14 and 3.15)

that together with an elaborate electronic system form the Tandem Fabry P  rot interferometer (TFPI) shielded inside a black box, and the multi channel analyzer (MCA) interfaced with the TFPI and the detector for observing the spectrum and recording data. A detailed explanation of the parts and working of the Fabry P  rot interferometer is given in the user manual [88], whose online version is found at [89]. The tandem operation is also described in [90, 91]. However, a brief explanation is given here based on the user manual.

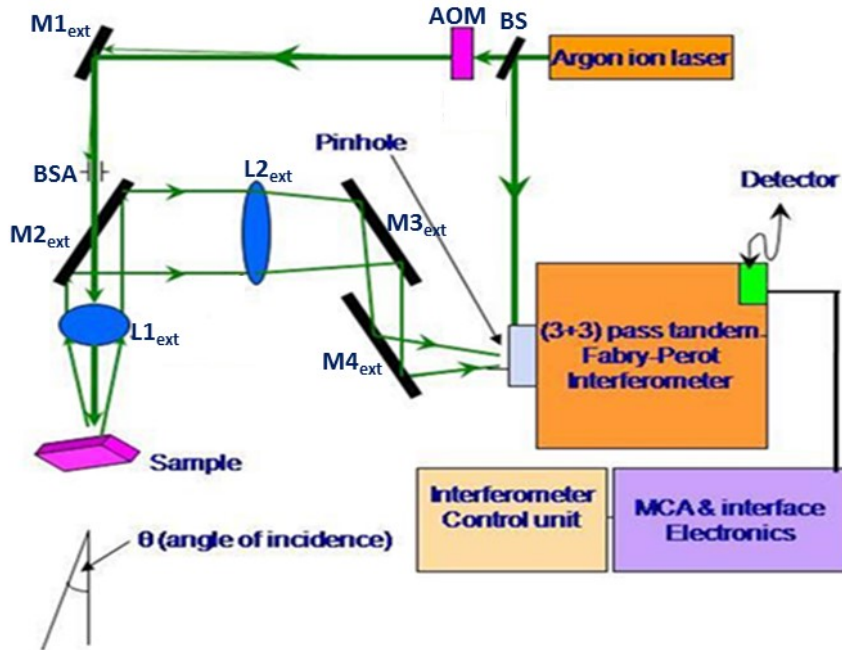


Figure 3.13: A schematic diagram of the external optics used for a Brillouin light scattering in the backscattering geometry. $M1_{ext}$ - $M4_{ext}$ are mirrors, $L1_{ext}$ and $L2_{ext}$ are lenses, the subscript ‘ext’ adopted here implies a component used in the external environment and different to that with similar nomenclature used inside the spectrometer (figures 3.14 and 3.15). BS, BSA and AOM are the beam splitter, beam selector aperture and acousto-optic modulator, respectively.

The polarity of the probing incident beam from an Ar^+ ion laser is maintained by the external optics. This is done by ensuring that the highly reflecting mirrors are mounted in such a way that the beam does not deviate from its path horizontally and vertically. The light should be able to retrace its path if it is reflected along the normal of any reflector. At the corners it is important to ensure that light

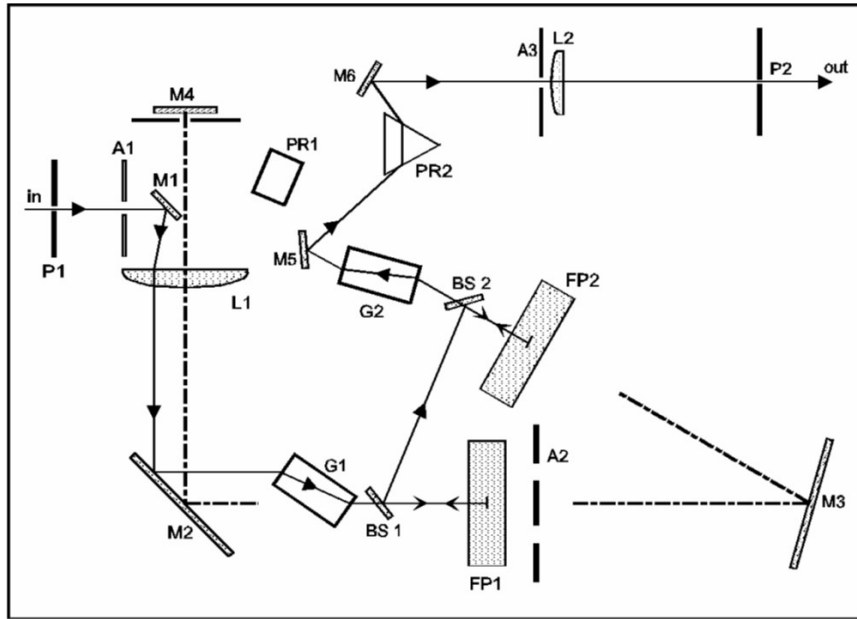


Figure 3.14: A schematic diagram of the internal optical components when in alignment (reflection) mode. P1 and P2 are pinholes that at inlet and exit from the spectrometer, prisms are abbreviated as PR, G1 and G2 are glass blocks while A1-3 are apertures. Two parallel mirrors form the Fabry Pétot (FP) 1 and 2, respectively.

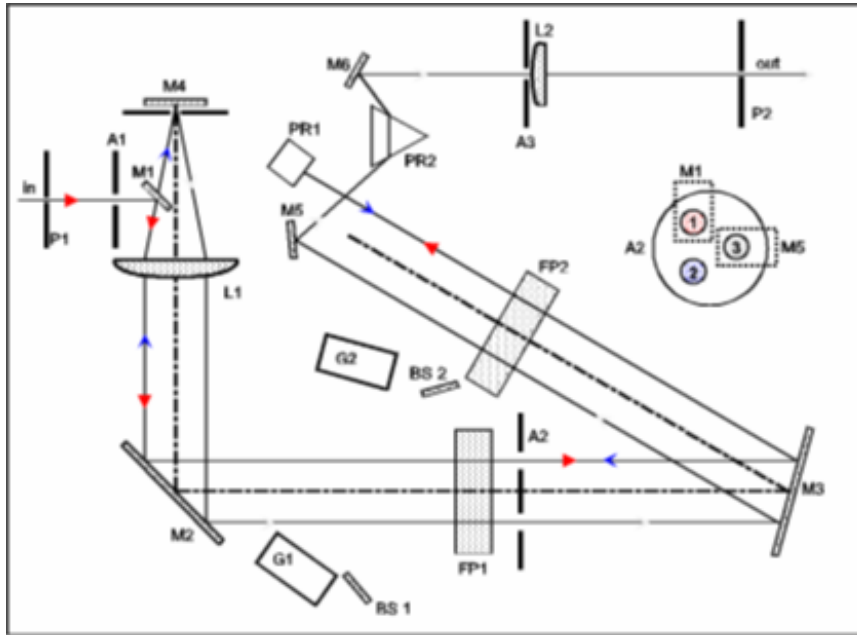


Figure 3.15: A schematic diagram of light travel and the internal optical components when in tandem (transmission) mode.

is reflected at a right angle by the mirrors. As much as is humanly possible, one should ensure that light is centred whenever it goes through an aperture. SBS measurements are sensitive to vibrations. A vibration and noise free environment is achieved by mounting the interferometer on the same optical table with the external optics set up. The interferometer is further cushioned by mounting it on two dynamic isolation mounts. The isolation mounts are stiff, compact and with excellent directional and positional stability. Other measures put in place to deal with vibration and sound disturbance are enclosing the contents of the interferometer in a thick metallic black box and electronic scan stabilization system.

3.5.1 Working of the Fabry P rot Interferometer

The FPI makes use of multiple reflections between two plane parallel surfaces of high reflectivity with spacing L as shown in figure 3.16.

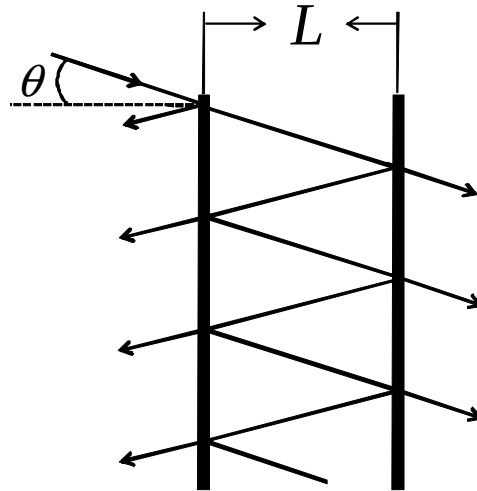


Figure 3.16: Fabry-P rot resonator.

The FPI consists of two plane mirrors mounted such that they are parallel to one another, with an optical spacing L between them. The output of the FPI consists of a series of peaks whenever there is constructive interference within the cavity. For a given spacing L , the interferometer will transmit only certain wavelengths λ

which satisfy the condition that $L = n.(\lambda/2)$, for integral values of n . If one of the mirrors is moved by means of piezoelectric transducers so that L varies by $\delta L - 1 \mu\text{m}$, a tunable filter is obtained. The transmission is given by the Airy-function [92]

$$T = \frac{\tau_0}{1 + \frac{4F^2}{\pi^2} \sin^2(\phi/2)}; \phi = \frac{2\pi}{\lambda} 2L \cos\theta. \quad (3.5.1)$$

where $\tau_0 (< 1)$ is the maximum possible transmission determined by losses in the system, F is called the Finesse, a quality factor that depends primarily on the mirror reflectivity and flatness.

The single FPI suffers from overlapping of interference orders of different spectral features of the scattered signal. This problem is solved by using equipment with two interferometers mounted on the same scanning stage at an angle α having different mirror spacings, L_1 and L_2 (tandem interferometer). If $L_2 = L_1 \cos\alpha$ then the relation $\delta L_1/L_1 = \delta L_2/L_2$ is satisfied, a condition required for synchronization of the two interferometer scans [93]. The total transmission curve is composed of a central elastic peak and small ghosts symmetrically positioned on either side representing weakly transmitted interference orders of the two interferometers.

The spacing between two subsequent maxima is called the free spectral range (FSR), $\Delta\nu$;

$$\Delta\nu = \frac{c}{2L}, \quad (3.5.2)$$

where c is the speed of light in air.

The minimum resolvable bandwidth (MRB), $\delta\nu$ is the full width at half maximum (FWHM) of each peak. Finesse can thus be defined in terms of FSR and MRB, equation (3.5.3) and shown in figure 3.17,

$$F = \frac{\Delta\nu}{\delta\nu}, \quad (3.5.3)$$

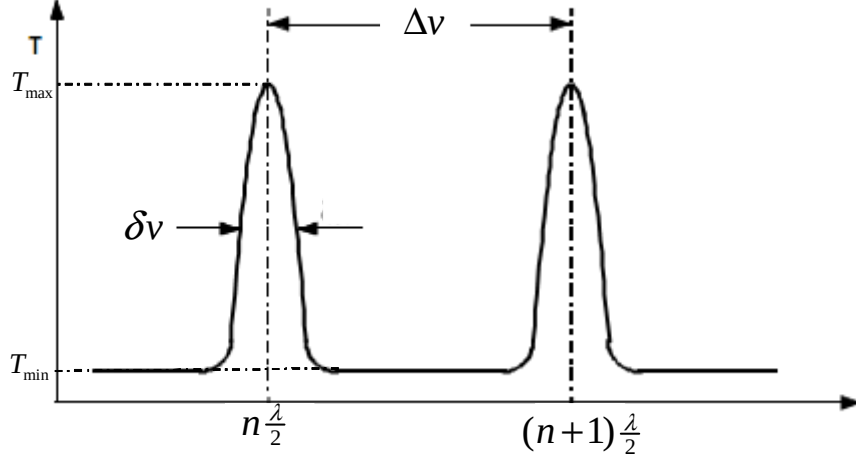


Figure 3.17: Airy transmission function [88].

It is also related to the mirror reflectivity by,

$$F = \frac{\pi\sqrt{R}}{1-R}. \quad (3.5.4)$$

Contrast describes the ratio between the maximum and minimum transmission,

$$C = \frac{T_{\max}}{T_{\min}} \simeq \frac{4F^2}{\pi^2}. \quad (3.5.5)$$

The resolving power, P is given by

$$P = \frac{\nu}{\delta\nu}. \quad (3.5.6)$$

The main function of the Fabry P erot Interferometer described in  3.5.1 is to receive inelastically scattered light from a sample and analyze it. It also receives elastically scattered light directly from a beam splitter, this forms the central peak in the spectrum apart from stabilizing the measurements of the instrument. The inelastically scattered light used in obtaining frequency shift is 10^4 - 10^5 times smaller

than the central elastically scattered light and hence a high contrast spectrometer is required [93]. For high resolution spectroscopy where resolutions of MHz to GHz are required, a Fabry-Pérot Interferometer (FPI) is ideal. Brillouin scattering easily handles frequency shifts of about 0.1 through 50 cm^{-1} and is done exclusively with FPI resonators [88].

In this work, the laser light was focused onto the sample by a lens of focal length 120 mm, the angle of incidence, θ_i on the sample was measured using a vernier protractor, the directional (azimuth) measurements were done with aid of a circular vernier. Upon scattering, the solid cone of scattered light is collimated by the lens and focused by mirrors into the Interferometer. The scattered light is analyzed in a (3 + 3)-tandem Fabry-Pérot-interferometer with a contrast better than $10^9 - 10^{10}$ [94, 95]. The tandem configuration (see figure 3.15) removes the ambiguity of the periodical transmission function of a single interferometer. For all measurements the incident power on the specimen was kept at a low value of less than 100 mW.

The scattered light through the interferometer is detected by a photomultiplier tube (PMT) with less than one dark count per second. Photomultiplier overload is avoided by attenuating the intense elastic peak with optical attenuators. The intensity of light reaching the sample is controlled by the acousto optic modulator (AOM). On the sample, the light is inelastically scattered before entering the interferometer for analysis. Obstructing the light path with an opaque object during alignment is also an important practice of protecting the PMT. However, good measurements are obtained when the external and internal optics are well aligned, the image formed after FP1 and FP2 have been optimized and calibration done using known samples. Alignment and optimization techniques are best achieved

through practice by carefully following the the instructions available in the authors manual which can be downloaded from the internet [96].

3.6 Raman spectroscopy equipment

All Raman spectroscopy measurements were carried out on the Jobin-Yvon T64000 Raman spectrometer. Figure 3.18 is a schematic functional diagram showing the light path for the different multiple configurations of the T64000 Raman system. A detailed description of the parts and working is well documented in [97], a summary of which is adapted here.

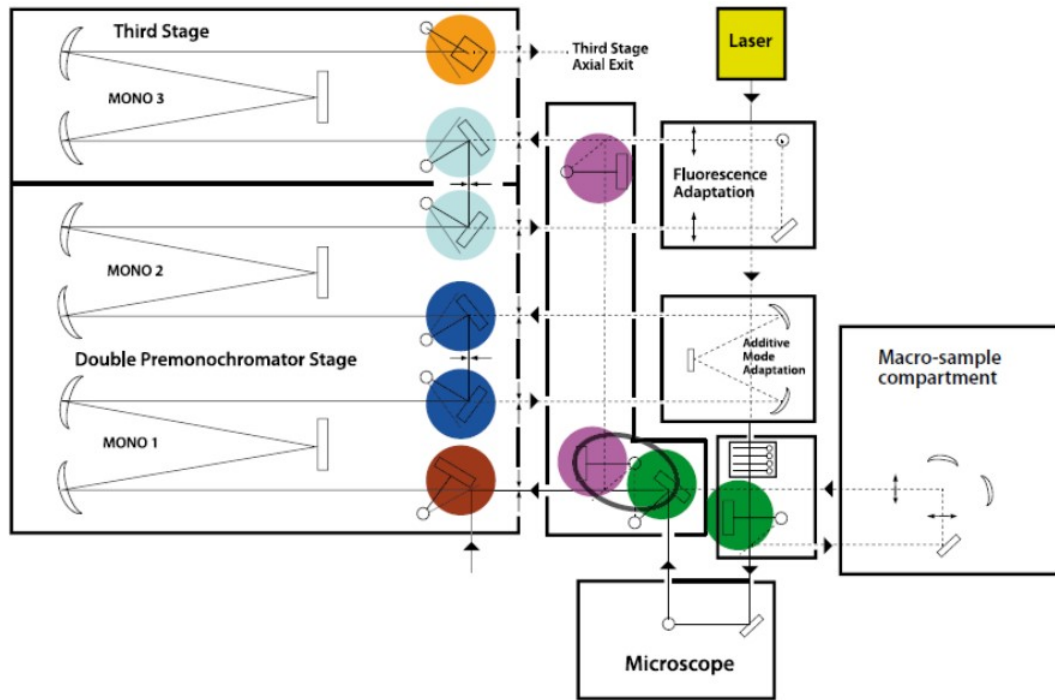


Figure 3.18: Schematic diagram of the Jobin-Yvon T64000 adapted from [98], illustrating the different light path permutations available to the user.

The source of probing light was a Coherent INNOVA Model 308 argon ion laser employing green single line light of wavelength 514.5 nm. The exciting light was focussed onto the sample placed on a motorized X-Y stage. The stage was therefore capable through computer control of moving the sample in x - y directions with a

step size of $0.1\ \mu\text{m}$. This allows the user to select specific spots (positions) along a line or randomly on the sample surface for investigations. Depth profiling (z -direction adjustments) was either done manually via a microscope focussing knob or automatically via a piezo-electric drive (in practice the two are applied complementarily) that moves the objective up or down. Scattered light was collected in the backscattering configuration with a microscope (Olympus BX40). The microscope is equipped with a CCD camera that is attached to a TV monitor. The TV screen aids in viewing and focussing the sample on the stage apart from pinpointing the exact spot on the sample.

Light from the sample gets dispersed in three possible ways; single spectrograph, triple additive or triple subtractive spectrograph modes, summarized in figure 3.18. The selecting wheel directs the light from the microscope by mirrors to the entrance slit of either the single or triple configurations. In single spectrograph mode, light is dispersed by the final stage spectrograph (mono 3, in this study a holographic notch filter was used), while in the triple configurations, it first passes through a double pre-monochromator (mono 1 and mono 2). In triple additive spectrograph mode, the light also passes through the additive mode adaptation. The sample properties and interesting features in its associated spectrum determine which mode is used. Whichever mode is chosen, there is always a trade-off between throughput and spectral resolution. In single spectrograph mode, there is higher throughput and rapid analysis time at the expense of spectral resolution and detection of low wavenumbers ($<200\ \text{cm}^{-1}$) peaks. The triple additive mode gives good resolution but low throughput. The triple subtractive mode offers excellent light rejection at the cost of low throughput. It is thus a mode of choice for analysis of features close to the exciting laser line. In this work the single spectrograph mode was used. This

ensured rapid accumulation and excellent throughput.

Data acquisition was done on a desktop computer connected to the detector. This was done using proprietary software from Horiba, the LabSpec v3.03 running on Microsoft Windows 95 platform. The data were stored in a proprietary format on a computer HDD. The data were then retrieved by exporting to text file format then importing it in programs that enable manipulation. Peak fittings were done using Lorentzian and Gaussian and other manipulation capabilities available in OriginPro v8 software.

3.7 The annealing furnaces

Annealing was done in two different furnaces. The second furnace (RF furnace) was brought in to address the limitations experienced when using the first furnace. Each furnace was used for the whole annealing cycle (from 200 to 1200 °C)

3.7.1 The “horizontal shoot-in furnace”

Isochronal annealing was done using the Carbolite Eurotherm 2416 furnace. In this type of furnace, the sample is put on to a crucible which is then pushed into the heating zone using an insulated rod. The ends are then sealed off and the desired gas introduced. It is therefore suitable for isothermal annealing. A modification to allow for isochronal annealing was achieved using a specially fabricated quartz tube shown in figure 3.19 designed by Dr. C. M. Levitt of Wits University.

This setup made it possible for the sample to be introduced when the tube has been purged with argon gas and the desired annealing temperature reached for at least 15 minutes. The sample was introduced by dropping the sample through

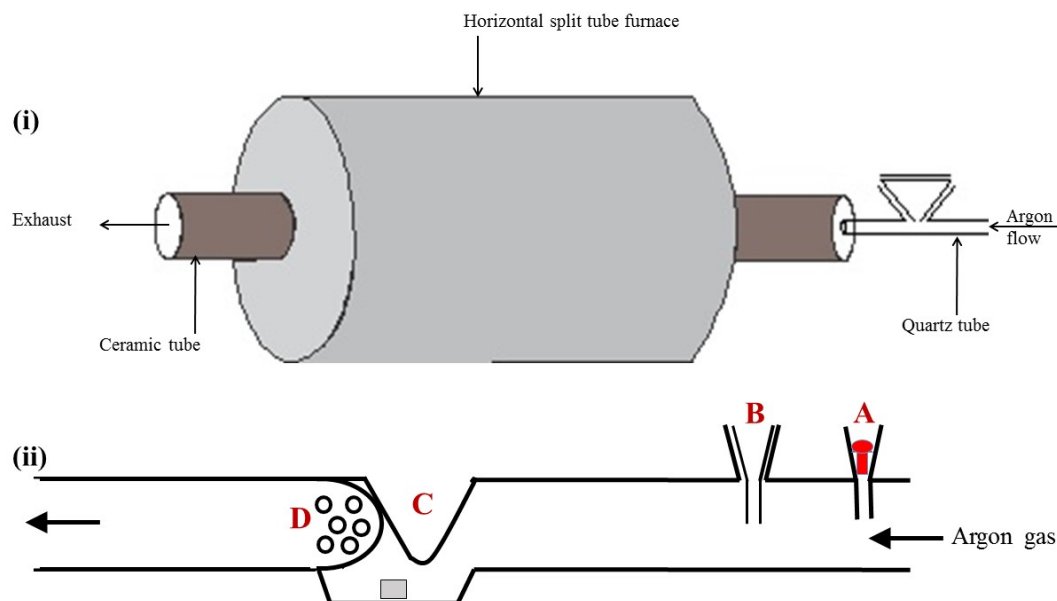


Figure 3.19: (i) The conventional furnace used with sample placed on crucible. (ii) A longitudinal cross section of the modified quartz tube used as sample holder for annealing.

funnel B then suddenly increasing the gas flow rate (shooting), exerting an impulsive force on the sample hence pushing it into the annealing section, C which sits within the heating zone. The sample falls into the depression at section C, where it stays during the entire annealing time. The perforated tube at D prevents the sample from flying past the heating zone, allows for expulsion of air in the heating ‘valley’ and also for exit of the continuous Ar gas. The gas flow rate was checked using the rotameter at A. Annealing would then take place for 30 minutes. At the end of this duration, the sample was then quickly withdrawn by pulling away the entire tube from the heating zone. The sample then cools in the still flowing cold Ar gas. The cooling was monitored with a thermocouple until temperature at the sample zone was $\leq 200\text{ }^{\circ}\text{C}$, then the gas was turned off. If diamond is kept in an oxygen atmosphere at temperatures above $600\text{ }^{\circ}\text{C}$, oxygen attacks the tangling bonds transforming the diamond to the more stable allotrope, graphite.

3.7.2 The RF furnace

Induction heating by RF electric current occurs when an electric conductor placed in an inductor is heated rapidly by induced eddy current caused by electromagnetic induction and hysteretic heat loss [99]. The RF frequency used for induction heating was 5000-9000 times higher than that supplied by the mains (50 Hz in South Africa). For instance in figure 3.20III where for a current of 52.8 A, the frequency was 413 KHz. Induced current flows only in the limited area near the surface of heated material because of skin and proximity effects. Skin effect is the phenomenon where RF electric current is confined to the area near the surface of a conductive material and proximity effect is when the primary current in the inductor and the secondary current in the conductive material pull each other since their directions are opposite and flow in the limited area near the surface where the distance is nearest each other. The penetration depth δ is the point where the RF electric current decreases to $\approx 37\%$ ($1/e=1/2.718=0.368$; e is the base of natural log) compared with the current at the surface and is calculated as [99]:

$$\delta = 5.03 \times \sqrt{\frac{\rho}{\mu f}}(\text{cm}), \quad (3.7.1)$$

where μ is specific permeability (magnetic material: $\mu > 1$, non magnetic material: $\mu=1$), f is the frequency (Hz) and ρ is the specific resistance ($\mu\Omega \cdot \text{cm}$). This implies theoretically that penetration depth reduces with increasing frequency hence heating would be concentrated at the surface. However, practically the heated depth may be larger due to conduction in the heated material.

The heating inductor induces RF current in the heating portion of a work-piece, a coil made of copper pipe with 3 turns (B in figure 3.20) inside of which water flows. Cooling of the induction coil was done by connecting the RF furnace to a

chiller that kept cooling water temperature at between 7 and 10 °C.

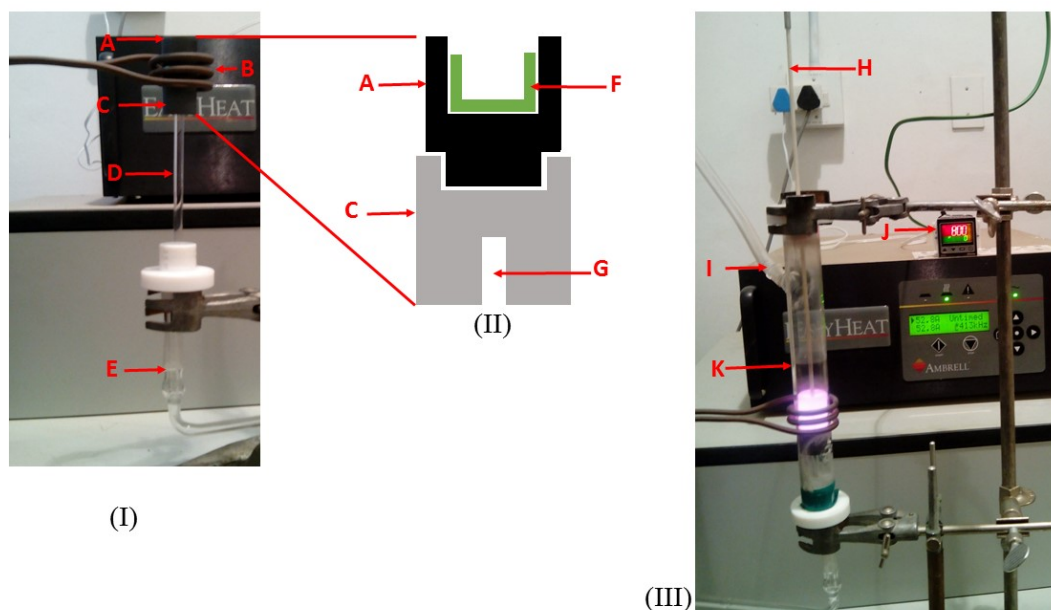


Figure 3.20: Modified parts for use with the RF furnace for annealing. A is a graphite (conductor) cylindrical hollow crucible in which a quartz pot F loosely fits. C is wonderstone (insulator) in which the crucible sits, on the lower end it is held by quartz glass rod, D at the hollow part G. E and I are the gas inlet and outlet tubes, respectively. H is a thermocouple rod that extends to the heating point on F and temperature readings shown on J. K is the quartz tube that encloses the setup to ensure that the samples are annealed under a sea of Ar gas.

There is clearance between the work-piece and the copper pipes which affects the power efficiency. However, for expansion of the heated work-piece and mechanical movements of contents, the gap is inevitable. There are gaps allowed between the different parts in (II), to cater for the different expansion rates. Unlike the “horizontal shoot-in furnace” §3.7.1, the RF furnace had the advantage of dropping the sample vertically through a capillary glass tube onto a clean quartz pot pre-heated to the desired temperature. The quartz pot was placed in a well fitting hollow graphite crucible that evenly distributed the heat all around it. The graphite crucible and its contents were enclosed in a long quartz tube. As can be seen in 3.20(III), heating is concentrated at the desired point as shown by the glowing graphite crucible. There was a gas inlet at the bottom and outlet at the top

that ensured that Ar gas was continuously supplied during the rapid ramping, isochronal annealing and cooling processes. The sample was totally immersed in a sea of Ar gas. Ar gas is heavier than air and displaces all the air from the tube. No air can enter when top cover is removed to replace the thermocouple that was formally held on the quartz pot with the sample since there is a continuous flow of Ar gas during the changeover process. Gas flow through the quartz tube is monitored by observing bubbling in a water bath placed at the end of the outlet. The probability of contamination of samples or oxidation is minimal when using this furnace. Annealing was done for 30 minutes then the furnace switched off. The temperature falls off first while the sample is still under Ar gas flow. At temperatures below 200 °C, the gas was turned off. The sample could then be removed anytime later.

In summary, the chapter has provided a description of the samples and their treatment in different equipment. The equipments used and the physics behind their operation have also been explained.

Chapter 4

Experimental theory, practice and analytical techniques

4.1 Introduction

This chapter is about interaction of matter with matter and matter with EM waves. Matter to matter interaction modifies the material while matter to EM waves interaction gives information about the material. The information obtained can be used in the study of elastic, optic, electronic, electrical and structural properties of the material. These interactions take place in special equipment and apparatus. The apparatus used in this study has been explained in the previous chapter. This chapter therefore gives the theory of ion implantation, the transformation of ion-implanted diamond due to heat treatment and the analytical techniques explored in studying the materials properties.

4.2 Ion-induced changes in materials

Semiconductor materials have been successfully used in electronic devices due to the possibility to alter their conductivity several orders of magnitude by introducing small quantities of dopant atoms [100]. The materials in group IV of the periodic table can be doped by introduction of the appropriate impurities during

crystal growth, by post growth in-diffusion or by ion implantation. Diffusion is a doping technique performed in furnaces at high temperature. Due to some of its limitations compared to ion implantation, it was replaced with ion implantation in the mid 1970s [101, 102]. Ion implantation is therefore employed in manufacture of semiconductors. This technique allows one not only to implant at certain desired temperature, but also enables one to a good degree to: independently control dopant concentration by amount of current used and time for implantation, profile/ spatial distribution by implanting with single energy or multiple times with different energies, and to place implanted atoms at the desired depth in the substrate accomplished by the ion energy. Figure 4.1 shows that it is possible to achieve precise doping in a selected volume using ion implantation as compared to diffusion.

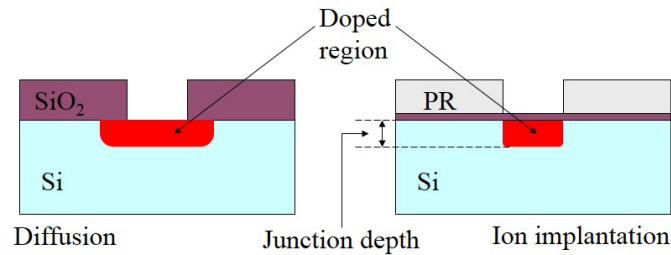


Figure 4.1: Comparison of final product of doping in Si using diffusion and ion implantation. Photoresist (PR) can be used in masking for ion implantation done at low temperature, something which can not be done in diffusion since doping temperature is always high. The lateral and vertical boundaries of the doped region are clear in the ion implanted Si wafer. [103]

During ion implantation, atoms are forced into the target's crystal regardless of the solubility or diffusivity of the dopant atoms in the target. Ion implantation therefore, is a process accompanied by much damage of chemical bonds which may itself give rise to electrical conductivity. In an as-implanted condition, the carbon implanted diamond has a structure of a defective matrix containing an elevated density of point defects. Appropriate annealing conditions must be found to remove

the lattice damage and to drive the implants to the desired lattice sites. Kalish [104] has argued that in diamond, the procedure for obtaining conductivities due only to the implanted dopants and lattice damage or graphitic islands is a complex one.

Since ion implantation can modify the near surface properties of any target material, it has been used to create new metastable phases, to harden metals, to change the optical properties of dielectrics and to modify the properties of semiconductors.

A projectile atom enters the target in a given direction of motion with kinetic energy. After some distance of relatively undisturbed motion with mainly electronic stopping, it collides with a stationary lattice atom in such a way that the primary suffers considerable angular deflection, transfers kinetic energy to the struck atom and continues through the lattice in a new direction with reduced energy. The process of collision continues until the primary atom has no more kinetic energy that can enable it to continue moving and hence comes to rest either as an interstitial or substitutional atom. The set of collisions and final resting point of the projectile atom is illustrated in figure 4.2. These collisions are consistent with the hard-sphere model, hence collisions are treated with hard-sphere approximations which incorporate the classical atomic scattering and to a good extent the aspects of Bohr atom and Rutherford scattering [105].

The incident projectile may transfer high enough energy to the lattice atom to dislodge it. The dislodged atom may leave its lattice site and itself become an energetic moving atom, leading to further displaced atoms, and thus a whole cascade process. The total path length L in figure 4.2 is computed by adding up the individual path segments:

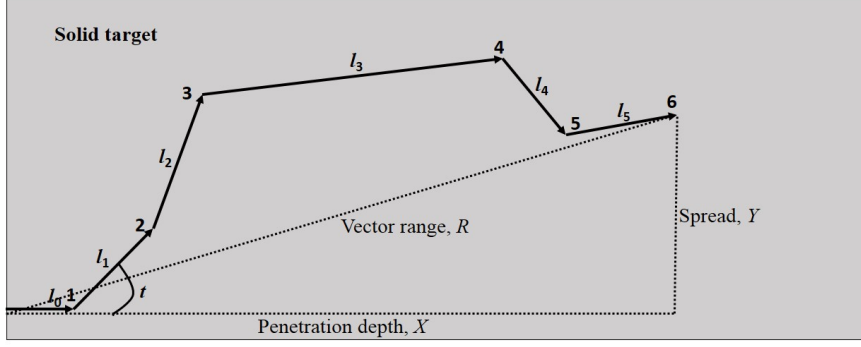


Figure 4.2: Schematic diagram of a hypothetical path (solid arrowed lines) of a lone projectile atom being slowed down by collisions and pertinent distances for range calculations, t is the angle through which the projectile is scattered when it collides with target atom at point 1 [106].

$$L = l_0 + l_1 + \cdots + l_5, \quad (4.2.1)$$

Since there are many atoms implanted into the solid, the average total path length over the distribution is then,

$$\bar{L} = \frac{1}{N} \sum_{i=1}^N L, \quad (4.2.2)$$

In actual sense the sample size is infinite, hence equation (4.2.2) passes over into an integral.

The collisions result in deviating the projectile from its initial direction. The vector range, R (magnitude of vector distance) is the distance from the point of entry into the solid to the final resting point of the primary. If the normalized spatial distribution of final resting position is $F(\vec{r}) d\vec{r}$, then the average vector range is given by;

$$\bar{R} = \frac{1}{N} \sum_{i=1}^N R = \int_1^\infty r F(\vec{r}) d(\vec{r}). \quad (4.2.3)$$

The penetration depth is the projection of the vector distance to the final resting position onto the original direction of motion, $X = R_{\parallel} = \vec{r} \cdot \vec{v}_0 / v$, where v_0 is the

velocity vector of projectile at the entry point into the solid. The spread, $Y = R_{\perp}$ is the projection of the vector distance onto a direction perpendicular to the direction of motion.

Ion implantation is a versatile and highly controlled technique for the modification of surfaces and the synthesis of buried layers of a material [107]. It is a violent process that breaks bonds and creates of defects in the target (radiation damage). The ion entering the sample is a moving charge which interacts with stationary target atoms. The nuclei of the target atoms recoil slowly as electrons move quickly and collectively in reaction to the approaching ion charge. The transfer of energy from the ion to the nuclei and electrons leads to ion energy loss as well as deflection from the original direction. By assuming an elastic collision and treating forces between the ion and atoms as being electrostatic, the final trajectory and velocities can be found from the conservation of momentum and energy of the system [108]. Generally, the interaction potential for two atoms is described with the basic contributions being Coulombic, kinetic and exchange energies:

$$V = V_{n-n} + V_{e-e} + V_{e-n} + V_k + V_x, \quad (4.2.4)$$

where the first three terms on the RHS are Coulombic, i.e. electrostatic potential between the nuclei of the ion and atom, the two electron distributions and the interaction of each of the nuclei and the other electrons, respectively. V_k is the increase in kinetic energy of the electrons in the overlap region due to Pauli excitation and V_x is the increase in exchange energy of these electrons.

Radiation damage is a disturbance of the periodic order of the lattice atoms in the crystalline material, and is often undesirable thus requiring rectification. The removal of the damage requires annihilation of the implantation related defects

normally achieved by imparting sufficient energy to the defects to allow the recombination of the interstitials and vacancies, for the case of elementary point defects, and to break up complex defect agglomerates [104]. Annealing also drives the ions to crystal's sites where they act as donors for n-type semiconductors or acceptors for p-type semiconductors. The relative concentration of randomly distributed lattice atoms, n_{da} can be determined as a function of depth X and is called the defect/damage concentration, $n_{da}(X)$. A value of $n_{da} = 1$ is commonly taken to indicate amorphisation [109]. Some parameters that have a direct bearing on the radiation damage are briefly discussed in the following sections.

4.2.1 Ion mass

The mass of ion determines the energy transferred to the target's crystal lattice. This means that heavier ions result in more damage if other factors are kept constant. During implantation the ions lose their energy by excitation of the electronic system (electronic energy loss) and through nuclear collision with the host atoms (nuclear energy loss), and finally comes to rest at a certain depth X . The main damage is produced by the nuclear energy loss which results in collision cascades, the density of which depends on ion mass. Electrons tend to absorb energy most efficiently from particles whose velocity compares well to their velocity. Much of the electronic energy loss occurs when the ion is still moving at high velocity in the target. Though the electronic energy loss is too low to produce significant damage in semiconductors, the electronic energy may influence the effect of the nuclear energy loss [110]

4.2.2 Target temperature during implantation

The temperature of the target determines what happens to the defects once formed. Working at elevated temperatures (room temperature or above) leads to intrinsic defects (interstitials or vacancies) becoming mobile. This allows for defect recombination within the primary collision cascades, which reduces the damage remaining after implantation. At low temperatures (liquid nitrogen temperature), thermal effects are widely excluded. If the implantation temperature is too low for any defect mobility, no annealing occurs and, consequently, more radiation damage occurs.

4.2.3 Ion flux

Ion flux is the number of ions implanted per unit area and time. It determines the time between two subsequent ion impacts or the time available for annealing of the damage produced by the previous ion. Moreover, high ion flux may locally warm the sample. The effect of ion flux on the formation of radiation damage is therefore, related to implantation temperature. For moderate temperature and reasonable fluxes used for common applications, damage concentration decreases with decreasing ion flux. Wesch [110] argues that under extreme conditions i.e. at high temperature and high ion fluxes, or extremely high ion fluxes, the process of damage formation becomes much more complex, and pure ion-flux effects may also occur.

4.2.4 Ion energy

The angle of incidence and to a greater extent the energy of the ion beam interacting with a surface determines what can occur [111]; reflection and adsorption (< 5

eV), surface damage and migration (5-10 eV), sputtering (3-10 keV), ion implantation (> 10 keV), chemical reaction or electron and photon emission. When the ion energy is increased, the maximum distribution shifts into larger depth. This is because the nuclear energy loss occurs mostly towards the end of the range of the implanted ions, when their velocity reduces. Before that, the electronic energy loss is the dominating process. Nuclear energy loss leads to an increase in straggling, and ion straggling may therefore be an important factor of ion energy. By considering a volume element (voxel) within a sample close to the maximum distribution, this voxel is much more often struck by low energy ions than for high energy ions due to the larger straggling in the later case. The enhanced straggling of the ions over the depth results in a reduction of the local ion flux at a fixed depth. This so-called local ion flux decreases with increasing ion energy.

Energy of the projectiles at the entry point and the random collision they encounter with the substrate determines the depth at which the dopants settle. This depth has some distribution as the collision with the target atoms is random. The total distance travelled by the projectile is called the range, R and its projection parallel to the ion beam is called the projected range, X (see figure 4.3). X is the average depth where most ions settle in the substrate. The projected straggle ΔR_p describes the statistical fluctuation of X [106].

4.2.5 Ion fluence/ dose

Ion fluence is the number of ions implanted per unit area in a material and is given by the product of the ion flux (usually constant) and time. Consequently, the damage concentration versus the ion fluence represents a time dependence and comprises information about the mechanisms of damage formation.

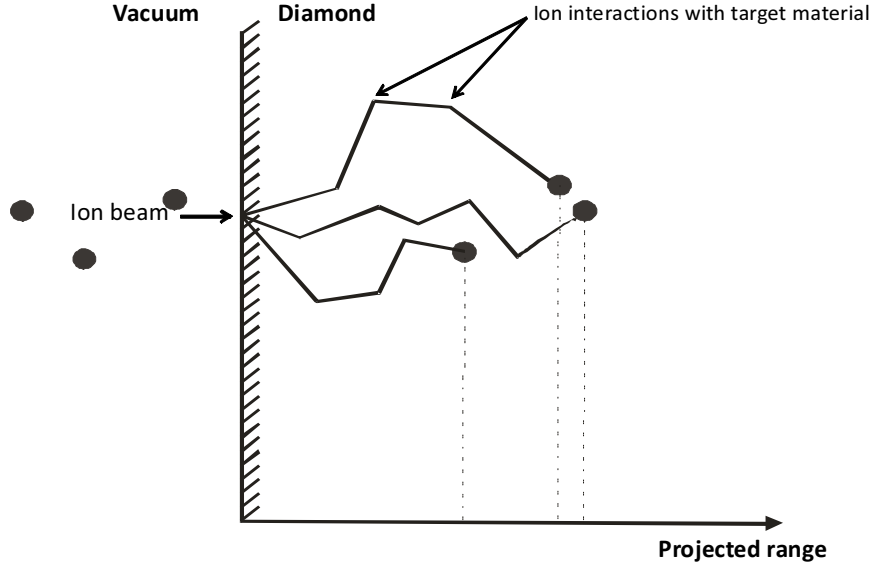


Figure 4.3: Schematic diagram showing ion interaction and penetration depth in a diamond target.

Key parameters that define the final implant are the fluence, Φ (ions/cm²) and the energy, E (keV). The fluence relates to the beam current I ,

$$\Phi = \frac{It}{q_i A}, \quad (4.2.5)$$

where, t is the implantation time, A is beam area and q_i is the charge per ion.

4.2.6 Ion stopping

Projected ions lose energy in the target due to effects of elastic collisions with the nuclei of the target material and inelastic collisions with the electrons. The loss is actually a transfer of energy from the ions to the target atoms. The energy transfer depends on the moving particles' initial speed and direction as well as the mass and charge of the two particles. The moving charge causes the stationary atoms in its neighbourhood to recoil and absorb some energy while the moving particle gets deflected in the process. Conservation of energy and momentum in the system determines the final velocities. The collision dynamics are well explained using

the laboratory and centre-of-mass coordinate systems [108]. Electronic stopping is an inelastic process where energy lost by incident ions is dissipated through the electron cloud into thermal vibrations of the target. The moving ion and stationary target ions undergo constant changes as the ion passes through. The perturbed target electrons polarize in front and around the ion, changing the local target electron density, the ion charge density also polarizes and changes its shape, losing energy in the process. The total stopping force S which is defined as energy loss per unit path length of the ion is thus mathematically defined as,

$$S = \left(\frac{dE}{dx} \right)_{nuclear} + \left(\frac{dE}{dx} \right)_{electrons} . \quad (4.2.6)$$

It can be seen from figure 4.4 obtained using TRIM simulation, that nuclear stopping dominates at low ion velocities (towards end of range), whereas at higher velocities, electronic energy loss dominates in the target material. Nuclear stopping results in denser damage than electronic stopping.

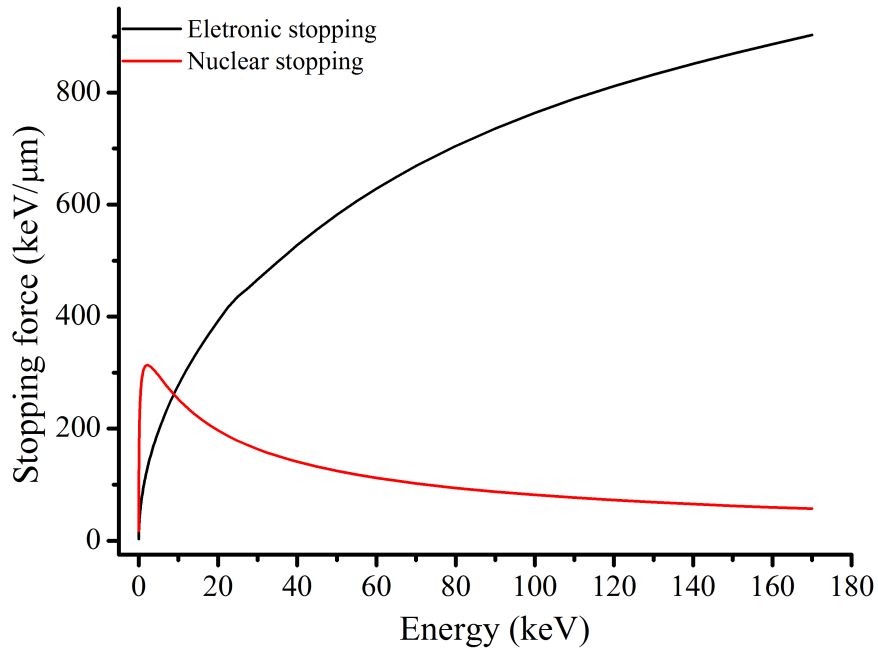


Figure 4.4: Ionization graph for carbon implanted diamond at energy of 170 keV. Other energies used in this study ionize in a similar way.

Nuclear stopping is an elastic process and can be simulated as the collision of two bare nuclei. If the separation distance between them is r then the coulombic potential while ignoring relativistic effects is:

$$V_c(r) = \frac{q^2 z_1 z_2}{4\pi \varepsilon_o r}. \quad (4.2.7)$$

where z_1, z_2 are either the ion or target atoms, ε_o is the permittivity and q is the electronic charge. The real potential has a screening function which accounts for the nuclear shielding effect by electrons at large distances:

$$V(r) = V_c(r) f_s(r). \quad (4.2.8)$$

The scattering angle for any incident ion trajectory can be calculated from the equations obtained from the interaction potential. From the centre-of-mass frame we have:

$$T = \frac{4M_1 M_2}{(M_1 + M_2)^2} E \sin(\theta/2). \quad (4.2.9)$$

where T is the energy lost by the ion, ion energy is E , θ is the scattering angle, and M_1, M_2 is the mass of either the ion or target atom. The energy loss due to nuclear collisions per unit length is an integral of the product of energy loss and probability of collision occurring:

$$S_n = N \int_0^{T_{\max}} T d\sigma. \quad (4.2.10)$$

where $d\sigma$ is the differential cross section and N is the target atoms per unit volume.

It may be expected that C^+ implantation into diamond would lead to a substantial reduction in the total number of vacancies in the implanted system due

to replacement collisions. The requirements for replacement collisions are met in such a system if collisions are taken as head-on i.e. the moving atoms are identical to the target atoms. The incident atom ends up with less energy than E_f (it stops in the target) and the struck atom has enough energy to move on (if energy is greater than the displacement energy, E_{disp}) [108]. Prins [112], found out that in a strong covalent lattice like diamond, the activation energy for interstitial-vacancy recombination is a much larger quantity E_c than the displacement energy E_d . E_c is an activation barrier that has to be overcome when an interstitial jumps from a ‘meet site’ to a ‘catch site’. This explains why there would still be damage of diamond when implanted with C ions.

4.3 Ion implantation in diamond

4.3.1 Implantation dopants

Possible dopants in diamond are boron and nitrogen, due to their atom size relative to diamond, they easily occupy substitutional sites. Nature has provided information on the preferred dopant in the case of p-type doping (B, found in type IIb diamond) and thus the electrical properties expected for B doped diamond. Boron is an acceptor atom in the substitutional position in diamond lattice with an activation energy of 0.37 eV [113]. The p-type doping of diamond with boron has been achieved by a variety of techniques including ion implantation [114, 115]. Phosphorus and nitrogen ought to be donors for n-type doping in diamond, but are deep lying donors with activation energies of 0.55-0.63 [116, 117] and 1.7 eV, respectively. There have also been attempts at using alkali metals (lithium and sodium) in obtaining shallow donors for n-type doping in diamond [118, 119, 120]. Carbon and noble gases have been used in ion implantation with the aim of introducing

damage in the diamond crystal. The damage induces conduction which depends on the volume density of the defects and on the implantation temperature as argued by Praver and Kalish [121]. The damage can be transformed by proper annealing. In diamond, the annealing temperature is very important due to metastability of the sp^3 bonds with respect to the sp^2 bonding. During annealing, the atoms rearrange to form the more stable and electrically conductive sp^2 bonds. This therefore implies that to achieve the desired results, one must be very careful when choosing the implantation and annealing conditions regarding the implantation energies, temperature, fluence, dose rate and the annealing temperature.

4.3.2 Amorphisation models

Ion implantation in diamond is challenging due to the tight bonding of the carbon atoms in the sp^3 hybridization and its metastable state. Lack of free bonding sites makes it difficult for impurities to occupy the required sites (usually substitutional) where they act as donors or acceptors. The tightness of the crystal also leads to slow diffusion of the implanted ions [9]. The structural sequence changes that occur during conversion from crystalline to amorphous states is a complex process. Sadana [122] argued that; (i) individual damage clusters are amorphous and complete amorphisation occurs as a result of accumulation of individual damage clusters, (ii) when defect concentration reaches some critical value in a crystal, the crystal becomes unstable and transforms to an amorphous state.

The Prins' ballistic model

Prins [123, 124] postulated that, in diamond, the defects (mostly point defects) that form in the collision cascades, although not homogeneously distributed, consists primarily of vacancies and interstitial atoms. He suggests that the major cause of

damage with the onset of implantation process is not graphite bond formation. In fact these bonds only form when the local vacancy density, as it relates to the material density, reaches a critical value. He further shows through equations for generation and accumulation of defects based on point defect creation and annealing that amorphisation in diamond, depends in part to implantation dose and to annealing temperature.

This model is appropriate to diamond because it has been argued by Prins and Derry [123] that it is not possible to anneal diamond without inducing graphitization, at temperatures where point defects are generated thermally. Other models that explain modification of other materials during ion implantation are briefly explained below.

The displacement thermal spike model

Change of lattice structure takes place as fast moving ions enter the target and makes many collisions with the lattice atoms displacing them from their lattice sites. During the slowing down process of energetic atoms, the kinetic energy of a moving ion is partially transferred to host atoms by elastic collisions. The displaced atoms, with sufficient recoil momentum, transfer part of their energy to other atoms before coming to rest. A cascade evolves resulting in the formation of a very hot, highly disrupted region inside the solid called a “thermal spike”. This is a short term local melting in the neighbourhood of the projectile affected region as shown in figure 4.5. That the time scale of quenching is so short (picoseconds), has been supported by the observations of Müller [125], who found that for Ar^+ into nickel at 150 eV, the thermal spike life-time is ≈ 0.2 ps. This model may therefore be suitable for materials with low melting point.

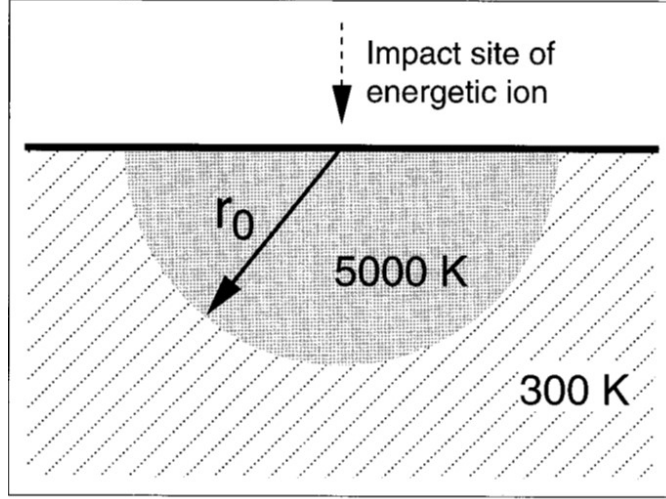


Figure 4.5: Schematic diagram of the thermal spike analytic model. The hemispherical spike with initial radius r_0 has much higher local temperature compared to the rest of the substrate [126]

The Morehead and Crowder model

The model assumes heterogenous nucleation of the amorphous layer at doses close to those which yield a continuous amorphous layer formed by overlap. It suggests that the path of each impinging ion is surrounded by a cylinder of damage whose radius R_o is determined by the energy lost by the projectile ion in nuclear displacement per unit path length [127]. This ‘cylinder’ of damage converts from an unstable disordered region, containing many dangling bonds, to stable amorphous region in relaxation time τ . The radius of the cylinder that converts to amorphous rather than crystalline material is reduced in this time by the ‘outdiffusion’ of ‘vacancies’ by an amount δR . The sheath from which the vacancies escaped recrystallizes, while the inner portion which retained the vacancies form a stable amorphous layer which has a lower mass density than the crystalline material. In brief the model stipulates that the density of the displaced atoms within the collision cascades can be so high that isolated regions generated within the material makes it temporarily unstable. Within a relaxation time τ , this unstable damage

converts to form stable amorphous regions. This model has been used to explain defect formation in silicon.

4.4 The annealing process

The annealing temperatures are described in §3.2. Isochronal annealing done in this study is a process where the annealing time is kept constant while annealing temperature varies in controlled steps. The other annealing process, isothermal takes place when the annealing times vary while the annealing temperature is kept constant. As stated earlier, ion implantation creates defects in solids. Concentrations of such defects beyond the thermal equilibrium tend to react to reduce the free energy of the solid. Annealing done in a controlled manner can be an effective tool for studying the damage evolution due to the effect of radiation damage. While some defects are mobile at low temperature e.g, interstitials in diamond at room temperature to about 500 °C [128] and possibly move faster at higher temperatures. Others require higher temperature to start moving. Vacancies start moving after 700 K [100].

When the source of irradiation is removed the defects in a crystal reach thermodynamic equilibrium. Below the mobility threshold temperature, the defects get ‘frozen’ in the crystal. Above the mobility threshold temperatures when materials have sufficient internal energy, it can be expected that properties of the solid induced by defects will change more rapidly. High temperatures, therefore induce defect decay. Annealing is therefore a process of change/ decay of property due to defects induced by temperature. It has also been defined in terms of the reduction of the original type of defects in crystals [129]. Defects contribute to certain properties of solids (e.g. optical, electronic, mechanical etc), their decay require some

energy for certain fate events to proceed and this in turn modifies the observable property of the solid. According to Kelly [130], the annealing rate of property may be described with equations similar to those of reaction kinetics:

$$\frac{dP(t)}{dt} = -AP_o(t)^\gamma e^{-E_m/\kappa_B T}, \quad (4.4.1)$$

where $P(t)$ is the remaining property from the original property P_o after time t at temperature T , γ is the reaction order, A is the effective frequency of vibration of the defect toward the saddle point (frequency factor), κ_B is the Boltzmann constant while E_m is the energy barrier which must be overcome by the activation energy for a reaction to proceed.

The thermally activated motion of ion-induced defects causes them to possibly encounter traps (e.g. impurities) where they are immobilized, be absorbed by sinks (e.g. surfaces, dislocations, grain boundaries). An interstitial may encounter a vacancy and the two become annihilated or the defects may form defect clusters where they act as traps among themselves. The thermal process therefore provides the activation energy that leads to the disappearance of excess defects when they migrate, recombine, form complexes or dissociate from clusters and traps.

4.4.1 Diffusion of interstitials

This section briefly summarizes from Wert and Zener [131], which through diffusion kinetics shows that it is interstitials that move, a concept that later researchers concur with [112]. Interstitial atoms diffuse by simply hopping between interstitial positions in response to thermal fluctuations, the direction of each particular jump being random. The diffusion is given by:

$$D = D_0 e^{-E_m/RT}, \quad (4.4.2)$$

while the theoretical diffusion coefficient for interstitial atoms in a cubic lattice has the form

$$D = \frac{\alpha d^2}{\tau}, \quad (4.4.3)$$

where d is the lattice constant, τ is the mean time-of-stay in one interstitial position between jumps and α is a coefficient whose numerical strength depends upon the location of the interstitial position. Over a limited temperature range, the mean time-of-stay of an interstitial requires heat of activation,

$$\tau^{-1} = \tau_0^{-1} e^{-E_m/RT}, \quad (4.4.4)$$

here

$$\tau_0^{-1} = n\nu e^{\Delta S/R}, \quad (4.4.5)$$

where n is the number of nearest neighbour interstitial positions, ν is the frequency of vibration of a solute atom in an interstitial position while ΔS is entropy of excitation interpreted as;

$$\Delta S = \frac{-\partial \Delta F}{\partial T}, \quad (4.4.6)$$

i.e. If all the work went into straining the lattice, then ΔF would have essentially the same temperature coefficient as the elastic moduli. ΔF is the work done in

transferring a mole of solute atoms from a constrained two-dimensional vibration about an interstitial position to a constrained two-dimensional vibration about a divide in a plane normal to the line joining the two neighbouring interstitial positions [131]. An upper limit to ΔS is thus obtained by setting

$$\Delta S \simeq -E_m \left(\frac{d \ln \mu}{dT} \right), \quad (4.4.7)$$

where μ is the shear modulus.

4.4.2 Decay of vacancies

In solids, an atom is tightly held in its lattice position due to bonding to other atoms. An atom and its neighbouring vacancy are separated by a potential barrier E_m which must be overcome for the atom to jump into the vacancy. A better understanding of the decay in vacancies as a result their annihilation by interstitials as briefly given in this section is exclusively from [112].

Given that there is an average density of N_v vacancies and N_i interstitials per cm^3 within an implanted layer of width d . When subjected to heat treatment, the interstitial atoms can either diffuse out of the layer (escape/ enter “another sink”) or can meet-up and annihilate vacancies. If the average number of jumps an atom requires to escape is μ_e and to capture and annihilate a vacancy is μ_c , then the probability P_{Rc} that an interstitial atom meets up and combines with a vacancy rather than another sink is given by,

$$P_{Rc} = \frac{\mu_e}{\mu_e + \mu_c} = \frac{\mu_e N_v}{\mu_e N_v + Q \left(1 + q \exp \left[\frac{E_C - E_D}{\kappa_B T} \right] \right)}, \quad (4.4.8)$$

where E_C is the activation energy and E_D is the migration energy of the interstitial defects, that on average makes μ_i jumps per second. κ_B is the Boltzmann constant and T is the annealing temperature. Q interstitial sites per unit volume while q is the ratio of the number of accessible interstitial sites to the number of catch-sites surrounding the meet-site.

The rate with which interstitial atoms recombine with vacancies κ_c is given by

$$\kappa_c = \left(\frac{\nu}{\mu_m} \right) \frac{\exp\left[-\frac{E_D}{\kappa_B T}\right]}{1 + q \exp\left[-\frac{E_D - E_C}{\kappa_B T}\right]}, \quad (4.4.9)$$

where ν is the frequency of the interstitial atom and μ_m is the number of jumps an interstitial has to make to ‘meet-up’ with a vacancy, this is different to μ_c which is the average number of jumps an interstitial makes to meet-up and combine with vacancies. The rate at which interstitials meet vacancies $\kappa_m = \mu_i/\mu_m$ can differ from the rate at which they annihilate them $\kappa_c = \mu_i/\mu_c$.

Three scenario arise from equation 4.4.9; when $E_C = E_D$ we have,

$$\kappa_c = \frac{\nu}{\mu_m(1 + q)} \exp\left[-\frac{E_D}{\kappa_B T}\right], \quad (4.4.10)$$

which is the recombination rate. If $E_C < E_D$ and $E_D - E_C < E_D$ then the migration energy for the interstitial atom diffusion determines the reaction rate. If $E_C > E_D$ and $E_D - E_C < E_C$ then the reaction rate is dominated by the activation energy.

In terms of equation 4.4.8, the kinetic equation for vacancy decay relative to interstitial atom decay may be written as,

$$\frac{dN_v}{dt} = P_{Rc} \frac{dN_i}{dt}. \quad (4.4.11)$$

Assuming that $N_v = N_i$ initially and integrating in terms of the final and initial vacancy densities, N_{vf} and N_{vo} , respectively, that

$$N_{vf} = N_{vo} \exp[-\gamma N_{vf}], \quad (4.4.12)$$

where

$$\gamma = \frac{\mu_e}{Q \left(1 + q \exp \left[\frac{E_C - E_D}{\kappa_B T} \right] \right)}. \quad (4.4.13)$$

Equation 4.4.13 was obtained by assuming that $E_C \neq E_D$ giving a more realistic value of γ [112].

NB: Howard and Lindiard [132] using statistical mechanics showed that migrating atoms have a jump frequency associated with the vibration of the atom between its original position and the saddle point of the Arrhenius equation form,

$$\nu = \nu_0 e^{-E_m / \kappa_B T}, \quad (4.4.14)$$

where ν_0 is the effective frequency of the defect towards the saddle point. The frequency of these atoms depends on the temperature of the crystal, this underscores the observable change in property as a factor of annealing temperature.

4.5 Analytical techniques

To study the interaction of matter with radiated electromagnetic waves, spectroscopic techniques were employed in this work. Light was the main probe tool as used in surface Brillouin scattering, Raman spectroscopy, UV/VIS and IR measurements. These optical spectroscopy techniques are based on the fact that when

light interacts with matter, it may be transmitted, absorbed, reflected or scattered. However absorption and scattering were more useful to this work. Optical spectroscopic techniques are non-contact, thus when used carefully are non-destructive. They therefore do not change the properties of the sample while providing useful information about the sample.

A brief description of the properties of electromagnetic (EM) radiation useful in spectroscopic techniques is hereby given. EM radiation is a form of energy described by the properties of waves and particles. As a wave, EM radiation is composed of oscillating electric and magnetic fields that propagate through vacuum and matter in a linear path. If the matter has constant optical density the radiations travel with constant velocity. The general equation of an EM wave propagating in matter is given by;

$$A_t = A_x \sin(2\pi\nu t + \phi), \quad (4.5.1)$$

where A_t is the magnitude of the electric/ magnetic field at time t and A_x is the electric/ magnetic field's maximum amplitude. The amplitude determines the EM wave energy as it travels through matter, ν is the wave's frequency and ϕ is the phase angle which accounts for the fact that A_t needs not be zero at $t=0$. Other properties in the wave nature of EM radiation are polarization, wavelength (λ) and its reciprocal, the wavenumber ($\bar{\nu} = 1/\lambda$) in units of cm^{-1} .

EM radiation can also be considered to consist of a beam of energetic particles, photons. When matter absorbs/ releases a photon, it undergoes a change in internal energy. A photon is said to be annihilated when matter absorbs it, and creation occurs when matter emits a photon. The photon energy in Joules in vacuum is given by:

$$E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu}, \quad (4.5.2)$$

where h is Planck's constant (6.626×10^{-34} J.s), c is the speed of light in vacuum, it is 2.99792×10^8 ms⁻¹; in matter the speed of light $v < c$. The difference between v and c is sufficiently small in air hence to three s.f, 3.00×10^8 ms⁻¹ is accurate enough for most purposes. However, diamond with a refractive index of 2.417, light travels at a much slower speed of 1.42×10^8 ms⁻¹

In spectroscopy measurements, EM interaction with matter leads to formation of dipoles (electric/ magnetic dipoles). An electric dipole is formed when a pair of charges of equal magnitude and opposite sign are separated by a given distance. If $\mathbf{s}$ is a vector oriented from a charge $-q$ to a charge $+q$, and whose magnitude is the separation of the charges, the dipole moment vector $\mathbf{P}$ (magnitude P) is given by equation (4.5.3)

$$\mathbf{P} = q\mathbf{s}. \quad (4.5.3)$$

A brief explanation of matter-EM waves interaction from Long [133] is hereby given. An unsymmetrical electron distribution in a molecule leads to permanent dipole. During a vibration, the magnitude of the dipole moment may change resulting in a dipole oscillating at the frequency of the vibration. If the electron distribution is symmetrical in a molecule and it has no permanent dipole in its equilibrium configuration, it is still possible for unsymmetrical vibrations to disturb the symmetry of the electron distributions and produce a dipole which again oscillates with the frequency of the vibration. External electric field may induce electric dipoles in molecules, such dipoles can oscillate and produce radiation. The frequencies of such dipoles are related to the frequency of the electric field and the

frequency of the molecular vibration. If the electric field is a static one, the induced dipole oscillates with the frequency of the molecular vibration. If the electric field is an oscillating one, e.g. one due to electromagnetic radiation, induced dipoles result which oscillate at the frequency of the electric field and also at frequencies which are beat frequencies between the electric field frequency and the molecular frequency. Analytical methods are particularly concerned with induced electric dipoles, since they are the principal source of Rayleigh and Raman scattering. The harmonic variation of any dipole oscillating with angular frequency ω may be expressed as;

$$\mathbf{P} = \mathbf{P}_0 \cos \omega t, \quad (4.5.4)$$

where $\mathbf{P}_0$ is the amplitude vector of the oscillating dipole. $\mathbf{P}_0$ (and hence $\mathbf{P}$) can be non-zero even if the system has no permanent dipole moment.

4.6 Brillouin and Surface Brillouin scattering

Vibrational excitation of atomic aggregates can interact with electromagnetic waves by absorption/ emission or by scattering (inelastic scattering). In crystals, the fundamental vibrational excitations have the form of modulated travelling waves, or phonons. Each crystalline cell has the translational degrees of freedom of its centre of mass (this gives rise to acoustic phonon branches), and the rotational and vibrational degrees of freedom of its internal motion (giving rise to optical phonon branches). Brillouin scattering (BS) and surface BS (SBS) are the inelastic coherent scattering of photons from bulk and surface acoustic phonons, whose wave vector, selected by the kinematics of scattering lies in a small neighbourhood of the centre of the Brillouin zone [66]. When laser light in the visible range is used as a probe, the phonon wavevector ($\mathbf{q}$) is very small and only zone centre phonons

($\mathbf{q} \approx 0$) are scattering active [134]. The huge difference in the dimensions of the Brillouin zone ($\approx 10^{10} \text{ m}^{-1}$) and the photon wavevector of the order of 10^7 m^{-1} ensures that only information about phonons near the centre of the Brillouin zone ($\mathbf{q} \approx 0$) is provided. In this region, the dispersion relation is linear for phonons and $\omega(\mathbf{q}) = v|q|$, where ω and v are the frequency shift and sound velocity inside the material, respectively [93].

In Brillouin scattering (BS), laser light is used as a probe to reveal acoustic phonons that are naturally present in the medium under investigation. The power spectrum of these excitations is mapped out from frequency analysis of the light scattered within a solid angle by means of a multipass tandem Fabry P rot interferometer described in section §3.5. The acoustic modes confined within the material can thus be revealed and their elastic constants determined [135, 136]. Comins *et al* [137] have defined surface Brillouin scattering as a non-contact measuring technique that exploits light scattering in the study of thermally induced surface acoustic excitations in the gigahertz (GHz) frequency range. These excitations can then be used to determine the elastic properties of opaque solids and thin supported layers. The scattered photons are supplied by a laser beam of moderately low power (less than 100 mW). This supposedly produces minimal heating, which is generally adequate for most materials studied in our lab. The laser beam is not therefore the cause of surface vibrations but rather a tool for their detection. Brillouin scattering is therefore the generation of sound waves using heat (internal energy in the material) then detecting the velocity and lifetimes of these waves using light. This is scattering from the acoustic branches and involves a frequency shift which is 10^3 to 10^4 times smaller than that of the Raman effect (scattering from optical branches) [65]. Therefore, information about the surface dynamics

is obtained from the inelastically scattered light which is a tiny fraction of the incident intensity [72].

Thermal fluctuations (‘thermal noise’) are governed by the equipartition principle of thermodynamics. By this principle we can say that at temperature T , each vibrational degree of freedom of a mechanical system has on average, an amount of energy $\kappa_B T$, where $\kappa_B = 1.3806 \times 10^{-23} \text{ JK}^{-1}$ is Boltzmann’s constant. The ‘Thermal noise’ can thus be seen as an incoherent superposition of all the acoustic modes (see section 2.4). In Brillouin spectroscopy, the scattering geometry selects a specific wavevector and probes the ‘thermal noise’ at that wavevector, therefore performing a sampling of the dispersion relation of the waves. Brillouin scattering fits well in the classical continuum model because the energies of phonons involved in scattering visible radiation are smaller than the thermal energy, similarly the wavelength of these phonons is much longer than the interatomic distance [138].

For opaque surfaces, light scattering by phonon vibrations causes the surface to appear as a moving grating, i.e. a ripple, capable by itself of producing diffraction and changing the frequency (Doppler shift) of the incoming light without invoking any modulation of the dielectric constant in the interior of the crystal [139]. The surface ripple mechanism dominates that by elasto-optic coupling as the skin depth diminishes. The frequency spectrum of the scattered light provides information on the surface dynamics and the near-surface elastic properties of material under investigation [137]. The dynamic rippling of the surface can be resolved into a superposition of harmonic waves, which act as moving diffraction gratings at the surface, travelling in the reverse (+) or forward (-) directions at velocity c_{acoust} .

In the case where the material is not totally opaque, the incident light penetrates deeper into the material to probe dynamic fluctuations in the strain field, ϵ_{ij} . The

elasto-optic scattering mechanism of a transparent solid has most of the scattered light emanating from the refracted beam in a region well away from the surface, and the kinematic conditions relating wavevector and frequency shift of the light pertain to bulk acoustic wave scattering [52]. The scattering in this case is mediated by the elasto-optic scattering mechanism, in which dynamic fluctuations in the strain field bring about fluctuations in the dielectric constant, and this in turn translates into fluctuations in the refractive index. There occurs therefore diffraction of the light at the air-sample boundary together with a Doppler frequency shift [72]. In partially opaque materials, both ripple and elasto-optic effects abound. The Brillouin cross section is therefore a combination of both contributions. The opacity of the material distorts the shape of the bulk phonon peaks, which appear shifted and show increased broadening [93]

For a highly transparent sample, like diamond, the spectrum is dominated by scattering from bulk longitudinal and transverse waves, for which scattering selection rule involves conservation of all three components of the wavevector [72]. The strength of scattering in transparent materials is proportional to the scattering volume and depends on the elasto-optic constants. The line shape for bulk phonons is Lorentzian with width proportional to the phonon lifetime.

When a sound wave of wavevector $\mathbf{q}$ and frequency $\omega(\mathbf{q})$ propagates through a medium, the associated compressions and rarefactions set up a modulation in the dielectric constant ε , in the interior of the crystal. Light may thus be scattered from this three dimensional phase grating in much the same way that a beam is Bragg scattered by a physical grating. Since the grating is moving with a velocity v , the frequency of the scattered light is Doppler shifted. In general, a discrete

frequency will be present for each branch, corresponding to $\mathbf{q}$. From the classical point of view, the scattering is a result of Bragg reflection from the optical stratification produced by the long wavelength acoustic phonons (elastic waves) in the medium [138]. The Doppler shift associated with these ‘moving mirrors’ produce the Brillouin components, inelastic light scattering from the elastic waves. For given incident (i) and scattered (s) directions, the frequency shift $\Delta\omega$ of the Brillouin components in a cubic crystal are given by (4.6.1)

$$\Delta\omega = \pm 2\omega_L n \frac{v_s}{c} \sin\left(\frac{\theta}{2}\right), \quad (4.6.1)$$

where ω_L is the excitation frequency, n the index of refraction of the medium, c the velocity of light in vacuum, θ the scattering angle, and v_s the velocity of the appropriate sound wave responsible for the Bragg reflection. The velocity v_s has three values corresponding to two quasi-transverse and one quasi-longitudinal sound waves. Sound velocity in the medium is calculated using equation (4.6.2)

$$v_s = \sqrt{\frac{X}{\rho}}, \quad (4.6.2)$$

where X is an appropriate combination of the elastic constants C_{ij} (the bulk longitudinal wave velocity is simply $\sqrt{C_{11}/\rho}$ while the phase velocity of bulk transverse wave is $\sqrt{C_{44}/\rho}$ for propagation along $\langle 010 \rangle$, and ρ is the density of the medium which was elaborated in section §2.1.3.

4.6.1 The basic principle of Brillouin scattering

Light is incident on a highly polished surface at an angle θ to the normal. Most of the light is specularly reflected, some is refracted at an angle θ' , or absorbed inside the material. Due to thermally excited dynamic fluctuations in the strain

field within the solid and dynamic rippling of the surface, some light is diffusely scattered, undergoing in the process a fractional change in frequency of the ratio $c_{acoust}/c_{light} \approx 10^{-5}$, where c_{acoust} is the acoustic wave speed and c_{light} is the light speed.

A derivation of surface acoustic wave velocity using the analysis of Mutti *et al* [93] is hereby given. To understand how surface Brillouin scattering takes place, we discard the problems associated with refraction and reflection of EM waves at the boundary and assume that a single acoustic phonon (thermal elastic wave) is propagating within the medium with wavevector $\mathbf{q}$ and frequency $\omega(\mathbf{q})$. The laws of momentum and energy conservation must therefore be obeyed in the scattering process. Conservation of total wavevector in the scattering process is given by ,

$$k_s - k_i = \pm \mathbf{q}, \quad (4.6.3)$$

where k_s and k_i are the vectors of scattered and incident photons. Frequency conservation in the medium and air is represented by a scalar equation of the form,

$$\omega_s - \omega_i = \Delta\omega = |\mathbf{q}| v, \quad (4.6.4)$$

whose dispersions relations are:

$$\omega_i = \frac{c}{n} k_i, \quad (4.6.5)$$

$$\omega_s = \frac{c}{n} k_s, \quad (4.6.6)$$

where c is velocity of light in ‘vacuum’ and n is refractive index of the medium.

From equation (4.6.4),

$$\frac{|k_s| - |k_i|}{n |\mathbf{q}|} = \frac{v}{c}. \quad (4.6.7)$$

The magnitude of the RHS of equation (4.6.7) in solids is typically 10^{-5} so that $|k_s| = |k_i| = k$, hence we can write an equation which is a variant of the Bragg law

$$2k \sin(\phi/2) = |\mathbf{q}|, \quad (4.6.8)$$

where ϕ is the scattering angle.

From the Bragg law

$$2d \sin(\psi) = \lambda, \quad (4.6.9)$$

and comparing equations (4.6.8) and (4.6.9), it can be seen that $\psi = \phi/2$, the grating spacing d equals the phonon wavelength and $\lambda = \lambda_0/n$ being the wavelength of incident photon in the medium. Substituting 4.6.5 and 4.6.6 into 4.6.7 then we get

$$\frac{2\pi}{|\mathbf{q}|} = \frac{2\pi v}{|\omega_s - \omega_i|} = \frac{2\pi v}{\Delta\omega}. \quad (4.6.10)$$

Measurement of angular frequency $\Delta\omega$ in Brillouin spectra in some fixed scattering geometry enables the measuring of sound velocity in the medium using the formula,

$$v = \frac{\lambda_0 |\Delta\omega|}{4\pi n \sin(\phi/2)}. \quad (4.6.11)$$

In backscattering $\phi = \pi$ hence equation (4.6.11) becomes

$$v = \frac{\lambda_0 |\Delta\omega|}{4\pi n}. \quad (4.6.12)$$

Surface acoustic phonons are completely characterized by their wavevector $\mathbf{q}_x$ parallel to the surface. For backscattering from surface acoustic waves (SAWs) where the refractive index of the medium is unnecessary, $\mathbf{q}_x = (4\pi/\lambda_i) \sin\theta_i$, the SAW phase velocity v_{saw} can be obtained from,

$$v_{saw} = \frac{\lambda_0 |\Delta\omega|}{4\pi \sin\theta_i}, \quad (4.6.13)$$

which gives

$$v_{saw} = \frac{\Delta\nu \lambda_0}{2 \sin\theta_i}, \quad (4.6.14)$$

therefore θ_i , the angle of the incident photon wavevector relative to the surface's normal and the peak position (frequency shift, $\Delta\nu$) must be known in calculating v_{saw} .

In the observed spectra, there is a central intense peak emanating from static inhomogeneities and surface roughness in the sample, not shifted in frequency, hence it lies at the reference point of the spectra. This is normally reinforced with the un-scattered light beam direct from the laser source, directed to the interferometer by means of a beam splitter. The intensity of this reference beam is small enough not to saturate the detector but large enough to keep the equipment from drifting.

The fluctuations in the strain field result in a spectrum with two more or less mirror image sidebands on either side of the central peak. Frequency shift therefore appears as either down-shifted or up-shifted events. The down-shifted frequency is the Stokes band resulting from the creation of a phonon, hence the scattered photon is less energetic than the incident photon, while the up-shifted one is the anti-Stokes band due to annihilation of a phonon. These two kinematic events are represented vectorially in Fig 4.6.

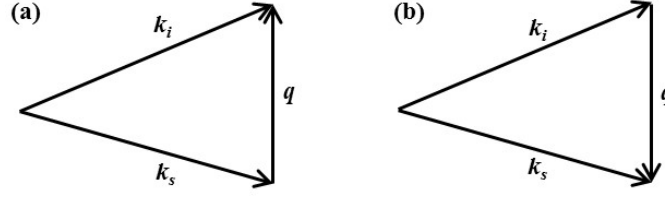


Figure 4.6: (a) Stokes and (b) anti-Stokes events that occur in Brillouin scattering [93].

Observable frequency shifts depend on the optical and elastic properties of the sample, the scattering geometry and the vibrational modes of the solid that the incident light is able to couple to. Since the average amount of energy per vibrational degree of freedom is $\kappa_B T$, the intensity of the inelastic spectrum is proportional to the absolute temperature (explaining the need to keep an almost constant temperature during measurements). These may also be explained using quantum mechanics, scattering where light loses energy may therefore be interpreted as a phonon creation (Stokes) while the process where the photon gains energy of the phonon is phonon annihilation (anti-Stokes). A quantum of energy $\hbar\omega$ associated with an oscillator of 30 GHz frequency corresponds to 1 cm^{-1} and to an equivalent temperature $\hbar\omega/\kappa_B$ of about 1.5 K [59, 70]. This implies that at even very low constant temperatures, Brillouin scattering measurements can be observed.

4.6.2 Scattering geometries

The scattering geometry which is defined by the direction of the incident light beam, the direction along which the scattered light is collected and the sample orientation identifies the probed phonon wavevector $\mathbf{q}$. Conventionally, the x axis is along the propagation wavevector in the sagittal plane of the sample and the z axis is along the normal, y axis is mutually perpendicular to the two axes. The incident beam of wavelength λ_0 , wavevector $\mathbf{k}_i$ impinges on the surface at an angle θ_i to the normal; along its trajectory of travel, it may be specularly reflected (θ_s), absorbed

or refracted at an angle θ' with wavevector q' , elastically scattered or inelastically scattered undergoing a frequency shift, $\Delta\omega$. Light emerging in the direction of the scattered wavevector $\mathbf{k}_s$ is collected and analyzed. This information is summarized in figure 4.7. For transparent samples where light penetrates matter, then light travel inside the material must be considered. Simply put: for a particular scattering geometry i.e. specific incident light wavevector q'_i and scattered light wavevector q'_s and both within the solid, the scattering wavevector $\mathbf{k} = q'_i - q'_s$, and only acoustic waves having precisely this wavevector $\mathbf{k}$ contribute to the detected signal (refer to figure 5.3) [140].

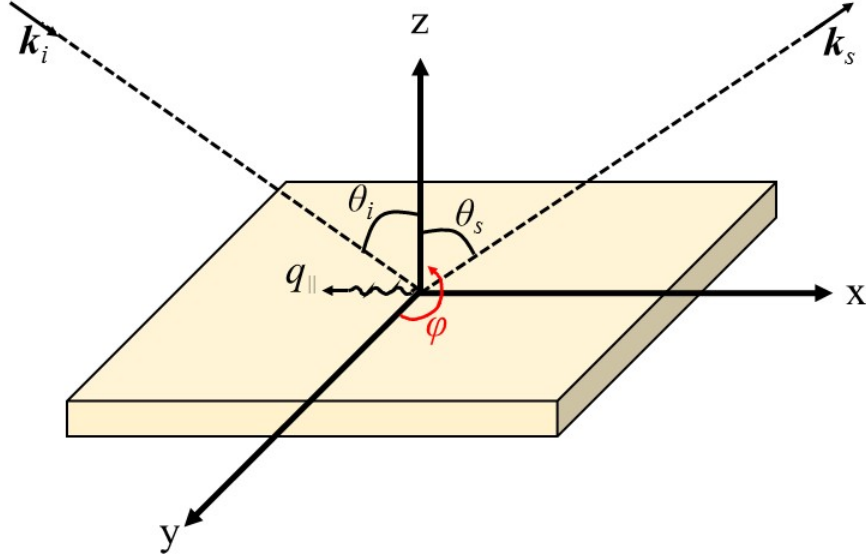


Figure 4.7: Schematic diagram of the general SBS geometry. The z axis points outwards and is normal to the sample's surface. By rotating the sample through φ at fixed angle of incidence θ_i the anisotropic properties of the material are studied.

The scattering geometry selects the projection on the surface of the scattering wavevector, $q_{\parallel}$, of the SAWs being probed; in backscattering, adopted in this work, the scattering geometry is fully specified by the incident angle θ_i : $q_{\parallel} = (4\pi/\lambda) \sin \theta_i$, λ being the laser wavelength. The wavelength of the phonons is $\lambda_{\parallel} = (2\pi/q_{\parallel}) \sin \theta_i = \lambda/2 \sin \theta_i$; the spectral shift $(\omega/2\pi)$ directly supplies the phase velocities v of the specific SAWs; $v = \omega/q_{\parallel}$. v varies with $q_{\parallel}$, the dispersion

being stronger when sound velocities of the film and the substrate are markedly different [63]. This implies that the Doppler frequency shift, $\Delta\omega$, in the light scattering is related to the surface wave velocity v_{SAW} by $v_{SAW} = (\lambda_{\parallel}/2\sin\theta_i)\Delta\omega$ [71]. The Brillouin spectrum obtained has sharp peaks at specific frequency shifts, for backscattering given by,

$$\Delta\omega = 2n k_i v, \quad (4.6.15)$$

where n is the refractive index of the medium, and v is the bulk L or T velocity for a particular direction. These peaks therefore yield bulk wave velocities from which individual elastic constants or combinations of elastic constants can be determined [55]. The factors n, k_i and v in equation (4.6.15) are such that the frequency shifts in bulk wave scattering (up to 150 GHz and more) are much larger than for the surface wave scattering (typically up to about 30 GHz or so) [72].

Zouboulis *et al* [141] have identified three different scattering geometries that can be applied in Brillouin scattering studies of transparent materials as represented using diagrams in figure 4.8.

Scattering from a bulk phonon shown schematically in 4.9 can occur only for a phonon wave vector $\mathbf{k}_B$ with components $\mathbf{k}_B^{\parallel}$ and $\mathbf{k}_B^{\perp}$ to the surface, respectively, which satisfy the wave vector conservation requirement [142];

$$\mathbf{k}_B^{\parallel} = \mathbf{k}_i \sin \theta_1 + \mathbf{k}_s \sin \theta_s, \quad (4.6.16)$$

$$\mathbf{k}_B^{\perp} = n(\mathbf{k}_i \cos \theta'_1 + \mathbf{k}_s \cos \theta'_s), \quad (4.6.17)$$

where $\sin n_i = n \sin \theta'_i$ and $\sin \theta_s = n \sin \theta'_s$, n is the refractive index of the material. The scattered light has a frequency shift $\delta\omega = v\mathbf{k}_B$, where v is the phonon velocity

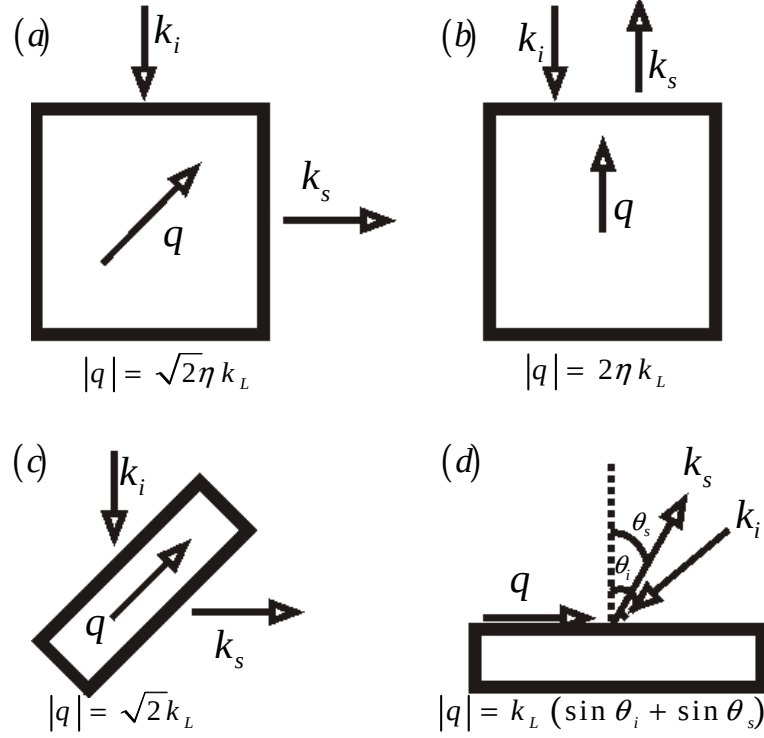


Figure 4.8: Scattering geometries used in Brillouin light scattering. (a) 90° scattering, (b) backscattering (180°), and (c) platelet scattering, (d) the more general backscattering geometry: k_i , k_s and q are the wavevectors of the incident and scattered light and phonon respectively [52, 141].

This study which seeks to study near surface changes will heavily rely Rayleigh mode $\mathbf{k}_R$ for interpretation of data. Generally, a surface wave travels parallel to the surface of an opaque material mediated by a light scattering mechanism known as surface ripple mechanism which relies largely on a reflective surface in order to realize sufficient scattering cross-sections. Thus the surface projected spectrum of long wavelength acoustic phonons of a homogenous semi-infinite body for a given surface phonon wavevector is the combination of a *discrete* (low frequency) set and a *continuous* (high frequency) set. In the discrete part, peaks corresponding to true surface waves (surface bounded modes) show up: true surface resonances. In the discrete part, *the Rayleigh wave* is found [143].

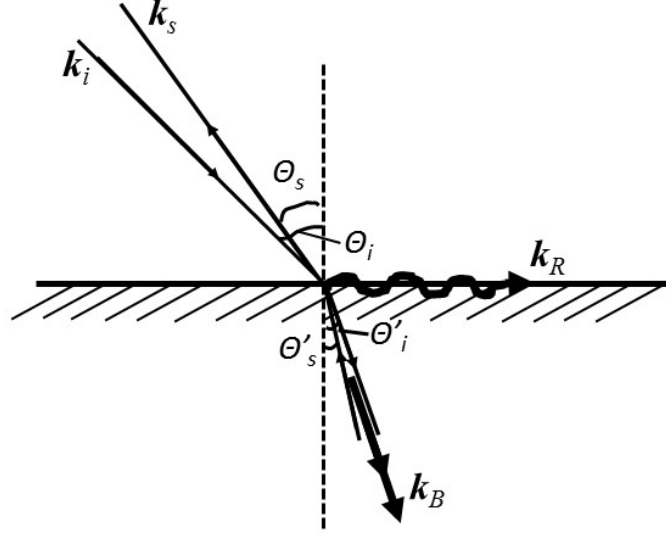


Figure 4.9: Conventional backscattering geometry adapted from [142] showing incident and scattered light wave vectors k_i , k_s and the surface and bulk wave vectors k_R , k_B .

4.7 EM Transmission

The interaction of the various diamond samples with EM radiation was studied. The study of the change in EM radiation after interacting with a material can give a lot of information about the sample. Transmission and absorption measurements were done using the UV-VIS-NIR 500 Cary spectrophotometer. In this instrument the sample is scanned from long to short wavelengths. However, our interest was in the visible light range since the main analytical technique, SBS, utilizes visible light. The transmission spectrum from the UV through near IR in un-implanted diamond showed that no UV is transmitted while there was a transmission of $\approx 70\%$ of the intensity of incident visible light and IR, agreeing well with observation of Coe and Sussmann [144] of 71.4%. This is in agreement with the predicted absorption-free transmittance of the Herzberger-type dispersion formula, $T_0 = \frac{2n}{1+n^2}$ for diamond interacting with radiation of wavelength $20 \mu\text{m}$ [145]. A perfect diamond will only absorb visible or ultraviolet radiation whose energy $h\nu$ (h is Planck's constant and ν is the frequency of radiation) is greater than the band gap energy of diamond as

shown in figure 4.10; transmission at some point in the UV region completely ceases where the energy of the radiation exceeds the band gap energy of the diamond sample. There was no transmission for radiation whose wavelength is less than 220 nm, the absorption edge for diamond [146].

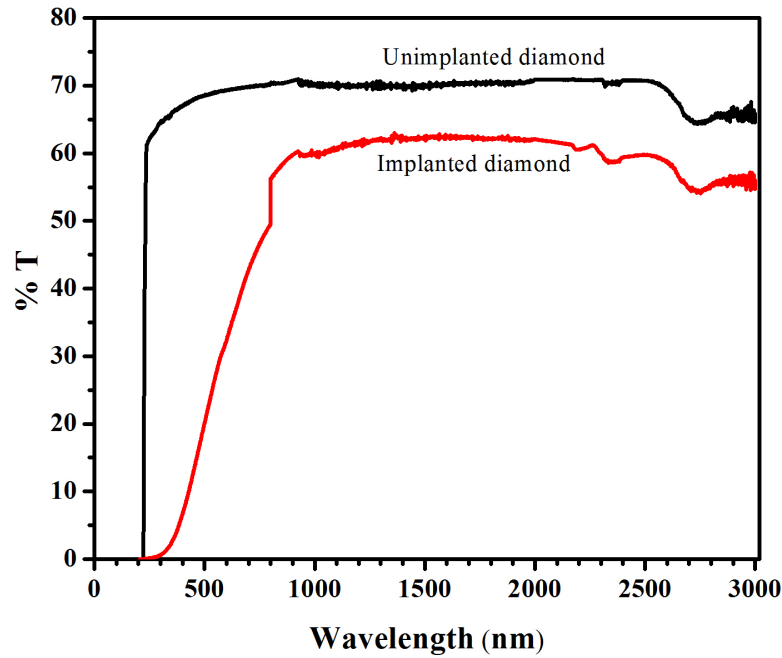


Figure 4.10: Transmission spectra of un-implanted and carbon implanted CVD diamond in the UV to IR range. There is no transmission below 220 nm, the absorption edge of diamond.

There is similar transmission in the IR region for the implanted diamond but it reduces drastically in the Vis region. McKenzie [8] has argued that the infrared spectrum of amorphous materials is an indicator of the vibrational density of states (VDOS) with matrix element weighted according to dipole moment produced by the vibrational mode. He continues to state that since there is no strong difference in the matrix element between sp^2 and sp^3 bonding, the VDOS of the network is reproduced in the IR absorption spectrum.

4.8 Raman Spectroscopy

Raman spectroscopy is an optical, non-destructive spectroscopic technique where analysis of materials depends on the interaction of EM radiation with matter. Raman scattering is basically the inelastic interaction of light with a material. In this classical interaction, the electric field of the incident light causes a perturbation of the molecule's dipole moment. Scattering is then generated by the oscillating electric dipoles induced by the electric field of the incident photon. Quantum mechanically, inelastic scattering is a process in which energy is transferred between an incident photon with energy $\hbar\omega_i$ and the sample resulting in a scattered photon of a different energy, $\hbar\omega_s$. The difference in energy equals the amount of energy transferred corresponding to the eigenenergy $\hbar\Omega_j$ of an elementary excitation labelled 'j' in the sample. The elementary excitation could be a phonon, a coupled plasmon-phonon mode, a plasmon, a polariton, a single electron or hole excitation,

$$\hbar\omega_s = \hbar\omega_i \pm \hbar\Omega_j, \quad (4.8.1)$$

where the '-' sign means a Raman process in which an elementary excitation is generated/ bands with lower frequency than exciting radiation (Stokes process, $\hbar\omega_s < \hbar\omega_i$), while '+' implies the annihilation of an elementary excitation (anti-Stokes process, $\hbar\omega_s > \hbar\omega_i$). From equation (4.8.1), it is clear that the scattered photon has a higher or lower frequency and therefore a different energy from that of the incident light, illustrated in figure 4.11. The intensity of the scattered light plotted against frequency difference $\Delta\omega = \omega_i - \omega_s$ yields peaks at eigenfrequencies Ω_j ; $j = 1, 2$ of the elementary excitations.

Raman measurement on implanted diamond shows a strong diamond signal in addition to a broad damage band. This agrees with the noted observation that

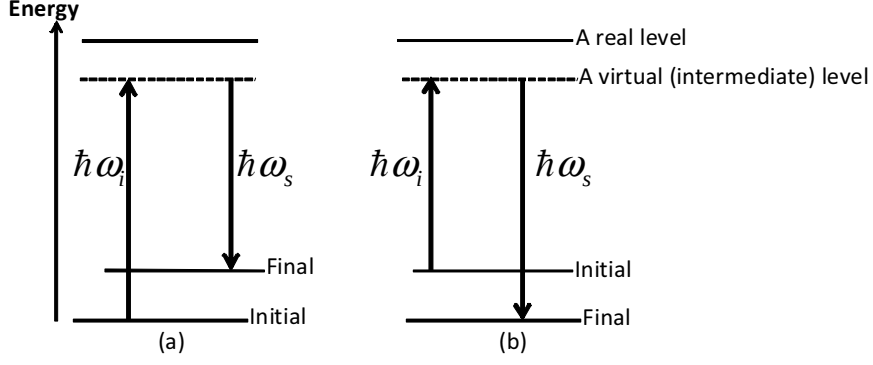


Figure 4.11: Schematic diagram of Raman events: (a) the Stokes $\hbar\omega_s < \hbar\omega_i$ and (b) anti-Stokes $\hbar\omega_i < \hbar\omega_s$ processes.

the smaller the crystal size, the greater the wavevector ($\mathbf{q}$) uncertainty. For very small crystal sizes nearly all the phonons in the Brillouin zone can participate in the scattering event (phonon confinement). The Raman scattering intensity of a finite crystal is given by [134]:

$$I(\omega) = \frac{n(\omega) + 1}{\omega} \sum_{\mathbf{q}j} C(\mathbf{q}, \omega_j(\mathbf{q})) |F(\mathbf{q})|^2 \times \frac{\Gamma/2\pi}{[\omega - \omega_j(\mathbf{q})]^2 + \Gamma^2/4} \quad (4.8.2)$$

where $n(\omega)$ is the boson occupation factor, Γ is the phonon lifetime broadening, $C(\mathbf{q}, \omega_j(\mathbf{q}))$ is the Raman coupling coefficient for a phonon of wavevector $\mathbf{q}$, branch j and dispersion relation $\omega_j(\mathbf{q})$, and $|F(\mathbf{q})|^2$ is the wavevector uncertainty of the phonons involved in the light scattering.

Annealing of the heavily implanted diamond results in an amorphous material whose Raman scattering intensity is governed by a formula derived by Shuker and Gammon [147]

$$I(\omega) = \frac{n(\omega) + 1}{\omega} C(\omega) G(\omega) \quad (4.8.3)$$

where $G(\omega)$ is the VDOS of the disordered material (usually rather different from that of the original crystal) while $C(\omega)$ is an often unknown coupling coefficient,

hence often neglected. This implies that all the VDOS of amorphous material is probed by Raman scattering.

From scattering by phonons and through evaluation of phonon frequencies, FWHM, line shape, peak shifts and their intensities, information about a crystal can be known. The information provided by Raman spectroscopic analysis includes lattice dynamics as well as electric properties. The lattice dynamics reflects not only structural information such as the identification of materials and compounds, including reacted phases at interfaces, but also aspects such as the composition of mixed compounds, layer orientation, stress and crystalline perfection. Furthermore, the resonance behaviour of the scattered intensity reflects the energetics of the critical points in the electronic energy bands [148]. Also information on the polarization state which shows the crystal symmetry and orientation can be obtained from Raman data.

In both Raman and Brillouin scattering, the incident photons scatter from the lattice inelastically by interacting with a quantized mechanical disturbance (phonons), conserving both energy and momentum. The optical branch of the phonon dispersion curve is responsible for Raman and produces fairly large wavelength shift in the scattered photon compared to the Brillouin scattering that involves phonons of the acoustic branch [149]. In comparison to electron spectroscopy methods like photoelectron spectroscopy (PES) i.e. (X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS)) and Auger electron spectroscopy (AES), Raman spectroscopy is advantageous for the investigations of buried interfaces, since the information depth of visible light may clearly exceed that of electrons. In PES experiments the information depth is restricted by the escape depth of electrons. The escape depth varies as a function of the K.E of

the electrons from a few monolayers at 40-100 eV typically achieved in ultraviolet (UPS) or in soft X-Ray photoemission spectroscopy (SXPS) to a few tens of atomic layers above 1000 eV obtained in X-Ray Photoemission Spectroscopy (XPS) [150].

In this study, Raman spectroscopy was handy in determining the quality of sample as-supplied. Raman measurements were also done to determine the structural changes taking place in the ion implanted diamonds as a result of heat treatment. This would in essence help explain the SBS observations.

4.9 Conclusion

An understanding of the macroscopic lies in uncovering the challenges hidden in the microscopic. This chapter has explained the matter-matter and Matter-EM radiation interaction. Matter to matter interaction was encountered in the ion-implantation process while matter-EM radiation interaction was explained in the analytical techniques employed in this experiment. The microscopic process causing transformation of a material due to heat treatment has also been discussed in the annealing process. In a nutshell this chapter sought to know how particles interact with one another and their surroundings.

Chapter 5

Back surface influence on Brillouin scattering in diamond

5.1 Introduction

This chapter lays the groundwork for the main observations reported in subsequent chapters. The results and deductions thereof form the basis of this work. It is rather like a tinkering process, where various hypotheses were tried out on the various samples. Description of preliminary measurements done on different samples that led to useful SBS results on transparent and semi-transparent as-implanted diamonds is given. These preliminary results led to the deduction of very important principles that not only drive the study to higher echelons but also lead to an avalanche of research questions.

Most of the previous research performed in our laser spectroscopy lab has focussed on thin opaque samples. These thin film samples, mostly on silicon substrates, attenuate light to orders of a half of a micron depth. For experiments dealing in thick opaque films, the nature of the surface at the back of substrates/film-substrate interfaces has therefore never been a research issue. In our conventional experimental setup (i.e. experiments involving opaque materials), the sample is held on an Al holder using a double sided tape. The present study on a

transparent single crystal CVD diamond started on the same premise of attaching the sample with a double sided tape on the usual Al holder. After a successful SBS measurement, the rest would be discovery/ proving/disproving already known facts. This chapter reports results for experiments done on pristine and as-implanted diamonds.

5.2 Sample modification

The study starts with pristine diamond (samples 1 and 4) which are later modified by ion implantation (samples 2, 3 and 5) §3.2. Ion implantation introduces radiation damage in the target, leading to lattice structural changes as a result of bond breaking and displacement of atoms from their lattice positions. In the work reported in this chapter, CVD single crystal (100) diamonds were irradiated with C ions in order to introduce lattice defects with the aim of inducing the phase transition to amorphous carbon and/ or graphitic states without introducing doping effects [151]. Proof that the sample had been modified was observed by Raman measurements and light transmission measurements. Attempts to increase the surface reflectivity and enhance the surface scattering profile of pristine and as-implanted diamonds was done by depositing a thin layer of aluminium on samples 1,2 and 3. The Al coated samples were then thoroughly cleaned in alcohol solutions and rinsed in distilled water after SBS measurements to totally clean the surface in preparation for other measurements.

5.2.1 Raman spectroscopy

The sharp peaks (characteristic peaks) observed in materials are related to lattice periodicity. In highly disordered materials, the loss of long range order results

in the absence of a well defined crystal momentum and a breakdown of the wave vector selection rules. Under such conditions a range of light scattering processes is allowed leading to broad peaks [152]. Raman measurements were done for un-implanted and implanted diamond to observe this argument. Figure 5.1 summarizes the observations.

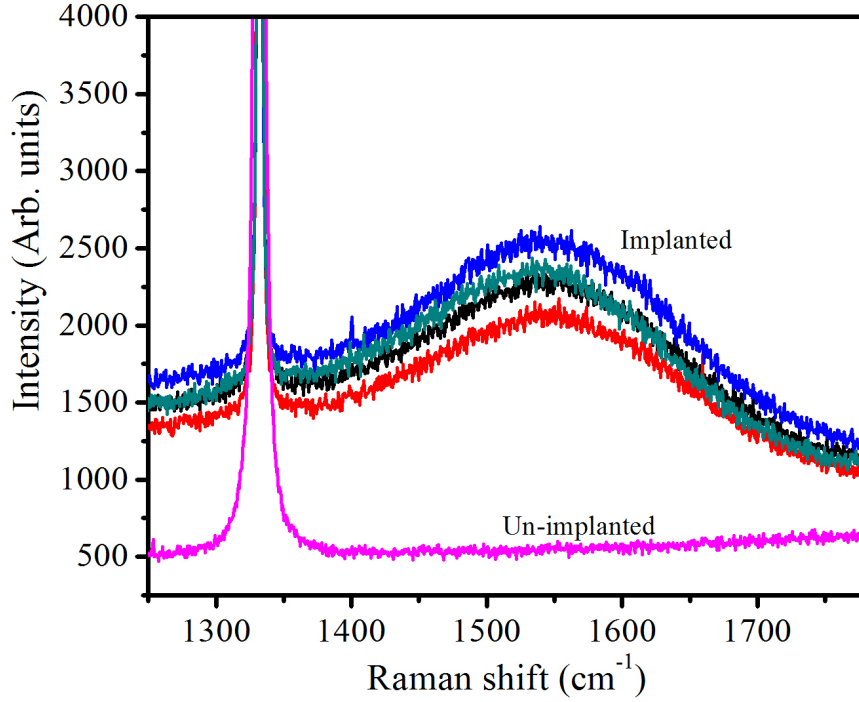


Figure 5.1: Raman spectrum done at randomly selected regions indicating uniform damage after ion implantation. Even in the implanted diamond, the Raman peak for diamond is still strong probably due to the sampling depth ($1\ \mu\text{m}$) which is far deeper than that of the implantation projected range [153].

The broad peak (wide range of scattering) indicating damage is centred around $1560\ \text{cm}^{-1}$ and did appear in both the single and multiple energy implants. Since Raman spectroscopy is sensitive to structural features that disrupt the translational periodicity of the atomic arrangement of solids caused by bond-angle distortions and particle size effects [154], the presence of the broad peak shows displacement of some atoms from their lattice sites hence loss of the diamond crystallinity after implantation. This peak is associated with sp^2 carbon bonds [4, 155]. The diamond signal at $1332\ \text{cm}^{-1}$ in un-implanted diamond is still strong in the ion implanted

samples and right shifted a bit to 1334 cm^{-1} ; however, it should be noted that the Raman line for diamond also emerges from scattering beyond the implanted range depending on penetration depth of the probing light. It was necessary to check for uniform damage by randomly selecting probe points. The similar Raman observations ensured reliability of results no matter the position on the surfaces where SBS measurements were taken.

5.2.2 EM Transmission, opacity measurements

Upon implanting diamond with carbon ions, there was an eye-visible physical change of colour from colourless to brown-like/ dark hue. This is in agreement with the observations of Spits *et al* [156] who report a golden brown hue, the intensity of which depends on the ion dose. There was no transmission for wavelength below 220 nm (absorption edge of type II diamond [157]), as expected. Transmittance is wavelength dependent for visible light, with a gradual reduction in %T of visible light towards the shorter wavelength, this has also been observed by Bhatia *et al* [151] for different carbon doses in diamond. The wavelength of interest in this work was the 514.5 nm since Raman measurements and most of the SBS data were obtained using it as a probe wavelength.

Figure 5.2 shows only the transmission in the visible range. The amount of light transmitted after ion-implantation was compared to that of pristine sample polished on both sides. There was a significant reduction in transmittance after ion implantation. The measurements show that pristine diamond transmits 69.3% of the 514.5 nm light. The transmission reduced to about 15.8% for as-implanted and up to anneal temperatures of 500 °C. However, the transmission after annealing at 600 °C show a drop to about 5% although the visible colour in white light remained

almost the same as it were in the as-implanted diamond. The transmission drops to below further to below 1% after annealing temperatures of 800 °C and above. Deposition of ≈ 20 nm layer of Pt reduced the transmission of pristine diamond to 28.3% and to 10.9% for the as-implanted diamond. Transmission measurements were important in determining the opacity the sample, an important factor in determination of the influence of the back surface.

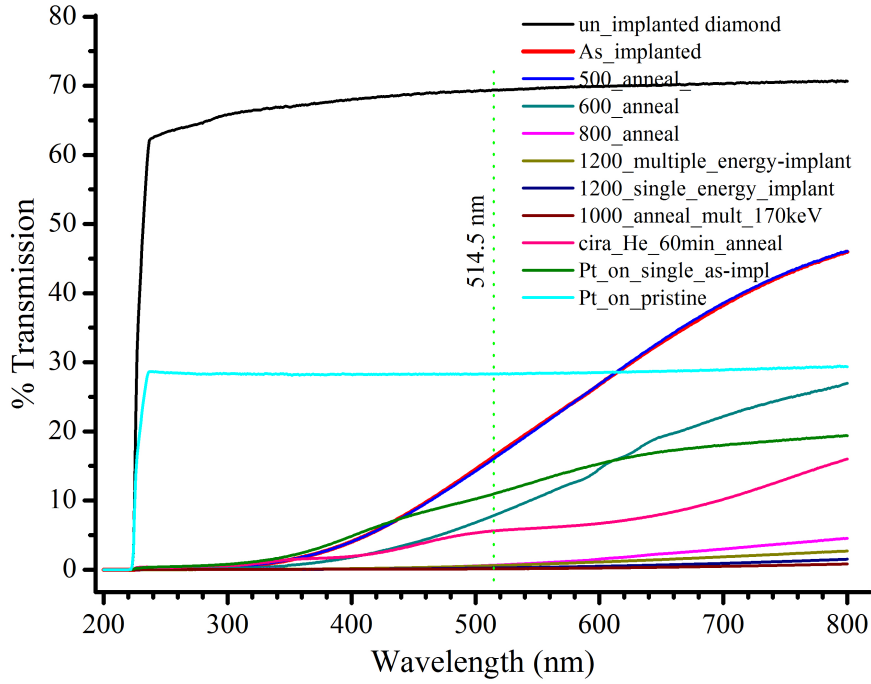


Figure 5.2: Transmission measurements after some selected annealing temperatures. Transmission reduced as annealing temperature increased though not linearly.

5.3 Brillouin Scattering in diamond

As earlier mentioned, the pristine diamond used in this work was a transparent plate, transmitting $\approx 70\%$ of visible. However, when laser light is incident on it, it is observed to produce a strong elastically scattered light. The data reported here first incorporate Brillouin measurements for bulk scattering carried out on pristine diamond then later a discussion of SBS results obtained from ion implanted diamond. It is however, important to mention that this work was not from the onset

focussed on bulk diamond characteristics but rather the near surface region where modification by ion-implantation takes place. Work reported on un-implanted diamond is purely for baseline referral to changes that occur after ion implantation.

5.3.1 Scattering mechanism in transparent sample

Reference is drawn from the work by Signoriello *et al* [140] on Brillouin scattering in silica and that of Beghi *et al* [69] to explain the scattering mechanism in a transparent sample with a reflective back surface. A brief explanation of the scattering mechanism is hereby explained basing on geometry schematically shown in figure 5.3 and discussions made with reference thereto.

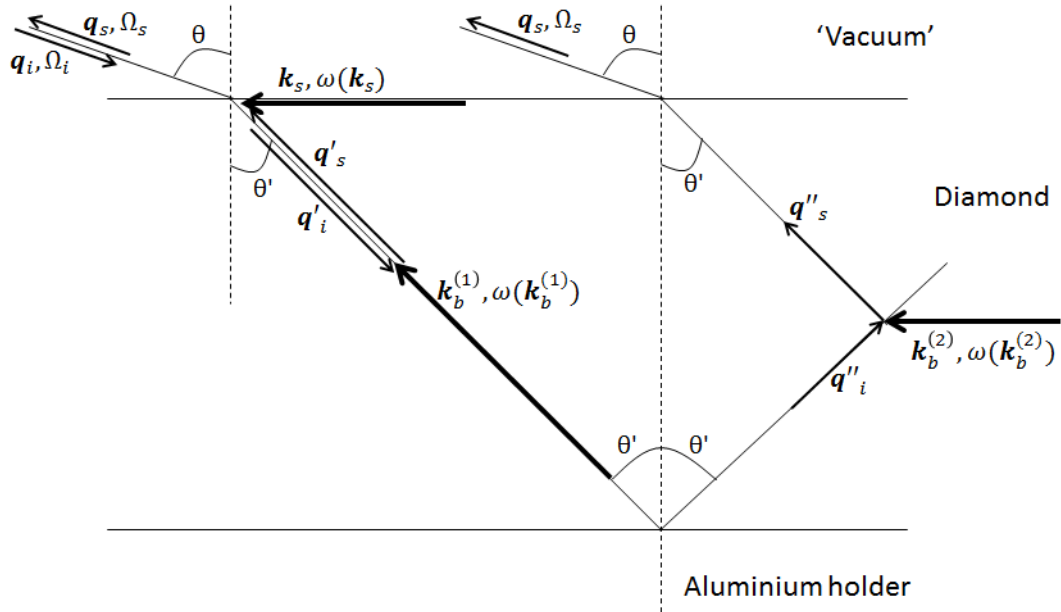


Figure 5.3: Scattering geometry which best represents a transparent sample like diamond held on a reflective aluminium holder. Optical wavevectors represented by thin arrow lines while thick arrows show acoustic wavevectors of bulk ($\mathbf{k}_b$) and surface ($\mathbf{k}_s$) acoustic waves [59, 140].

An incident photon of wavelength λ_0 , angular frequency Ω_i and wavevector $\mathbf{q}_i$ strikes the sample at incident angle θ with respect to the normal. It is then refracted with wavevector $\mathbf{q}'_i$ at angle θ' to the normal. Note that $|\mathbf{q}_i| = 2\pi/\lambda_0$ and that $\mathbf{q}'_i = n|\mathbf{q}_i|$, where n is the refractive index of diamond and also that $\theta > \theta'$,

since diamond is optically denser than air (‘vacuum’), the refractive index of air is taken as 1. These photons interact with a bulk acoustic wave of wavevector $\mathbf{k}_b$ and angular frequency $\omega(|\mathbf{k}_b|)$ and get scattered into an optical wave of wavevector $\mathbf{q}'_s$ and angular frequency Ω_s , it then emerges with wavevector $\mathbf{q}_s$. The optical wave has both longitudinal and transverse modes, hence $\omega = \omega_l = v_l|\mathbf{k}_b|$ or $\omega = \omega_t = v_t|\mathbf{k}_b|$, where v_l and v_t are longitudinal and transverse velocities, respectively. Since momentum and energy are conserved, we have:

$$\mathbf{q}'_s = \mathbf{q}'_i \pm \mathbf{k}_b \quad (5.3.1)$$

$$\Omega_s = \Omega_i \pm \omega, \quad (5.3.2)$$

where (+) and (-) signs refer to anti-Stokes and Stokes events.

The large difference between the velocities of light and sound and the requirement to conserve momentum and energy imply that $|\mathbf{q}'_s| \cong |\mathbf{q}'_i|$. The direction of $\mathbf{q}_i$ and $\mathbf{q}_s$ is determined by the scattering geometry, their direction in turn determines the wavevector $\mathbf{k}_b$ being probed. In the backscattering geometry as used in this work, $\mathbf{q}_i = -\mathbf{q}_s = 2(2\pi/\lambda)\sin\theta$, the SAW velocity $v = \omega/|\mathbf{q}|$ can then be calculated. Analysis of figure 5.3 shows that *three* possible scattering events can take place.

The *first* takes place through direct scattering of an incident photon by a bulk acoustic wave of wavevector $\mathbf{k}_b^{(1)}$. The backscattering means that $\mathbf{q}'_i = -\mathbf{q}'_s$, which maximizes $|\mathbf{k}_b|$. In this case, $|\mathbf{k}_b| = 2|\mathbf{q}'_i|$ and the spectrum of the scattered radiation contains a doublet at angular frequency shifts $(\Omega_s - \Omega_i)$;

$$\Omega_s - \Omega_i = \pm\omega(|\mathbf{k}_b|) = \pm 2v|\mathbf{q}'_i| = \pm 2\pi(2nv/\lambda_0), \quad (5.3.3)$$

where $v = v_l$ or $v = v_t$. These doublets are dependent on the refractive index of the

scattering material and are non-dispersive i.e. they are independent of the angle of incidence.

The *second* takes place through scattering by a surface wave of wavevector $\mathbf{k}_s$ which is always parallel to the surface. There is lack of translational invariance in the direction normal to the surface hence equation (5.3.1) becomes,

$$(\mathbf{q}_s)_\parallel = (\mathbf{q}_i)_\parallel \pm \mathbf{k}_s \quad (5.3.4)$$

Snell's law requires that upon refraction, $\mathbf{q}'_\parallel = \mathbf{q}_\parallel$. In this case, however, the distinction between $\mathbf{q}$ and $\mathbf{q}'$ is immaterial. The scattered radiation contains a doublet too at frequency shifts,

$$\Omega_s - \Omega_i = \pm\omega(|\mathbf{k}_s|) = \pm 2v_r |\mathbf{q}_i|_\parallel = \pm 2\pi v_r (2\sin\theta/\lambda_0), \quad (5.3.5)$$

the velocity v_r being substituted by the appropriate velocity in the case of scattering by different types of surface waves. These doublets are independent of the refractive index of the scattering material and are dispersive i.e. they are dependent on the angle of incidence.

The *third* takes place by the indirect scattering by a bulk acoustic wave of wavevector $\mathbf{k}_b^{(2)}$ from the reflected photon in the back side of the diamond plate. This type of scattering can take place in a transparent film sitting on a reflecting substrate or transparent material with a reflective, smooth, free back surface. The scattering is from the beam of wavevector $\mathbf{q}_i''$ that is reflected from the film-substrate interface/ back side of the free surface of the material/ holder. The collection of backscattered light with $\mathbf{q}_s = -\mathbf{q}_i$, selects the light scattered by the wavevector $\mathbf{k}_b^{(2)}$, which is parallel to the surface. As in case *two*, invariance of wavevector upon refraction implies that $\mathbf{k}_b^{(2)} = \mathbf{k}_s$, but unlike case *two* where the

detected wave is a surface wave, these are bulk waves whose direction of propagation is parallel to the surface. The scattered radiation contains another doublet at frequency shifts,

$$\Omega_s - \Omega_i = \pm\omega(|\mathbf{k}_b|) = \pm 2v|\mathbf{q}_i|_{\parallel} = \pm 2\pi v(2\sin\theta/\lambda_0), \quad (5.3.6)$$

where $v = v_l$ or $v = v_t$. These doublets are independent of the refractive index of the scattering material and are also dispersive.

5.4 Brillouin Scattering in diamond in extended FSR

The main phonon modes involved in this scattering are the $\mathbf{k}_b^{(1)}$. The peaks observed from measurements involving $\mathbf{k}_b^{(1)}$ were at high frequency values, hence are called high frequency modes in this study. In seeking to distinguish some peaks, optical half wave plates were used to polarize the light in certain preferred planes. This is to confirm the works of Mutti *et al* [93] who observed that light scattered by transverse phonons is completely depolarized; i.e. it does not keep the polarization of the incident wave. In this work, the laser beam reaching the sample was always polarized in the sagittal plane of the incident light. This was thus referred to as the plane polarized light. Scattering by longitudinal phonons is fully polarized while it is expected that there is no scattering by transverse phonons polarized in this scattering plane for an isotropic material. By choosing the polarity of the incident beam to be either plane (primary) polarized (p-p) or horizontally (secondary) polarized (p-s) to the scattering plane, spectra due to both the polarized (p-s) and unpolarized (p-p) light were obtained to check the wave mode. Thus, by polarizing light it is possible to say conclusively whether a peak is transverse/ longitudinal or

not.

A single wavelength beam of light, 488 or 514.5 nm, was used and revealed similar spectra. Figure 5.4 shows the longitudinal peaks obtained when the diamond crystal was illuminated with unpolarized (p-polarized) light using the scattering geometry described in figure 5.3 which requires a back reflecting surface. The transverse waves are clearly suppressed. The transverse peaks appeared enhanced when incident light was s-polarized, as shown in figure 5.5. The peaks appearing within the 50 GHz range were initially suspected to be surface modes. Since surface characterization was the aim of this work a free spectral range of ≈ 60 GHz was set and used in studying these modes. These peaks are dealt with extensively in section §5.5 where it is shown that in the absence of a Al back-reflector, these peaks are absent.

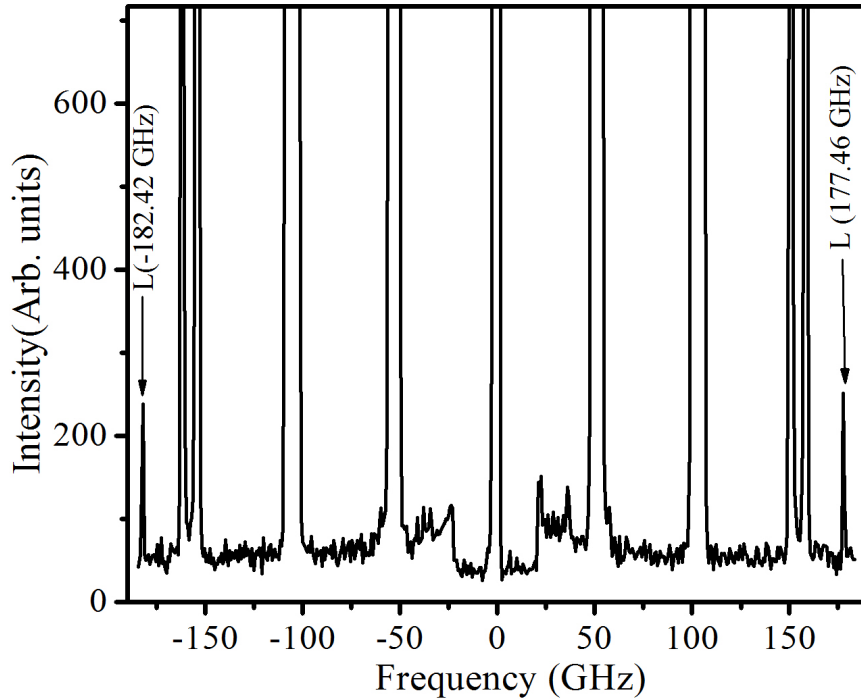


Figure 5.4: Brillouin scattering spectrum for pristine (100) diamond surface showing position of longitudinal modes for 488 nm light incident at 45° to the crystal normal with aluminium reflecting surface behind the sample. Scattering done in the p-polarization.

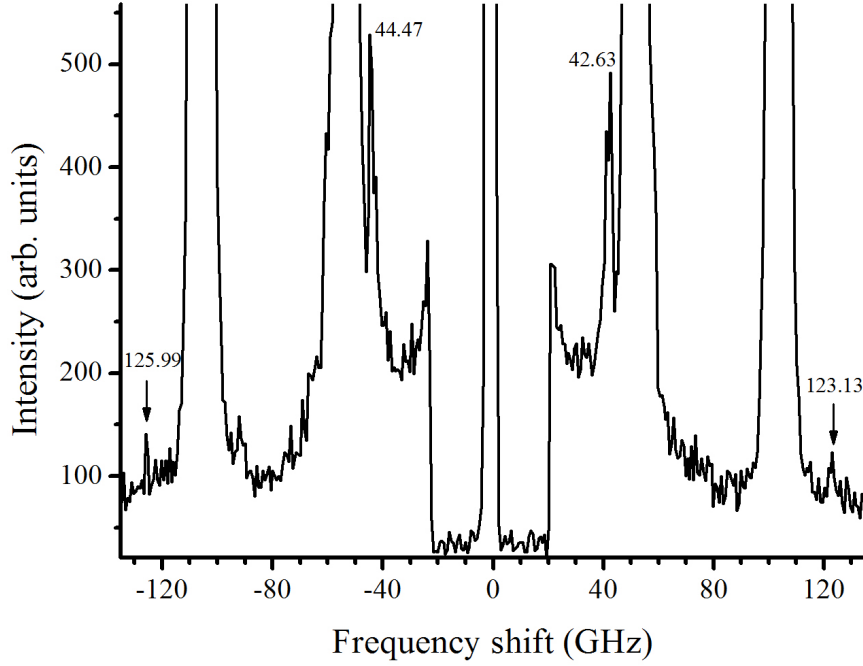


Figure 5.5: Brillouin scattering spectrum for diamond showing transverse modes at both low and high frequencies for green s-polarized light incident at 60° to the crystal normal, with an aluminium reflector behind the crystal.

To determine the elastic constants of diamond using bulk peaks at high frequency, the refractive index of the material is required. The Sellmeier equation (5.4.1) [17] was used to determine the refractive index of pristine diamond when using either blue (488 nm) or green (514.5 nm) laser light,

$$n = \sqrt{\left(\frac{0.3306 \lambda^2}{\lambda^2 - 175^2 \text{ nm}} + \frac{4.3356 \lambda^2}{\lambda^2 - 106^2 \text{ nm}} + 1 \right)}, \quad (5.4.1)$$

where λ is the wavelength of the incident light (nm). From this relationship, the refractive index of diamond when using the blue laser beam was 2.435 while it is 2.429 when using the green laser beam. Table 5.1 shows the longitudinal and transverse velocities of sound determined from:

$$v_L = \frac{\lambda \nu_L}{2n} \quad (5.4.2)$$

and

$$v_T = \frac{\lambda \nu_T}{2n}, \quad (5.4.3)$$

where v and ν are velocity and frequency shift, respectively.

Table 5.1: Bulk velocities of diamond

Mode	Frequency shift (GHz)	Velocity (m/s) (this work)	Velocity (m/s) (other works)
Longitudinal	180	18037	18000[158], 18038($\pm 0.30\%$)[159]
Transverse	124	13132	12834($\pm 0.26\%$)[159], 12390-13030[160]

The sound velocity in single crystal diamond is direction dependent. For instance in the work by Wang *et al* [159], it was shown that longitudinal and transverse velocities were higher in [111] direction as compared to the [110] direction. They report longitudinal velocities of 18784 ms^{-1} and 18182 ms^{-1} and transverse velocities of 12719 ms^{-1} and 12146 ms^{-1} for CVD diamond in the aforementioned directions, respectively. In single crystal natural diamond they report longitudinal velocities of 19039 ms^{-1} and 18038 ms^{-1} for [111] and [100] directions, respectively. The reported sound velocities are in agreement with the ones obtained in this work.

The engineering constants $E=1140 \text{ GPa}$, $B=380 \text{ GPa}$ and $\nu=-0.01$ were then calculated from the bulk wave velocities using equations (2.1.33) to (2.1.35). These values lie within those reported by other researchers, the range of values of Young's modulus reported for CVD diamond are $536\text{-}1224 \text{ GPa}$ [161]. However, in [162], the Young's modulus, bulk modulus and Poisson ratio for CVD diamond in the (100) plane are 1106 GPa , 442 GPa and 0.0569 , respectively. The deviations in reported values by different researchers may be attributed to variation in the direction of the wavevector probed owing to the anisotropic nature of CVD diamond.

The bulk modes (longitudinal and transverse) appear at much higher frequency shifts than surface modes, partly due to the higher velocity and also partly due to

the higher wave vector as derived from $[|\mathbf{k}_B| = (n/\sin\theta_i)|\mathbf{k}_R|]$. These bulk modes lie outside the spectral range of the broad central dominant mode seen up to ≈ 60 GHz in figure 5.4, the quasielastic scattering. This mode has been explained to arise due to entropy fluctuations. It was originally observed in perovskites, KTaO_3 and SrTiO_3 by Lyons and Fleury [163] and also in semiconducting Si [142]. To study the width of this mode Stoddart *et al* [164] excluded the transverse and longitudinal bulk peaks since it was observed not to extend past the transverse peak. In our quest to study the modified diamond surface due to ion implantation, this served as a pointer to limit the spectral range so as to avoid bulk modes.

5.5 Surface Brillouin Scattering in diamond within a limited FSR

The phonon modes involved in this section are $\mathbf{k}_b^{(2)}$ and $\mathbf{k}_s$. The primary interest of this study was to determine the modes that are true SAWs as they would give information regarding the elasticity of the near-surface region. This is the region that is later ion implanted. From the analysis of equations (5.3.5) and (5.3.6), it is clear that $\mathbf{k}_b^{(2)} = \mathbf{k}_s$, both being parallel to the surface, hence the question, “Which one of these modes gives the Rayleigh equivalence?” In the context of this work these modes are referred to as low frequency modes (LFM). Though the discussion in this section deals with measurements done with limited free spectral range (FSR), some explanations need the limited and extended FSR simultaneously. Hence limited FSR will not be used exclusively in the sections hereafter.

Elastodynamic Green’s function methods have been widely used in understanding the surface dynamics of opaque or semi-opaque solids [72, 73]. Green’s functions

simulations have been used to theoretically fit SBS data obtained from such materials. The Fortran based programs developed by A. Every have been adopted by many researchers in the SBS field [165]. The programme code requires an upper material (film) to have a finite width while the substrate can be considered to have an infinite width. In this work the simulation is done whilst neglecting the elasto-optic coefficients of diamond. The ion damaged region was simulated as the film that is basically diamond and bulk diamond as the substrate. The diamond's elastic constants were reduced by $\approx 2\text{-}4\%$ and the density by 17%. These values were then used to mimic the hypothetical film. It was then possible to predict the theoretical spectra of 'diamond' as-implanted at different angles of incidence as shown in figure 5.6. In this simulation, a 'film' thickness of 400 nm was used, being thick enough only to produce Rayleigh modes. The film representing the as-implanted diamond was considered largely isotropic with respect to the pristine diamond. The assumption to work with is, a similar mode at almost same position for a particular angle of incidence obtained experimentally using the backscattering configuration is a Rayleigh mode of diamond.

In 1978, Sandercock [142] wrote a paper in which he asserted that *using backscattering geometry, it was impossible to observe a Rayleigh mode in any transparent medium*. The reason he gave for this was "Opacity is a requirement. This is qualitatively to be expected for an electron-mediated coupling mechanism to the phonons, for in opaque materials the light is absorbed close to the surface and thus many electron-hole pairs are produced in the medium just in the region where the surface wave exists". Surface Brillouin scattering studies in this chapter discusses the observed spectra off pristine/ ion implanted diamond with the opacity consideration

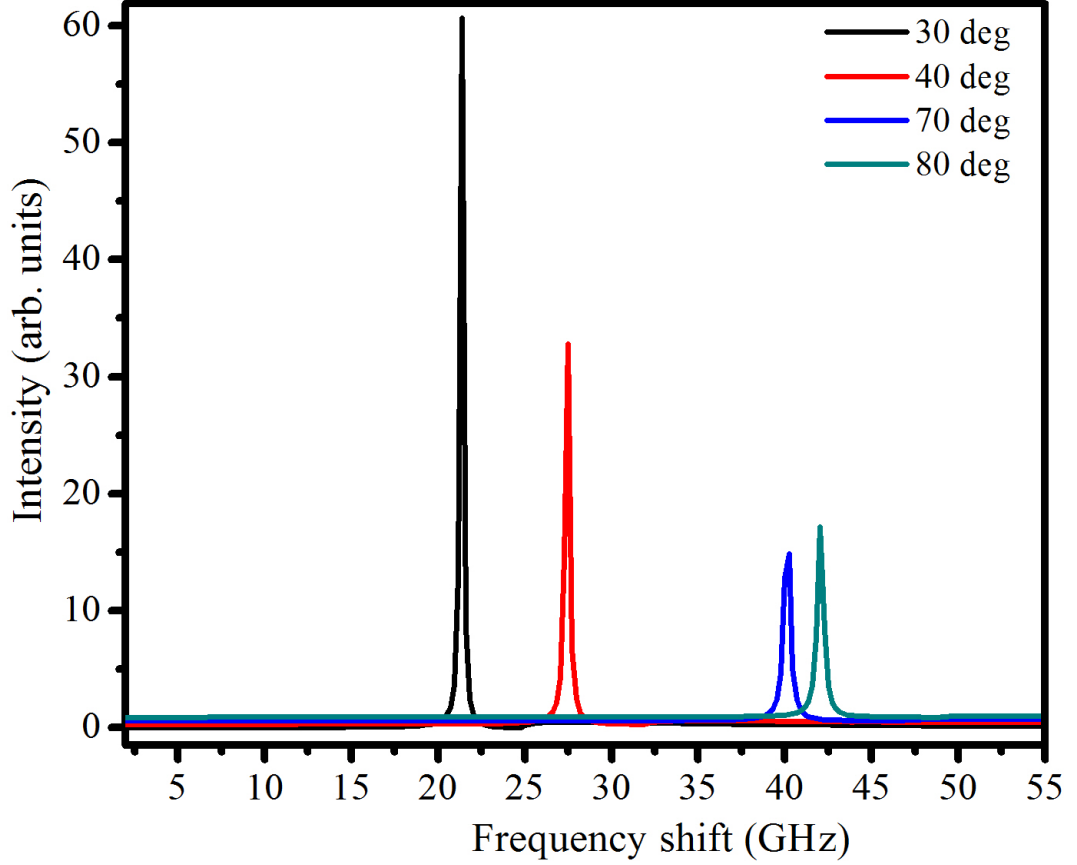


Figure 5.6: Simulated surface Brillouin scattering spectra for different angles of incidence on a hypothetical 'layer' that mimics a damaged diamond region created using $C_{11}=1054.9$, $C_{12}=122.7$, $C_{44}=555.2$ GPa and a density of 3.0 g/cm^3 . The substrate (diamond) was modelled using elastic constants in [166] i.e. $C_{11}=1076.4$, $C_{12}=125.2$, $C_{44}=578.3$ GPa and a density of 3.52 g/cm^3 using [100] plane orientation.

in mind. The Krüger geometry [167] was employed in studying the transparent unimplanted and the semi-opaque as-implanted diamonds. The schematic diagram of the Krüger scattering mechanism is shown in figure 5.7, where in the presence of a metal reflector (R), the incident photons undergo direct scattering ($q180$) as well as indirect scattering ($q2\alpha a$) off the acoustic phonons near the free end attached to the metal.

As reported in section §3.2, the samples were $\approx 0.3\text{-}0.5 \text{ mm}$ thick. There is therefore a huge geometric scattering volume for the pristine diamond. Also from the end of range to the back of the sample, the width is very large compared to the wavelength, $514.5/488 \text{ nm}$ of light beam used. It is expected that only the

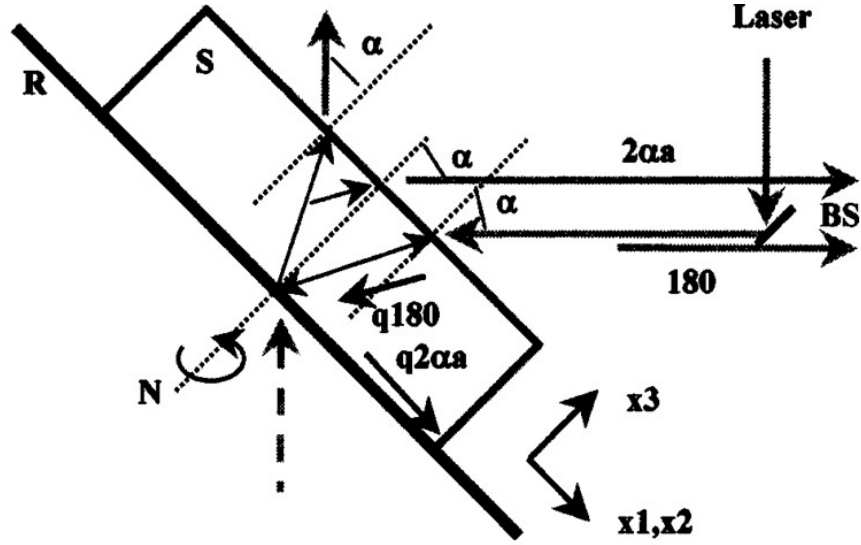


Figure 5.7: Schematic representation of the backscattering geometry and the reflection on the substrate giving rise to the $2\alpha A$ scattering geometry. S: sample. R: Reflecting substrate. N: Normal and possible rotation axis. [94].

scattering taking place at the front and/ or back of a free surface of the sample can give rise to surface modes. We try to find out which of the two locations was responsible for the detectable modes. It was important to check if light at the front or that reaching the back side actually scattered back into the limited area of the detector. To do this, Brillouin measurements were carried out with a translucent double sided tape (hydrocarbon based material) behind and in front of the sample consecutively. The results in figure 5.8, show that there are similar features observed on the sample with light impinging on the tape (tape in front) and tape at the back.

There was need to ascertain the source of the observed peaks between 7-18 GHz and the one at around 44 GHz. Another test was done with the sample on a clean aluminium holder without the tape. The peaks at 7-18 GHz were conspicuously missing while the one at 44 GHz was noticeably tall and sharp. It can therefore be concluded that the peaks at 7-18 GHz were scattered from inside the tape since they did not scale with the angle of incidence as shown in figure 5.9. The peak

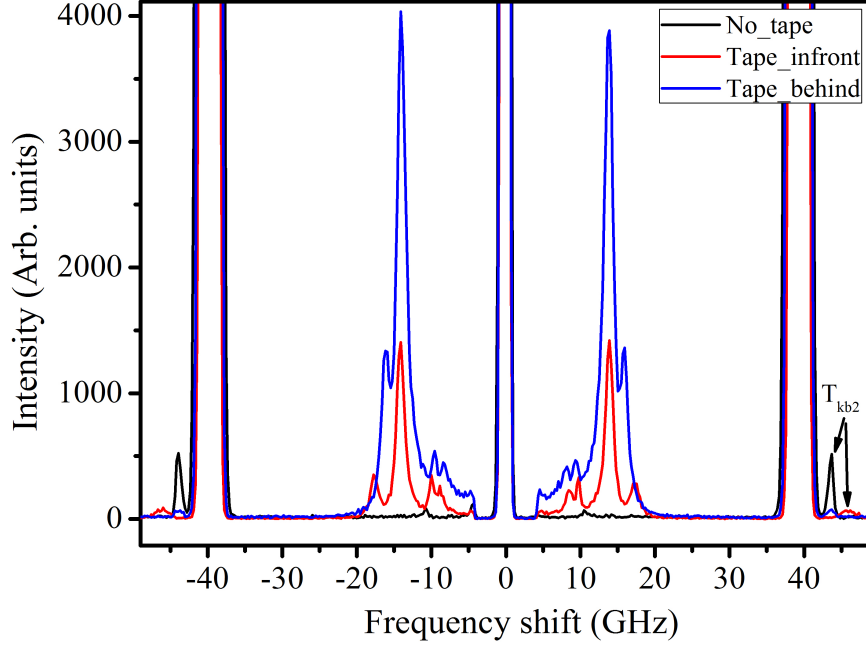


Figure 5.8: Brillouin spectra for different tape positions. Similar features appear when the double sided tape is in front and at the back of the sample. There is a peak, T_{KB2} that appears in both tape-present and no-tape situations, however it is highly suppressed where the tapes were present. Light of wavelength 514.5 nm was used as a probe.

labelled L_{KB2} on the other hand originated from diamond. The peak was poorly resolved when the tape was in front or back of the diamond but was sharp with higher intensity when no tape was used. This could be attributed to the fact that the tape at the front or back absorbed most of the photons reducing the intensity of scattered photons. This peak is also as a result of indirect scattering since it is affected by the relative position of the tape. Its appearance in both the tape-in-front and tape-at-back scenarios shows that in transparent material, the probing light travelled the whole length of the sample hence scattering from the tape. Though it has low intensity and was poorly resolved when light passes through the tape, it nevertheless scaled with the angle of incidence.

Figure 5.10 read in tandem with figure 5.3 explains the scattering mechanism that can take place in such a huge width. The thick arrows q_s , bulk, and S are representations of phonons at different locations in the sample. Directly scattered

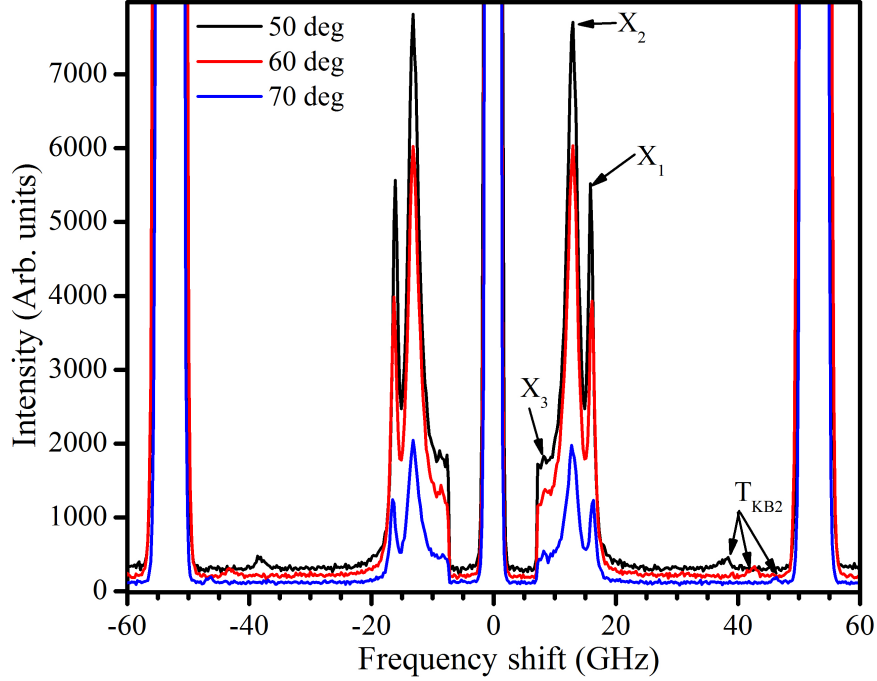


Figure 5.9: Brillouin spectra for different angles of incidence where the sample was mounted on the holder using a double sided tape. Peak T_{KB2} scales with the angle of incidence while peaks X_1 to X_3 at 7-18 GHz do not change with change in angle of incidence. Blue light of wavelength 488 nm was used as a probe

photons q'_s and those scattered after reflection (r), q''_s by phonons q_s are the only ones that reach the detector (PMT) in this setup. The indirectly scattered photons must travel parallel and very close to those scattered directly in order to fall within the collection angle of the detector. Those scattered indirectly from regions that lie far away from point of reflection such as ‘bulk’ and S can not enter the detector.

Figure 5.10 also shows a special slot on the Al holder with a clean smooth finish at the back that held diamond samples without the need of the double sided tape. This ensured the exclusion of the unwanted peaks lying at 7-18 GHz in figure 5.9. There were no peak(s) that could be traced to Al when the diamond was attached to it. One possibility is the lack of intimate contact between the Al holder and diamond. Moreover, with such a thick optically hard over soft material, there would be no Sezawa modes [168] even if thin films were being considered. However, the fact that peaks associated with the double sided tape could be seen even when the

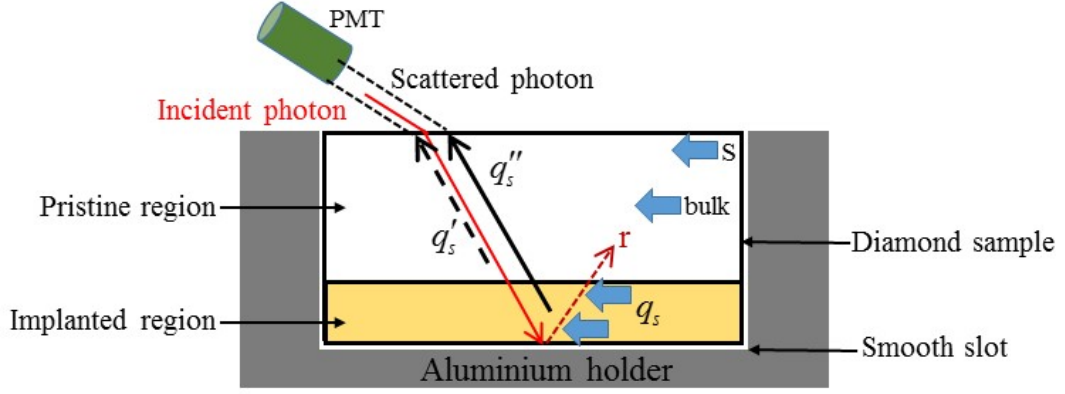


Figure 5.10: Schematic diagram of possible scattering mechanism of light when translucent material is in intimate contact with a transparent material and away from the impinging light.

tape was positioned at the back (intermediate between diamond and Al holder) may mean that the lack of any peaks due to Al was due to a poor Al-diamond boundary. The layer of air between diamond and Al holder is practically so large it causes the diamond back surface to behave as a free surface.

5.5.1 The one side polished surface question

Having ascertained that it is possible to eliminate other unwanted peaks and obtain only peaks related to diamond by having a clean Al back surface, investigations were further done using pure diamond polished on one side. The diamond sample was placed in the Al slot with the unpolished surface facing the light and then flipped over for the polished surface to face the light. The same sample was placed such that unpolished side rested on the double sided tape, the tape being used to fill up the space between the rough surface of the diamond and the smooth Al holder. Brillouin scattering measurements were done for each scenario. In all the three cases, the peak associated with diamond (appearing at $\approx 44-48$ GHz in figure 5.8) was not observed. Neither were the peaks (X_1-X_3) in figure 5.9 originating from the tape observed. These observations show that it is impossible to perform

surface Brillouin measurements by indirect scattering on diamond polished on one side, irrespective of which surface is probed. The lack of any peaks when the unpolished surface faces the light, due to roughness, was observed earlier by Riobóo and Belmahi's [94] who then subsequently stated that it is impossible to observe any Brillouin spectrum on the front of an unpolished diamond surface. Mortet *et al* [169] noted that an unpolished surface has high roughness which interferes with good propagation of surface acoustic waves. Lack of spectra when the unpolished surface is positioned at the back correlates directly with the fact that the Krüger geometry fundamentally relies on specular reflection from the back off the metal reflector. Diffuse reflection at the rough diamond surface implies that the photons that select the wavevector of interest are too few to show any meaningful spectrum. A rough interface means that the diffusely reflected light from the back surface causes phonon wave vector and momentum conservation to break down. Therefore, an unpolished diamond surface forming this interface results in a featureless spectrum. The high frequency modes, the longitudinal and transverse peaks due to direct scattering were observed on a set-up with the un-polished face away from the impinging beam as can be seen in figure 5.11. This implies that the scattering of photons took place only along q'_s and not due to reflection at q_s (refer to figure 5.10). Any further investigations focussing on this diamond peak were done on diamond polished on both sides.

5.5.2 Incidence angle dependence of the diamond related peaks

A clean diamond that was polished on both sides was placed on the clean smooth Al holder. A FSR that allowed for observation of HFM from direct backscattering

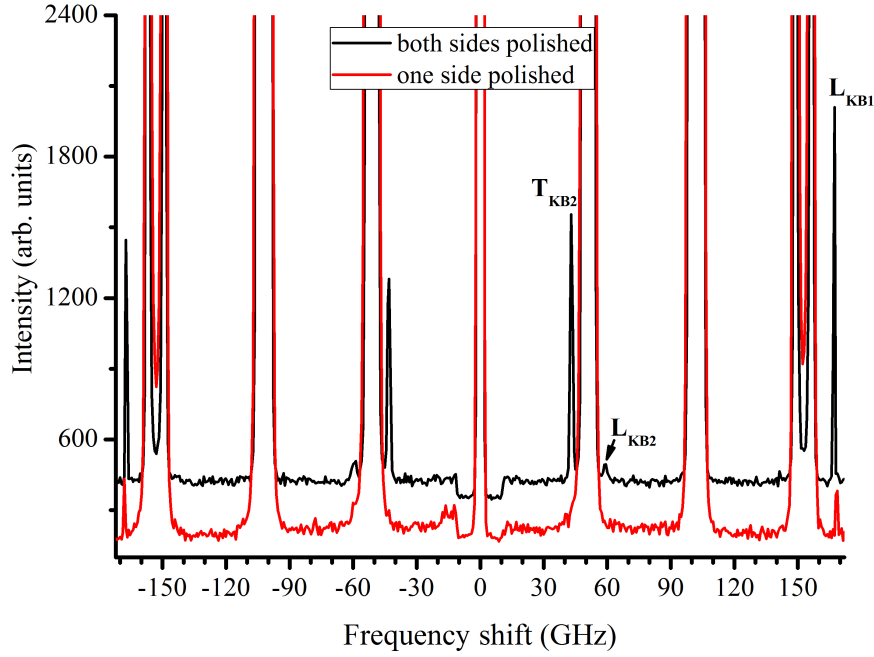


Figure 5.11: Brillouin spectra for a sample polished on one side (red) shows only one peak at 167 while that polished on both sides shows this peak in addition to two bulk peaks T_{KB2} and L_{KB2} due to indirect scattering.

of photons by phonons was employed. Figure 5.12 shows spectra taken with p-polarized incident light. Two modes labeled T_1 - T_3 and L_{KB1} are observed, barring obstruction of other peak(s) by the instrumental ghosts. The acoustic mode at low frequencies ≈ 22 -30 GHz was observed to scale with the sine of the angle of incidence while the HFM at around 166.7 GHz does not. The low frequency modes (LFM) therefore exhibit a surface wave-like characteristic.

The measurements done on pristine diamond within the low frequency (LF) range at different angles of incidence yielded single peaks shown in figure 5.13. These peaks correlate very well with those predicted using Green's functions simulations in figure 5.6. The simulated spectrum therefore correctly predicted the experimental spectrum. These peaks were better resolved and took a shorter time to accumulate than those where double sided tape was used at the back. This suggests they originate from indirect scattering of photons after reflection where minimal loss of photon intensity has occurred.

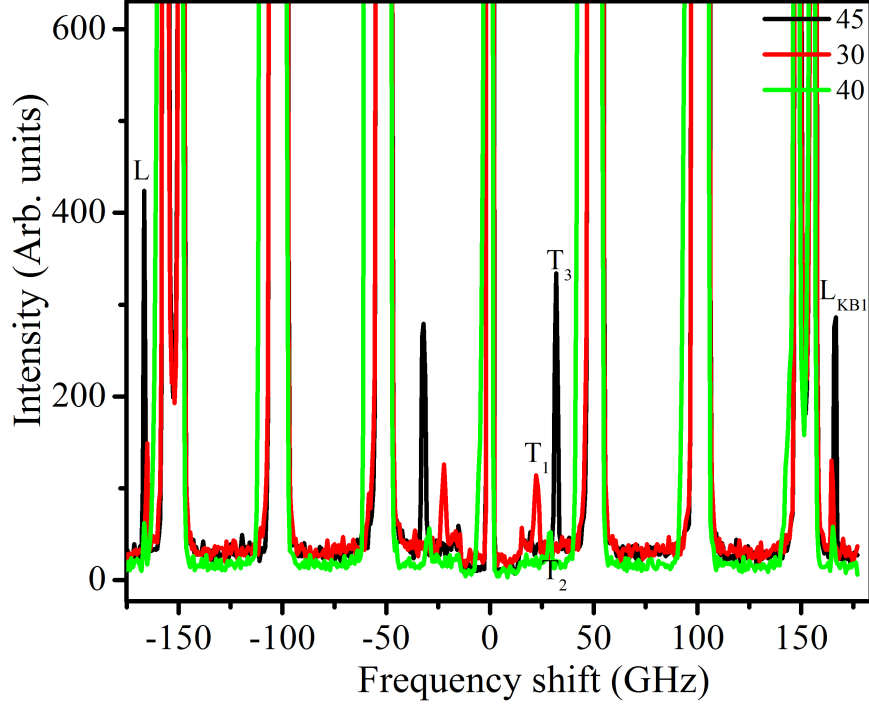


Figure 5.12: Brillouin spectra for different angles of incidence on virgin diamond. The peaks at lower spectral range, T_1 , T_2 and T_3 corresponding to incidence angles 30° , 40° and 45° respectively, vary with the angle of incidence while the high frequency peak, L_{KB1} is fixed for the same angles of incidence.

A graph of frequency shift relative to the sine of the angle of incidence is shown in figure 5.14. The figure is a representation for the results obtained from measurements of pristine diamond and of as-implanted samples 2 and 3 described in section §3.2. The peaks obtained from the 3 samples were well resolved. It can also be observed that the peak width is not the same though the collection time was almost the same. The peaks obtained using steeper beams (small angle of incidence) were more broader than those from large (grazing-like) angles. Table 5.2 summarized by figure 5.15 shows how the peak width changes with $\sin\theta_i$. The position where instrumental ghosts occur, depends on mirror spacing and FSR chosen; for ease of comparison these were kept constant, however the ghosts obscured the peak for angle of incidence 50° and 60° (not shown in figure 5.13).

The peak width reduced as the angle of incidence increased, hence the narrow

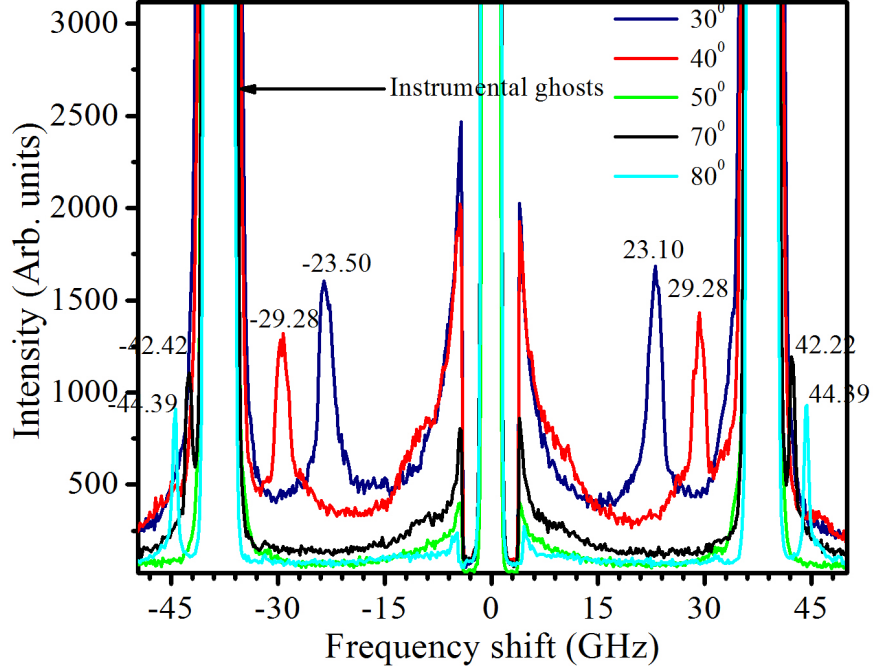


Figure 5.13: Brillouin spectra for different angles of incidence where the sample was mounted on the holder using a specially made slot without the double sided tape. Peaks appearing at 7-18 GHz in figure 5.9 are clearly absent.

Table 5.2: Peak width at half maximum for different angles of incidence for samples 1, 2 and 3.

$\sin\theta$	Un-implanted diamond (sample 1)	Multiple-energy implanted diamond (sample 2)	Single energy implanted diamond (sample 3)
0.50	2.29	2.29	3.60
0.64	2.12	2.02	3.03
0.94	1.43	1.10	0.99
0.98	0.65	0.67	0.73

ones were well resolved. This is in agreement with the observation made by Sandercock [142], who showed that for a range of finite number of scattering angles, θ_s has no effect on bulk phonon wavevector $\mathbf{k}_B^\perp$ when centred around θ_i in backscattering. However, it is apparent from $\mathbf{k}_B^\parallel = \mathbf{k}_i \sin\theta_i + \mathbf{k}_s \sin\theta_s$, that there results a range of values for k_s and so a broadening in the surface phonon spectrum. The broadening becomes less severe as $\theta_s \rightarrow 90^\circ$. He further argued that to compensate for this, one requires smaller apertures on the spectrometer for smaller θ_s . Measurements at $\theta_i = 70^\circ$ and/ or 80° are preferred since its peaks are well resolved.

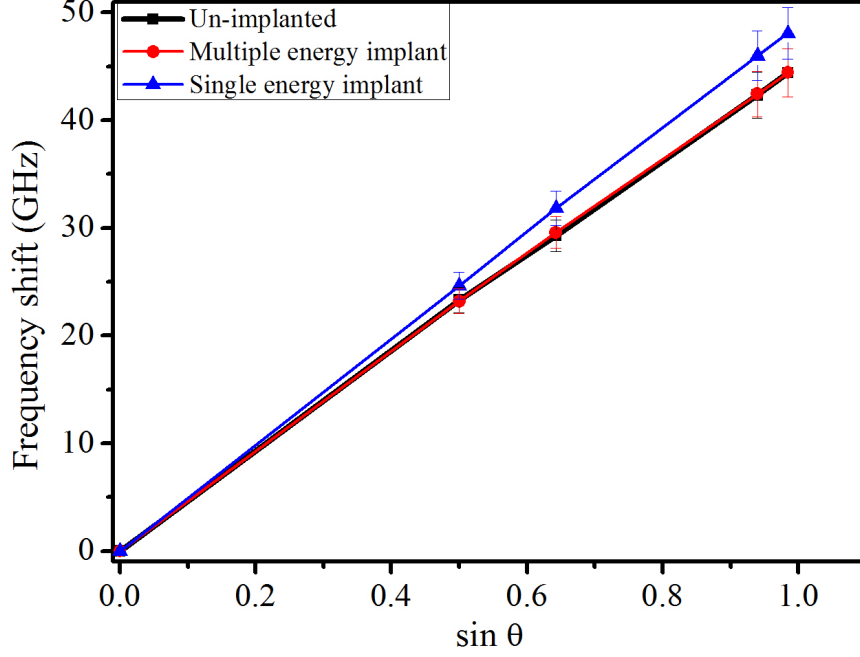


Figure 5.14: Variation of frequency shift with the angle of incidence for both pristine and as-implanted diamond (100) surface.

5.5.3 The scaling bulk modes paradox

The question of whether the observed peak associated with diamond was a bulk or surface mode compelled an increase in the free spectral range to determine if there was another peak with similar behaviour in its neighbourhood. Scaling with angle of incidence was earlier seen among the T peaks of figure 5.12 for s-polarized light. Adjusting the mirrors of the Fabry P  rot to 3 mm and increasing the spectral range to 179 GHz, two peaks were obtained for p-polarized light as shown in figure 5.16. Peak L_{KB2} scales with the angle of incidence and was only visible at certain azimuthal directions of the sample while peak L_{KB1} does not scale but was visible at all orientations.

Peak L_{KB2} showed a dispersive behaviour; its velocity can therefore be calculated without incorporating the refractive index of the material using equation (4.6.14). The velocity calculated for this peak was 18005 m/s for $\lambda = 514.5$ and laser beam incident at $\theta_i = 70^\circ$ to the sample surface's normal. Peak L_{KB1} shows

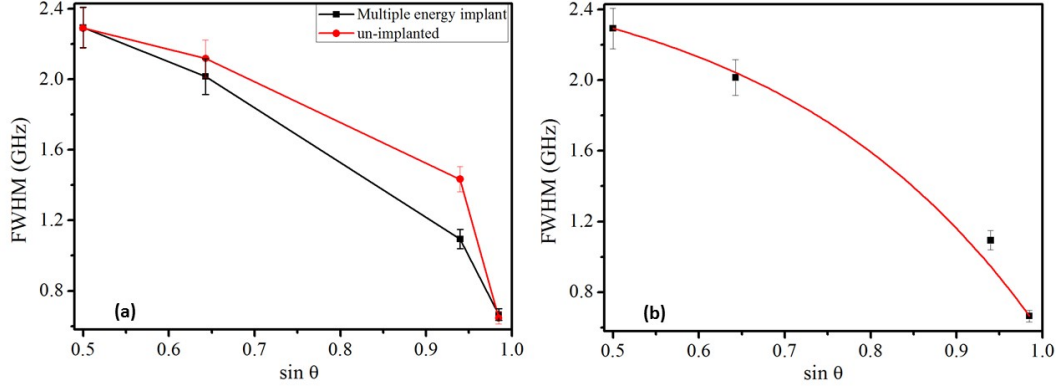


Figure 5.15: Peak width scaling with the sine of the angle of incidence for un-implanted diamond (100) surface.

non-dispersive characteristics of a bulk mode whose velocity is calculated using equation (5.4.2). The two peaks are basically the same modes in the same sample under similar conditions of pressure and temperature in the same crystal direction, so their velocities must be related. Therefore equating (4.6.14) and (5.4.2), the refractive index of diamond was determined using:

$$n = \frac{\nu_{dir}}{\nu_{ind}} \sin \theta_i, \quad (5.5.1)$$

where ν_{dir} and ν_{ind} are the frequency shifts for peaks L_{KB1} and L_{KB2} , respectively. This gives the value of n as 2.435, a deviation of +0.25% from 2.429 that was calculated for 514.5 nm wavelength using the Sellmeier equation (5.4.1). Within the limits of experimental error, peaks L_{KB1} and L_{KB2} are the same mode but observed at different frequency shifts since L_{KB1} and L_{KB2} are not strictly propagating along the same direction; even more for angle of refraction 70 °C for which the angle of refraction is ≈ 23 °C. Hence their velocities could not compare perfectly well because of the high anisotropy of diamond.

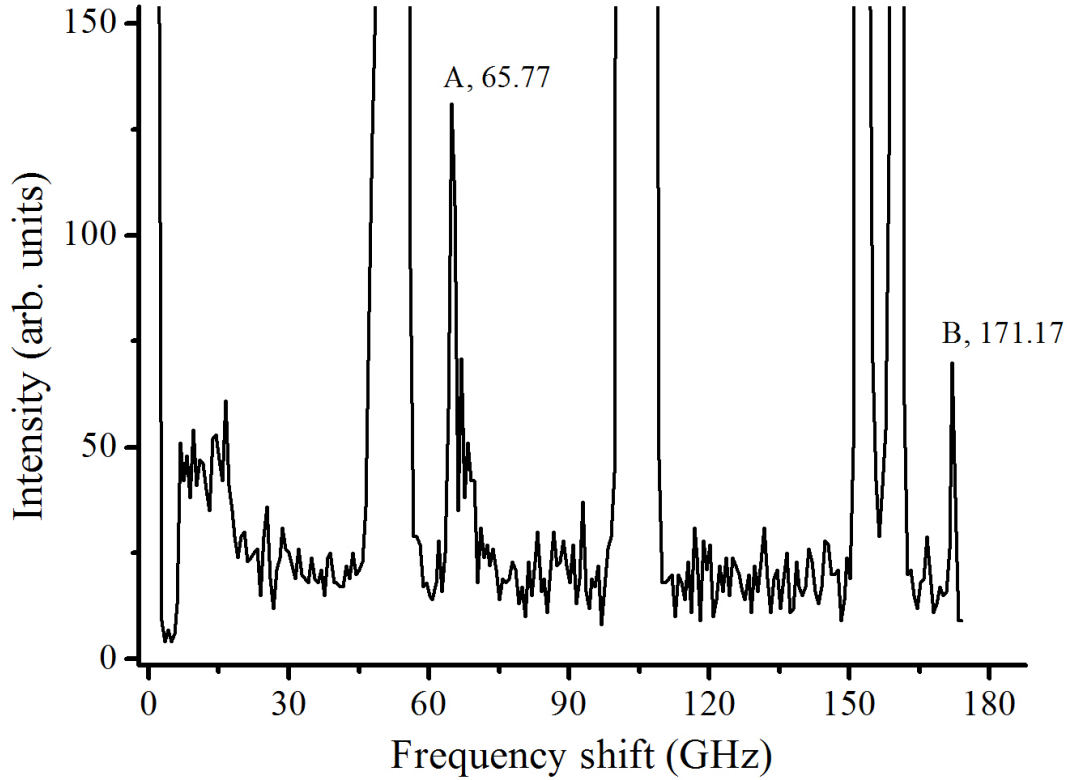


Figure 5.16: Longitudinal peaks on the anti-stokes side of Brillouin scattering in pristine diamond for light incident in the p-polarization. Peak A (L_{KB2}) is due to indirect scattering while peak B (L_{KB1}) is due to direct scattering measured along the same wavevector.

5.5.4 The light polarization factor

Djemia *et al* [135] have shown the effect of polarization of the incident light on the peaks observed in polycrystalline and smooth grained diamonds. They showed that for non-polarized light three peaks RW, SHM and LM are observed; for p-polarized light RW and LM appear while for s-polarized, only the SHM is observed. In this study two peaks, namely transverse and longitudinal for non-polarized light, were observed within a frequency shift range similar to that of Djemia *et al* [135]. This is in agreement with the other reported results on CVD diamond observed by the same author *et al* [136]. The effect of light polarization is clearly shown in figure 5.17.

The peak of interest (T_{KB2} at 47.8 GHz) appears in both the p- and s-polarizations.

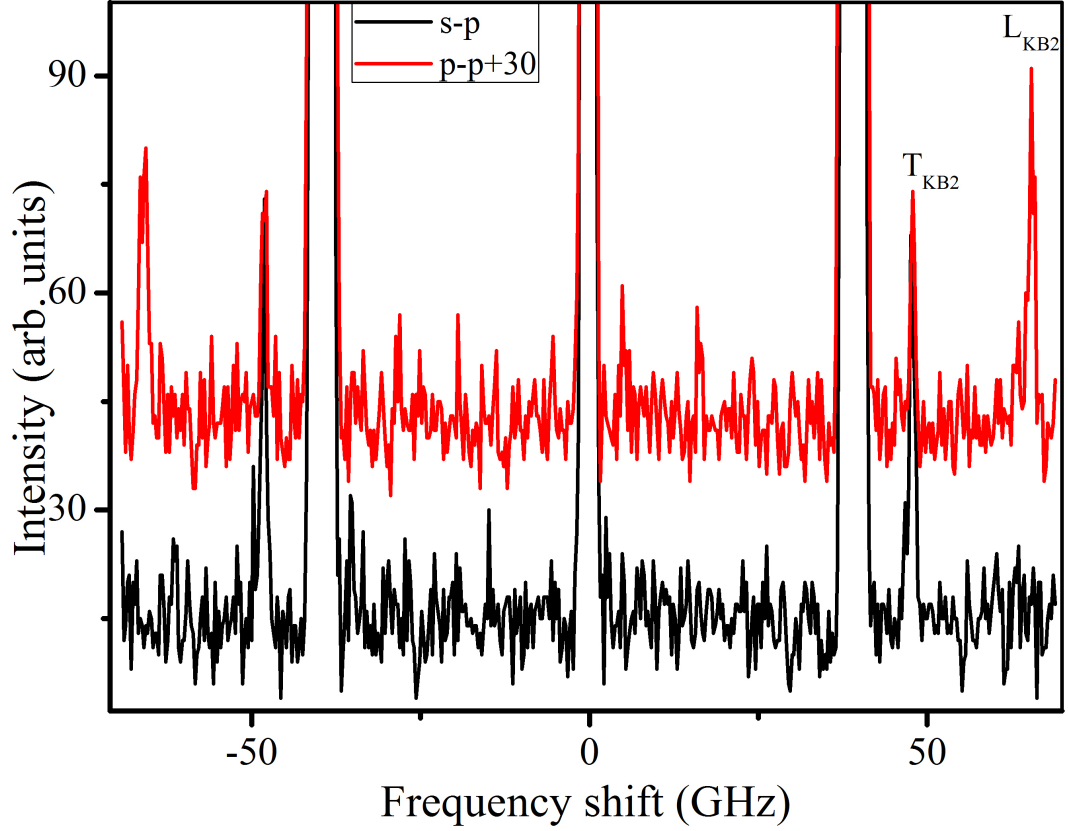


Figure 5.17: Spectra obtained for p- and s-polarizations at incidence angle of 70° . The peak T_{KB2} that has been seen previously in all measurements having Rayleigh-like behaviour is observed in both polarizations. The bulk L_{KB2} does not appear in the s-polarization as expected. Spectrum due to p-polarization has been displaced by 30 units for clarity.

This seems to contradict the observations of Djemia *et al* [135] above. If this peak was a pure transverse mode then it should not appear when the sample is probed with p-polarized light, however, it is expected for s-polarization while L_{KB2} is not. The appearance of the T_{KB2} mode in both cases in single crystal diamond is intriguing. As explained earlier in section §5.3.1, for light impinged on a transparent material, the invariance of wavevector upon refraction implies that $\mathbf{k}_b^{(2)} = \mathbf{k}_s$. The detected surface wave and bulk results from phonons whose direction of propagation is parallel to the surface. It is also possible that T_{KB2} can be a vertical-transverse mode that can scatter light with p-polarization with no rotation of polarization. Hence in this work a hypothesis is put forth that peak T_{KB2} is degenerate for both

the RW and SHM in this transparent sample, the scattering volume notwithstanding. Peak L_{KB2} at 65.7 GHz only appears in p-polarization as expected, and is definitely a longitudinal mode.

5.6 Brillouin scattering in as-implanted diamond

As stated earlier, the as-implanted diamond had a golden brown hue, with a lower transmittance of 15% for light of wavelength 514.5 nm as shown in figure 5.2. The question we sought to answer is where does coupling of the surface mode with the incident photon take place? Is it at the front where the reflected light scatters off the phonons on the implanted side or does it occur at the back surface when treating the diamond as a free surface? Brillouin scattering measurements were taken on as-implanted samples 2 and 3. In one measurement, the implanted layer faced the light and in the other set of measurements, the layer faced the holder, schematically shown in figure 5.10. For consistency, a wavevector in the same direction had to be probed. The mark at one corner of the sample shown in figure 3.1 was used as a reference. To attain this, the sample was flipped over front to back then rotated through a clockwise direction of 90° as shown in figure 5.18. The end result is the wavevector on the opposite faces are in the same direction. Representative Brillouin spectra done for these set-ups are shown in figure 5.19.

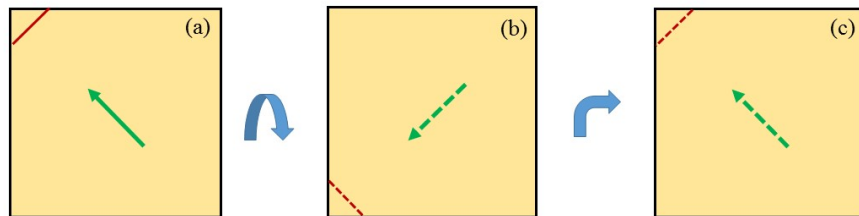


Figure 5.18: (a) Implanted layer facing the impinging light, (b) Front to back flip over of the sample and (c) after 90° clockwise rotation.

Measurements done on the implanted layer facing the impinging light and when

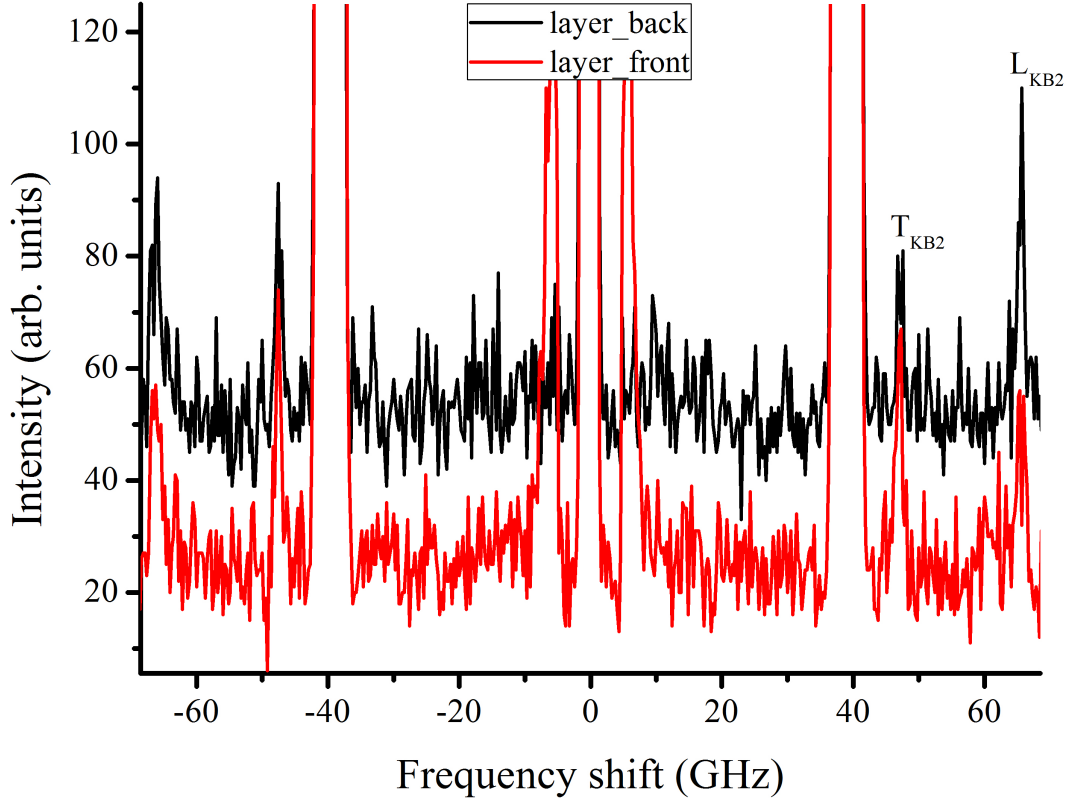


Figure 5.19: Brillouin spectrum obtained from implanted layer facing and away from the impinging light.

turned away from the light show that there was no significant change in peak positions of T_{KB2} and L_{KB2} . The same modes observed in pristine diamond appear in as-implanted diamond. The lack of new modes or change in frequency shift from the ones observed in pristine diamond may suggest the similarity in the elastic properties of the ion implanted region with its neighbouring host and/ or lack of true surface acoustic waves due to the opacity of the layer. Raman spectroscopy, however shows a new broad peak in addition to the diamond Raman line (1332 cm^{-1}) after ion implantation (see figure 5.1). Discussions on as-implanted diamonds are based on results obtained by the procedure described in figure 5.18 and the representative result of figure 5.19. We see that from the Brillouin scattering viewpoint, the implanted diamond still very much maintained the vibrational properties of pristine diamond. The technique does not manage to detect vibrations due

to disorder and the sp^2 bonding created in the as-implanted samples. In Raman data the sp^2 cross-section for green light is strong and the diamond signature is also very strong even after ion implantation because light probes the pristine substrate beyond the implanted region where stresses have been introduced by growth processes or ion implantation [4, 152, 155]. In surface Brillouin scattering, opacity is a factor but as long as light could still transit through the implanted layer, similar results as for pristine diamond were obtained. Hence the results obtained in pristine diamond and extensively discussed in sections above were repeatable in as-implanted diamonds.

5.6.1 Direction dependence of Brillouin scattering in implanted and pristine diamond

To investigate whether the implanted layer was contributing to the Rayleigh-like mode (peak T_{KB2}), sound velocities in different azimuth directions at constant incident angle of 70° on un-implanted (sample 1) and as-implanted with different doses (samples 2 and 3) were measured. The data obtained are presented in figure 5.20.

On the un-implanted surface, velocities measured were in the range 11810 - 13120 ms^{-1} , and those for where damage depth was evenly spread by multiple energy implantations were 11780 - 13030 ms^{-1} while the sample with highest dose supposedly concentrated within a small region by a single energy implant was in the range of 11660-12870 ms^{-1} . This suggests that there is a wide range of velocity values one can obtain from the same sample if the direction is randomly probed. For similar diamonds it would be expected that the average velocity would be the same. Variation in average would imply modification of the surface as a result of

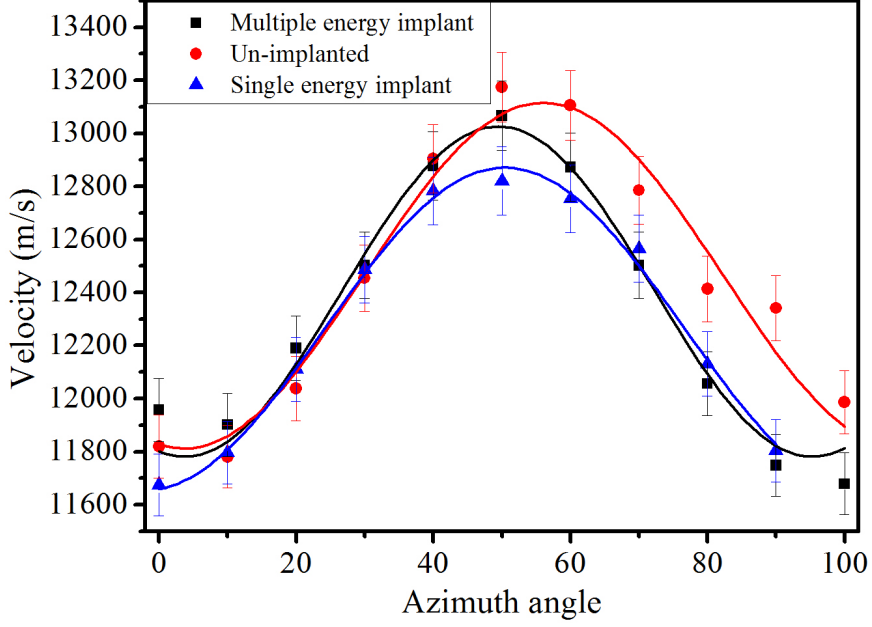


Figure 5.20: Variation of velocity on the surface of implanted and un-implanted diamond (100) surface at different azimuth angles and incident angle of 70° .

ion implantation. Average velocities versus their respective azimuth angles when fitted with a sine function, $A = v_o \sin \theta_A$ for each of the samples 1, 2 and 3 gave average velocities v_o and velocity variation A for each sample as shown in Table 5.3.

Table 5.3: Rayleigh-like velocities in pristine and near surface damaged diamond. y_0 is the average velocity for that sample while A is the deviation from average.

	Un-implanted	Multiple energy implant	Single energy implant
Dose (atoms/cm ²)	0	1.0×10^{16}	1.5×10^{16}
v_0 (m/s)	12500.0 ± 40	12400.0 ± 30	12300.0 ± 30
A (m/s)	670 ± 50	620 ± 40	610 ± 20

This small decrease in acoustic velocities suggests that ion implantation to doses of 1×10^{16} ions/cm² and 1.5×10^{16} ions/cm² does not affect the diamond lattice significantly. Directional velocity measurements help remove the erroneous picture which a cursory look at the velocity of the Rayleigh-like mode from figure 5.14 portrays. In that figure, it can erroneously be concluded that the single energy implanted diamond had the highest velocity, yet it's possible that it was oriented

in the direction of its higher velocity compared to the other samples. However, the fact that the decrease in velocity corresponded to the level of fluence show that there were defects created by implantation which mildly destroyed the periodic diamond lattice resulting in somewhat reduced acoustic velocities. Moreover, the azimuthal dispersion for the three samples reveal a fourfold symmetry even after ion implantation that is consistent with the diamond (100) plane [170] implying insignificant damage on vibrational symmetry of diamond in as-implanted samples.

Experiments were also carried out to ascertain authenticity of using average velocities obtained from the azimuth measurements. Sample 6 was used for this studies. Measurements were conducted by varying the incidence angles between 30-70° after each annealing cycle from the as-implanted up to 500 °C. A specific wavevector was probed by orienting the sample with the aid of the groove as shown in figure 3.1 on the 20° mark of the circular vernier. The velocity of the SHM peak (A) was obtained using equation 4.6.14. In another set of measurements, a constant incident angle of 70° was used in determining the frequency shift positions of the SHM peak recorded at different azimuth angles. A sine fitted plot of velocity against azimuth angle is shown in figure 7.15(a), from which the average velocity was obtained in a similar way to that shown in figure 5.20 and table 5.3. Comparison between the velocities obtained from the azimuth and scaling peak measurements are shown in table 5.4

Table 5.4: Rayleigh-like velocities measured by the scaling angle and different azimuth orientations.

Annealing temp (°C)	Freq. shift Vs $\sin\theta_i$ (m/s)- v_{KB2}	Velocity Vs azimuth angle (m/s)- v_{az}	Ratio ($v_{az} : v_{KB2}$)
As-implanted	13140	12493	0.951
200	12918	12355	0.956
400	12820	12248	0.955
500	12877	12249	0.951

There is a slight decrease in velocity with increase in temperature up to 400 °C as observed by both techniques. The relationship between these velocities which is reported for the first time by this study is given by equation 5.6.1

$$v_{az} = 0.953v_{KB2}. \quad (5.6.1)$$

5.7 Aluminium coated diamond

From the foregoing discussions, there had been limited success in accessing true surface waves in transparent and semi-opaque diamond using SBS measurements. There was need to improve surface excitations on transparent media by increasing reflectivity at the surface. Some researchers, contrary to assertion made by Sandercock that it is difficult to observe SAW modes on transparent medium, have reported successful studies when a thin metal layer is deposited on the surface to enhance reflectivity. All agree that in transparent materials, the scattering from the Rayleigh mode is too weak to measure. To increase intensity, it has been suggested that a thin Al film, < 40 nm be coated on the surface. Sussner *et al* [171] used a thin reflective Al front surface coating on quartz and sapphire, Andrews *et al* [86] deposited Al on 6H SiC, Mroz and Mielcarek [172] on silica glass SUPRASIL. Riobóo and Belmahi [94] deposited a 40 nm thick Al on 12 μ m CVD diamond and obtained SAW velocities of 8575 m/s (nucleation) and 9350 m/s (growth). These values are smaller compared to the expected Rayleigh velocity discussed in section §5.7.1. Jiang [173] observed that such treatment underestimates the Rayleigh frequency of diamond. The thin metallic coating provides the required high reflectivity while its low mass does not significantly influence the surface waves on the underlying transparent medium. This section reports on attempts made to find

the surface mode of the samples 1, 2 and 3 when coated with a thin Al film.

Al deposition on clean samples was done using a physical thermal evaporator. Al films were deposited on diamond and Si substrates simultaneously after optimizing the variables to ensure repeatability. The large sized Si wafer was important for further analysis such as thickness determination that required a larger surface. Moreover, Al deposited on Si remained firm for a long time compared to that deposited on diamond which tended to degrade with time. As analysis was being done on the Al deposited on Si, the metallized diamonds were immediately taken for SBS studies. A ‘thin’ Al film of interest among the many that were tried out was deposited for 2 minutes and had a thickness of 23.8 nm measured using profilometry and 20.1 nm using XRR. XRR fitting using the LEPTOS 7.05 software shows that its roughness was 0.24 nm. The XRR fit is shown in figure 5.21.

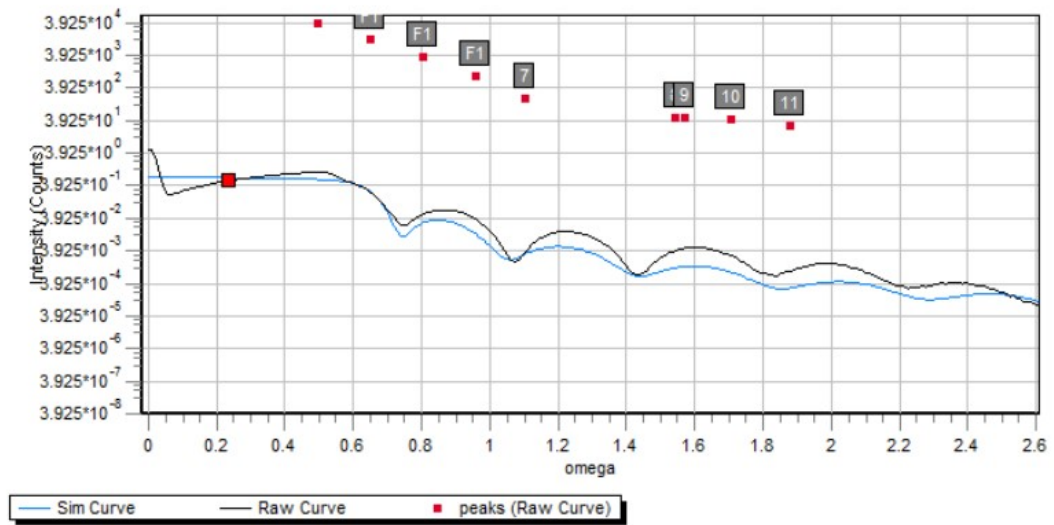


Figure 5.21: XRR fitting for a thin Al film on diamond. The average thickness of the Al film was estimated to be ≈ 22 nm.

Al deposited on diamond for 5 minutes under similar conditions as those for 2 minutes above was 43.7 nm, “thick”. This was ≈ 40 nm value suggested by Sussner *et al* [171] as ideal for reflectivity enhancement purposes on transparent media. A representative SBS spectrum of Al on sample 3 is shown in figure 5.22.

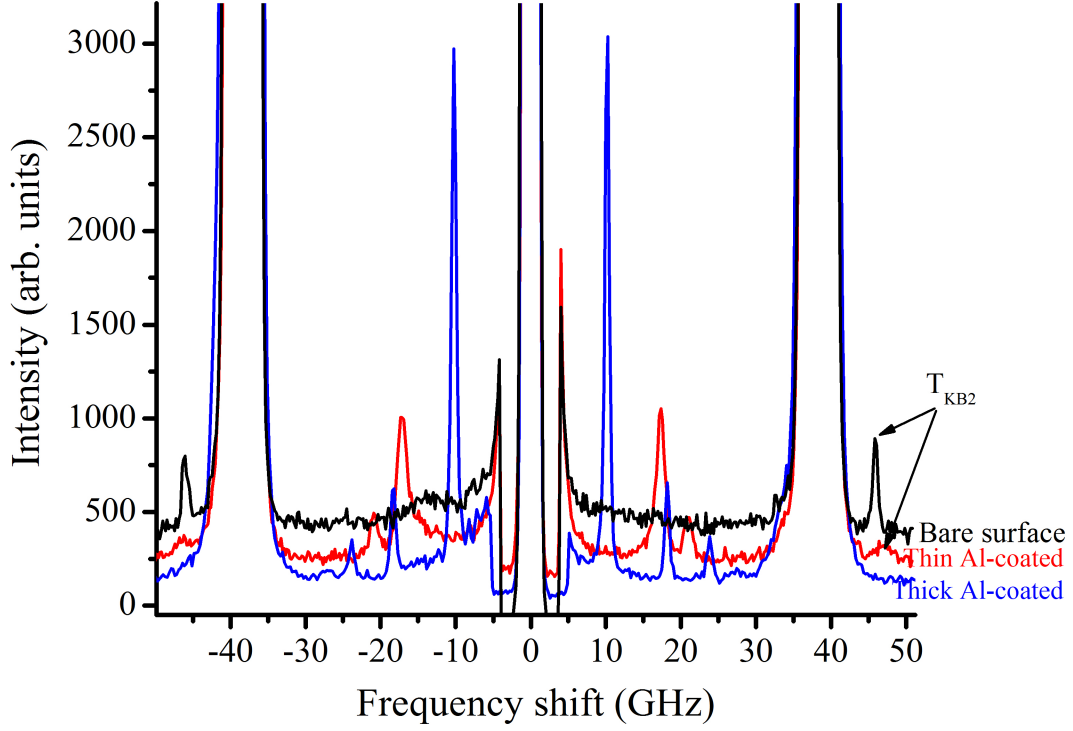


Figure 5.22: SBS spectrum of “thick” Al film on as-implanted diamond compared with that obtained from the same sample before Al deposition and when coated with a “thin” Al film. The Rayleigh mode for a “thin” Al film appears at 17.3 GHz while that for a “thick” Al film is at 10.2 GHz. Spectra taken at angle of incidence 70° .

It can be observed that the presence of a ‘thin’ Al film introduced other modes, a modified Rayleigh mode of Al due to the diamond substrate as well as Sezawa modes. There is however the mode T_{KB2} already identified as originating from diamond at almost the same position (directional effects ignored). This mode was diminished and took long to appear possibly due to reduced photon intensity reaching the diamond due to the metal film on the surface. This mode is completely absent in the ‘thick’ Al-coating. There were more Sezawa modes as a result of the presence of the Al film. The Rayleigh mode appears at a much lower frequency shift than for the ‘thin’ Al-coated case. The observations made from this study do not convincingly support the hypothesis that Al coating can help in measurement of the elusive Rayleigh mode of diamond. However, the higher order Sezawa modes that travel within the film can be used not only in the study of Al film but also of

the diamond substrate.

5.7.1 Theoretical considerations: Dispersion curves

Theoretical simulations were handy in predicting the extent of damage and interpreting the observations made. TRIM simulations showing the extent of damage are described in section §7.2. However, in this section Green's elastodynamic function was specifically employed to find out the theoretical value of Rayleigh mode velocity in diamond. Dispersion curves of Al film on diamond was used for this purpose. Dispersion curves are obtained by either varying the angle of incidence and holding the film thickness constant or vice versa. A velocity against $k_{\parallel}d$ was plotted for an Al film of thickness 250 nm on diamond. The incidence angle was varied in the range 40-80°. The positions of three prominent peaks were recorded and their dispersion fitted on to the dispersion generated using elastodynamic Green's functions as shown in figure 5.23. Pristine diamond was modelled using the elastic constants in [174] ($C_{11}=1076$, $C_{12}=125$ and $C_{44}=576$) and a mass density of 3.515 g/cm³ while those for Al film which was considered elastically isotropic were $C_{11}=107.3$ and $C_{44}=28.3$ [175].

The simulation shows that the transverse threshold for diamond was calculated as 12800 m/s. Also, as $k_{\parallel}d \rightarrow 0$, the RW $\rightarrow$ 10800 m/s. This value of Rayleigh velocity is in agreement with that calculated by Jiang *et al* [176] of 10753 m/s on polycrystalline CVD diamond. In the same work, they gave an experimental value of 10326 ± 470 m/s using SBS. Apart from the Rayleigh mode they were also able to measure the velocities of slow and fast transverse modes on the (110) surface but only one transverse mode on the (100) surface. They report the slow and fast transverse velocities to be at 11582 ± 380 and 12437 ± 250 m/s, respectively.

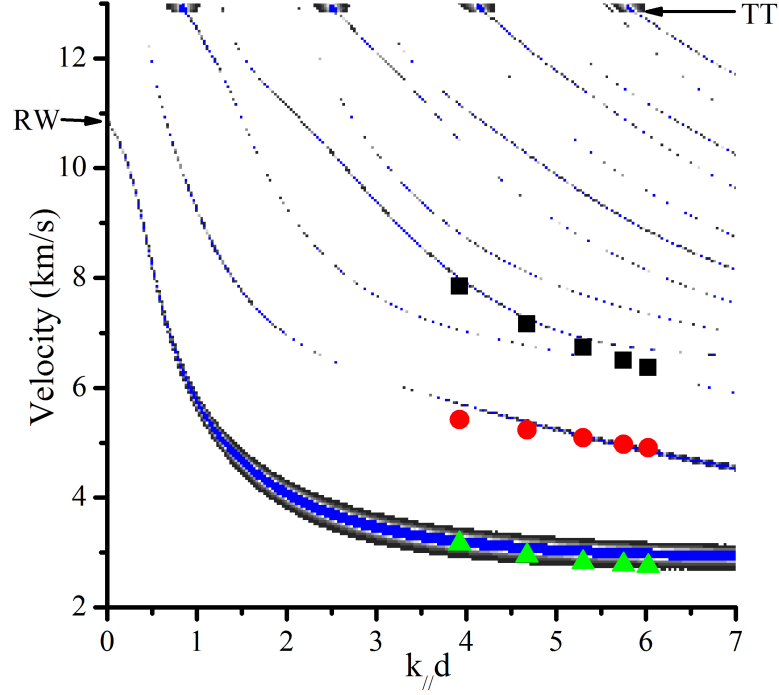


Figure 5.23: Dispersion simulation curves of Al layer on diamond. Triangles, circles and squares are the experimental values fitted into the simulated curves. The initials RW denotes Rayleigh wave and TT, transverse threshold of diamond.

Philip *et al* [177], reported a Rayleigh velocity of 10750 ± 80 m/s for nanocrystalline diamond of thickness $3.61 \mu\text{m}$ measured using broadband surface acoustic wave pulses. Djemia *et al* [135] obtained a Rayleigh velocity of 10800 ± 300 m/s on polycrystalline diamond using SBS. Whitefield *et al* [178] report Rayleigh velocities of between 11000 and 12000 m/s on (100) surfaces of polycrystalline diamond films measured using the laser ultrasonic technique. However, in analyzing acoustic waves in CVD diamond Flannery *et al* [170] assert that the acoustic properties of CVD diamond have not been successfully characterized by conventional acoustic techniques. They fail to pinpoint the exact Rayleigh velocity for CVD diamond due to the large SAW velocity variation between the extrema along [100] and [110] directions. The range of SAW velocities they reported was 10250-11082 m/s, a variation of nearly 10%. They therefore choose to use the phrase ‘Rayleigh type’ acoustic waves. They observe that such waves propagate on the surface of

diamond at all possible angles on the (100) surface. Van de Rostyne *et al* [179] employed a fitting routine using Lamb wave dispersion data and they reported a transverse wave velocity of 10500 ± 500 m/s in CVD diamond films measured using a laser beam deflection technique. It can therefore be deduced that there is a big variation in the values of Rayleigh mode velocity for diamond and this may not be converging any time soon. The variation seem to depend on manufacture route process, growth rate, thickness of sample, composition, wavevector projection and substrate preparation. These factors lead to difficulty in ensuring uniformity and repeatability of measurements between samples.

This study's samples had a thickness of 0.3-0.5 mm which is comparable to those in some of the other work reported here, but the values of the Rayleigh-like mode observed are higher than those reported by the cited researchers. It is therefore logical from the range of velocities reported in section §5.6.1, to argue that the observed modes were from bulk phonons travelling parallel to the surface. Scattering from such modes takes place when the laser light is reflected from the back of the sample, yielding a wavevector transfer in the scattering process which is parallel to the surface with Rayleigh-like character [173, 140]. However, the work of Van de Rostyne *et al* [179] does lead us to question whether what others have reported was actually a Rayleigh mode of CVD diamond.

5.8 Conclusion

The objective of this chapter was a search for the true surface mode of pristine CVD diamond as well as establish the basic best practices and principles for carrying out SBS measurements on transparent and semi-opaque diamond. By identifying this mode precisely, its finding would help in pinpointing the ion implantation effects

on the elastic properties of diamond. By improving on the factors studied, it is easier to take this research further to study the effect of varying ion fluence. The study has shown that to work with transparent and semi-opaque samples, both the opposite sides must be optically flat. The supporting holder must be reflective as well. This has helped to unravel how not to work towards finding the mystery behind determining without ambiguity the Rayleigh mode of CVD diamond.

Chapter 6

The diamond-amorphous carbon interface: a “mirror”

6.1 Introduction

Analysis of Brillouin measurements employing the scattering geometry summarized in figure 5.3 in chapter 5 does not give distinguishable SAW modes of pristine and as-implanted diamond. Moreover, it was observed that the SBS data of implanted region at the annealing cycles below 500 °C was not optically distinct from the pristine diamond, and thus elasto-optic scattering mechanism was unable to yield information specific to the implanted region. At exactly what part (front or back of the sample) of the free surface would scattering take place for these to be observed as a SAW? Apart from the samples used being thick, the transparent nature of the sample implies that the scattering cross-section of photons scattering off the acoustic modes at the free surfaces was too small to produce observable surface modes. There was therefore a need to try and get a thin film of diamond which would confine the scattering events close to where surface measurements could be carried out. Owing to instrumental limitations, the deepest implantation available to the group using the lightest element that can cause substantial damage to the diamond lattice was used (He ion at 160 keV). This chapter details a technique of

forming a reflective layer below a thin film of diamond by ion-bombardment and annealing. The reflective property of the diamond-damaged region interface was utilized in Krüger geometry to obtain an SBS spectrum on a recrystallized thin film at the surface. This technique is premised on the following facts about ion damage in diamond: (1) Most of the radiation damage due to ion implantation occurs near the end of range where nuclear scattering dominates and hence the damage can be placed at an appropriate depth depending on implantation energy. (2) The damaged layer can be graphitized by annealing and this layer has sharp boundaries because of the well defined critical damage density required for conversion of diamond to amorphous/ graphitic carbon [180, 46]. The interface between diamond and the graphitic layer was found to give reflective properties. (3) The critical damage density (D_c) is of general nature, independent of ion species or implantation energy [34]. The damage density depends on implantation conditions such as implantation temperature T_i , ion dose, ion energy and ion species.

6.2 Single energy He ion-implanted diamond

The study sought to find a Rayleigh mode of diamond in a reduced volume where modes from the top (surface facing impinging light) could be detected. This can be made possible by implanting diamond with the lighter He ions so that the main damaged region lies at a pre-determined depth and then annealing at 1200 °C. Such a treatment creates a graphitic/ amorphous carbon region which has both absorptive and reflective properties. The reflective property is the one that is exploited in order to employ the SBS technique. Four samples were implanted: two at 80 keV and two at 160 keV. For each set of these energies, one sample was implanted at liquid nitrogen temperature while the other was implanted at room

temperature. The same fluence of 6×10^{16} ions/cm² was implanted in the four samples. The samples implanted at liquid nitrogen were carefully transferred from the implanter into a liquid nitrogen bath and finally dropped into a preheated RF furnace for rapid annealing at 1200 °C in flowing argon gas. Like the samples under cold implant rapid anneal (CIRA) treatment, those implanted at room temperature were also rapidly annealed at 1200 °C. The CIRA treated samples were such that the implanted face was polished while the reverse side was unpolished. A TRIM simulation for He⁺ in figure 6.1 shows that a section within the region traversed by ions and very close to the surface lies below the critical damage density (6×10^{22} ions/cm³). Regions below D_c reconstruct by recombination of vacancies and interstitials and not by solid state epitaxial growth from the boundary outwards, this is why sharp boundaries are formed. This region therefore is expected to reconstruct to diamond after the heat treatment resulting in a thin layer of transparent diamond sitting on an opaque layer of amorphous carbon. The thin layer can then be implanted with additional ions and studies done. Upon annealing, the damage density of amorphized carbon that forms the boundary with diamond on the implanted side is gradual, it is abrupt on the un-implanted side. The quality of ‘mirror’ is therefore expected to be better on the un-implanted side.

6.2.1 Transmission and diffuse reflectivity measurements

Transmission measurements conducted on two of these samples which had both surfaces polished showed that there was less than 0.5% transmission of 514.5 nm light after annealing as shown in figure 5.2. Diffuse reflectance measurements in the visible range was conducted to determine the presence of a thin transparent

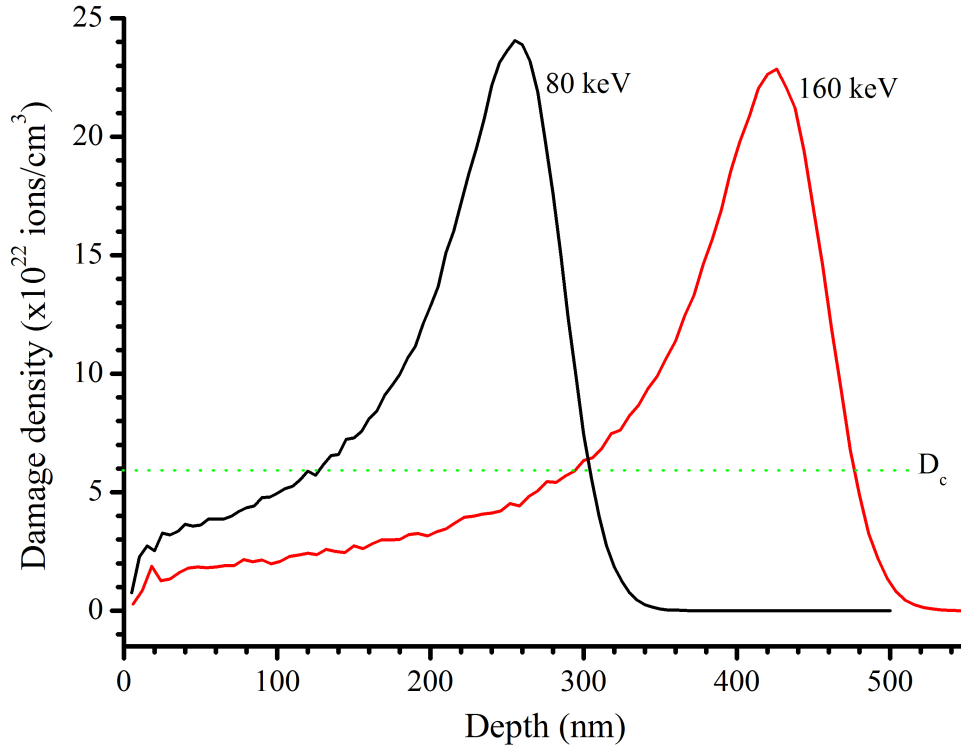


Figure 6.1: TRIM simulation for the two He^+ energies used.

medium sitting on an opaque reflecting surface. Figure 6.2 shows the diffuse reflectivity graphs of different surfaces measured using the UV-VIS-NIR 500 Cary spectrophotometer. It was observed that those surfaces with thin transparent diamond on an opaque graphitic layer (He-ion implanted samples) resulted in a sine-like curve due to interference of waves reflected from the surface and the ‘mirror’ interface. The sine ‘wavelength’ reduced with the wavelength of the light (blue shift). Diffuse reflectivity of the light of interest (514.5 nm) lay in the range of 36-37%. Thick samples like pristine diamond do not show any interference fringes. Samples where implantation damage reached the surface like the multiple energy implanted sample 6 did not show the interference fringes. Similarly those samples where measurements were taken from the back face (un-implanted), implying that the width between the end of range of ions and surface was infinitely large compared to the range of implant, did not show interference fringes. The lower the percentage of diffuse reflectivity, the better the specular reflector.

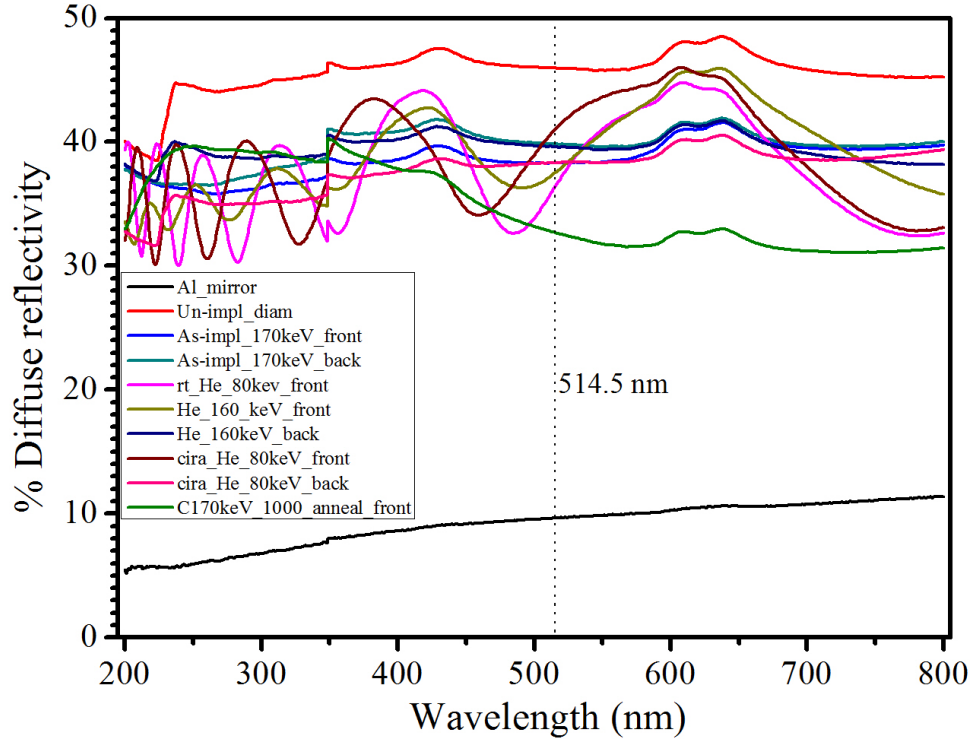


Figure 6.2: Diffuse reflectance measurements on selected samples, back means measurements taken from the un-implanted side while front means the implanted side.

6.2.2 Raman measurements

Raman measurements using a single line mode of wavelength 514.5 nm was conducted on the room temperature He-ion implanted diamonds in the unannealed state. A first order diamond line was observed at 1333 cm^{-1} wavenumbers with FWHM of 3.1 cm^{-1} (not shown). The measured signal was probably from the region close to the surface where the damage was lowest and possibly a small fraction from the virgin diamond below the damaged region. Raman measurements on all the four He ion implanted diamond samples after annealing showed six peaks. Peak positions from the CIRA treated samples are shown in figure 6.3 and summarized in table 6.1. The D peak (IV) was clearly visible using the 514.5 nm light around 1344 cm^{-1} . The G peak (VI) was observed to lie between $1603\text{--}1605\text{ cm}^{-1}$ for both 514.5 and 785 nm light beams. There is therefore no dispersion in the G peak which implies that the opaque implanted layer had some graphitic order. The peak

I (1055 cm^{-1}) that are associated with sp^3 [181] vibrations were observed prominently using green light alongside all the other sp related peaks. This implies that the layer contained a mixture of sp^2 and sp^3 carbon bonds.

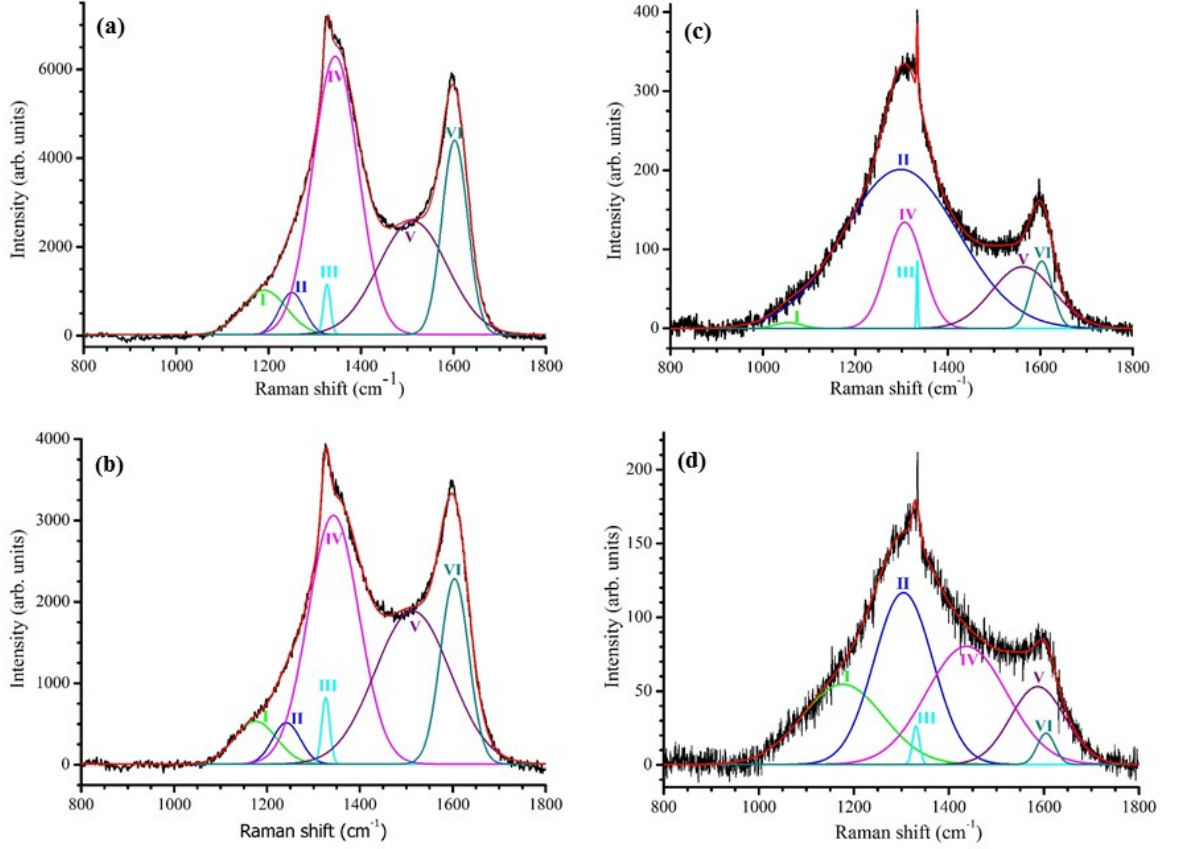


Figure 6.3: Raman spectra of the CIRA treated He ion implanted diamond after annealing $1200\text{ }^{\circ}\text{C}$. Figures (a) and (c) were implanted at 160 keV while (b) and (d) were implanted at 80 keV . Light of wavelength 514.5 nm was used to produce spectra (a) and (b) while that of wavelength 785 nm produced (c) and (d). Peaks I, II, III, IV, V and VI are the multiple Gaussian fits of each individual spectrum

This particular experiment was concerned with investigating the presence of recrystallized diamond on the surface, hence the implications of peak positions, heights or widths will not be discussed. The presence of a broad D peak (IV) implies that there was disorder in the ion damaged region; however, a first order diamond peak (III) was observed possibly from the strained recrystallized top surface since the damaged layer below it was totally opaque after annealing at $1200\text{ }^{\circ}\text{C}$. The first order diamond signal was observed around $1326/1327\text{ cm}^{-1}$ using the 514.5 nm light

Table 6.1: Peak positions for He⁺ implanted diamond upon annealing at 1200 °C with their corresponding peak heights in {} brackets.

λ (nm)	Energy (keV)	Peak positions					
		I	II	III	IV	V	VI
514.5	80	1175	1242	1327	1343	1514	1604
		{526}	{508}	{817}	{3057}	{1880}	{2278}
	160	1191	1250	1326	1344	1512	1603
		{1001}	{951}	{1139}	{6270}	{2559}	{4380}
785	80	1177	1304	1331	1437	1587	1605
		{54}	{116}	{26}	{80}	{53}	{21}
	160	1055	1298	1334	1307	1562	1603
		{7}	{201}	{87}	{134}	{78}	{85}

in figures 6.3a and 6.3b. It was however around 1331 and 1334 cm⁻¹ for the 785 nm light, implying that the recrystallized diamond generally experienced tensile stresses [182]. It has been reported that deeply implanted regions in diamond with He ions (from MeV energies) could recrystallize upon annealing even where D_c had been exceeded [183]. The Raman and diffuse reflectance measurements show a recrystallized diamond film that obviously forms a cap on the buried graphitic region. According to the Orwa model, it could be argued that the top restraining cap did not provide a sufficiently high enough pressure to recrystallize the damaged region below the thin layer of diamond at the surface.

6.2.3 Surface Brillouin measurements on He⁺ implanted diamond

The He ion implanted and annealed system could be visualized as a thin transparent recrystallized diamond (film $\approx$ 120 nm for 80 keV and 300 nm for 160 keV implanted samples as predicted by TRIM in figure 6.1) on an opaque amorphized layer of thickness 180 nm in both cases. The amorphous layer with a sharp boundary at end of range sits on pristine diamond. This is basically an optically hard material on a soft one. The expected behaviour of such a system for opaque samples is the

observation of a Rayleigh mode of the layer only [168]. The transparent nature of the thin diamond film therefore means the scattering volume and film-substrate interface properties has the potential to affect the outcome.

Brillouin measurements were done on all the four samples. During SBS measurements, the unpolished surfaces (for CIRA treated samples) lay far beneath the opaque graphitic layer and away from the impinging light as shown in figure 6.4.

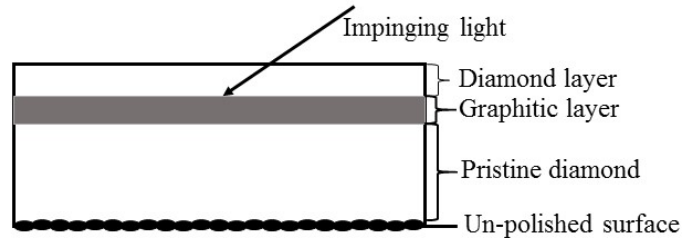


Figure 6.4: Cross-section of the He ion implanted diamond (not drawn to scale).

It was proven earlier that there is no transmission through the opaque layer (section §6.2.1) and also that there can be no spectrum obtained from indirect scattering when the unpolished side lies on the Al slot (figure 5.11). The experimental setup of figure 6.4 therefore guarantees that any spectra observed to be emanating from indirect scattering must be from the diamond sitting on top of the opaque reflective layer. Measurements involving an extended FSR produced L_{KB1} after a very long collection time as expected due to the limited scattering volume of the top thin diamond layer. The longitudinal peak due to direct scattering was therefore from strained diamond sitting on the opaque layer. The accumulation time was longer because of the small scattering depth of the layer.

Brillouin measurement targeting the peaks due to indirect scattering following the scattering geometry of figure 5.3 was employed for analysis. Weak peaks were observed in positions L_{KB2} and T_{KB2} using p-polarized (see figure 6.5) and s-polarized light, respectively. These peaks would however disappear (‘wipe out’) as

measurements progressed. The L_{KB2} peak observed after 19000 counts (close to 4 hours) seems to have been completely wiped out after 101000 counts (20 hours) but seems to be growing again after 166000 counts (34 hours). The appearance of these peaks means that with an increased scattering volume, the top layer can be studied without ambiguity.

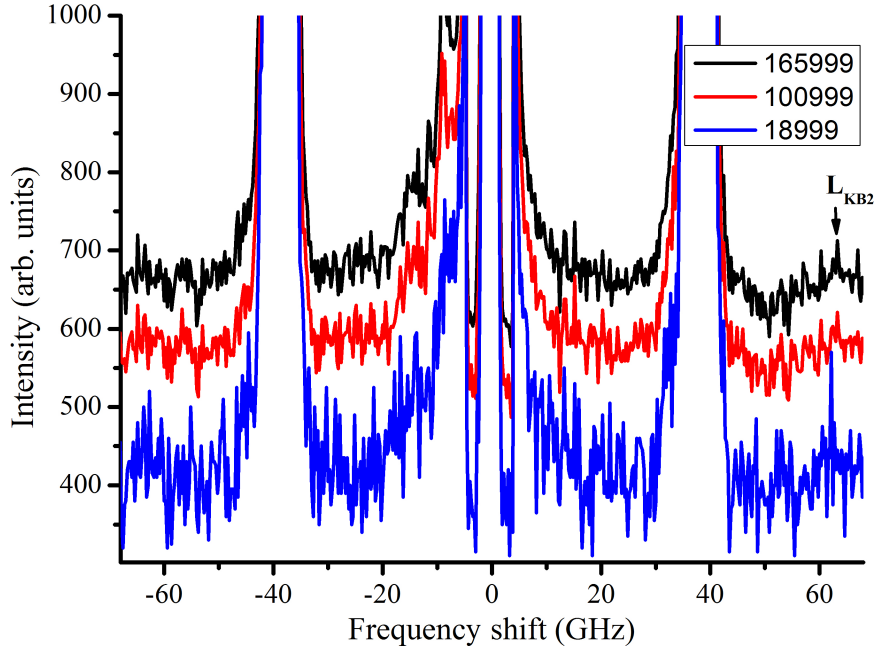


Figure 6.5: SBS spectra collected at the front of a 160 keV CIRA treated sample.

Beghi *et al* [59] assert that in indirect backscattering (also called $2\alpha A$ and only applicable to transparent materials), bulk acoustic modes are probed if the geometric wavelength (λ') is shorter than the film thickness. If however, the film thickness is smaller than the geometric wavelength of the probing light, other surface waves like Sezawa waves may be supported. In this section, where it is intended to get light reflect off the deep-seated ‘mirror’ and back through the diamond, the geometric wavelength of the layer would be important. In such a configuration the geometric wavelength $\lambda' = \lambda_o / 2 \sin \theta$, is independent of the refractive index of the transparent film. Thus for angles of incidence that vary between 30° and 80° , the film thickness needs to be greater than 514.5 nm and 261.2 nm respectively, to

observe the bulk waves due to indirect scattering. The bulk waves were observed in 0.3-0.5 mm thick samples as reported in chapter 5. Similarly, Beghi *et al* [59] studying bulk silica (2 mm thick) and thin silica film (2 μm thick) were able to observe a weak Rayleigh peak in bulk silica using backscattering ($2\alpha\text{A}$) geometry but they do not report observing it in the forward (90R) or transmission (90A/ platelet) geometries on the bulk or thin film samples. In their large samples they were able to observe the bulk modes (transverse and longitudinal). Therefore, probing a thin transparent diamond on a reflective opaque layer using the backscattering ($2\alpha\text{A}$) geometry in this work was appropriate. This work sought to reduce the scattering volume to a level where the T_{KB2} and L_{KB2} peaks can just be observed in the recrystallized volume as shown in figure 6.6. This volume can then be implanted with carbon ions and studies made for different parameters such as fluence and annealing temperature.

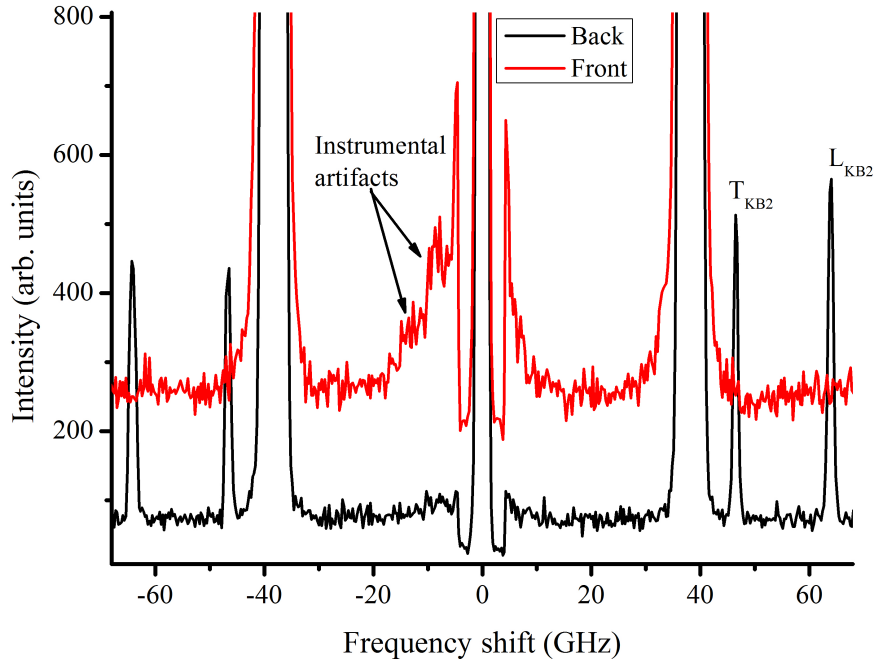


Figure 6.6: SBS spectra collected at the front and back of a 160 keV room temperature He ion implanted sample. Though it took longer to collect from the front, no obvious peaks were observed. Measurement from the back rapidly yielded the indirectly scattered peaks T_{KB2} and L_{KB2} .

The ‘wipe-out’ effect, instead of growing of the spectra with increase in accumulation time was intriguing. This phenomenon was attributed to multiple reflections leading to what can be perceived as multiple sources of coherent inelastically scattered light being detected. Interference effects by division of the amplitude would be expected when light is incident at an angle on such surfaces (two reflecting surfaces). In this scenario, part of the amplitude is reflected from the top surface and the other is reflected at the interface. When these reflected beams overlap, interference effects (contour fringes) are observed due to the path difference travelled by light. As shown in figure 6.7, the optical path difference is $2nt \cos \theta$, where n is the refractive index of the medium between the reflecting surfaces, t is the distance between the surfaces and θ is the angle made with the normal by the light path in the medium. The approximate intensity of light detected due to multiple reflections between $\approx 100\%$ reflective “surfaces” is calculated in Appendix B. From these calculations the ideal calculated total reflectivity was 37% but this could be much less owing to absorption of the layer on the implanted side. Which explains the long time scales required for accumulation of photons scattering of the phonons to yield the indirect scattered peaks that later undergo a ‘wipe-out’ effect.

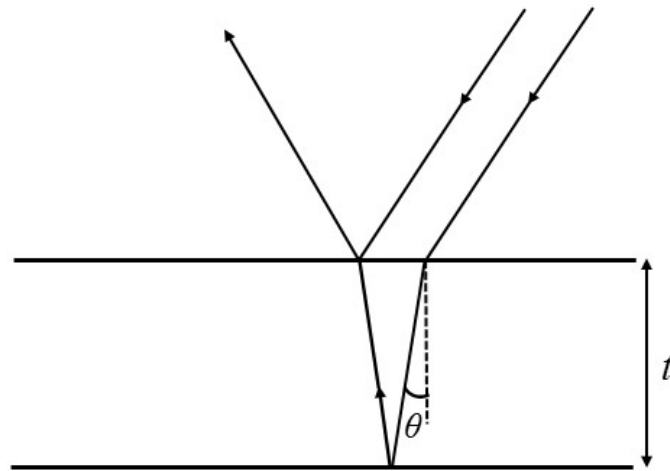


Figure 6.7: Two parallel reflecting surfaces which form contour fringes

Even though the idea did not succeed to produce steady peaks due to the ‘wipe-out’ effect, this study does present new opportunities to study diamond. This may be possible if the “mirror” is created in a sample that is polished on both sides and have a pre-determined scattering volume. The side not affected by radiation damage (end of range side) should then be positioned such that light impinges on it.

6.2.4 Finite element modelling (FEM) for He⁺ implanted diamond

The TRIM simulations of figure 6.1 show that the simulated critical D_c of He ion implanted diamond lies between ≈ 120 -300 and 290-480 nm, respectively for 80 and 160 keV. It would therefore mean that upon annealing the width of the regions below D_c recrystallize back to diamond. This is however, practically not the case when the system is treated thermally. TRIM simulates ion implantation in pristine materials, does not take into account implantation temperature, vacancy saturation or changes in the target as implantation progresses. Non-linear processes such as self-annealing, ballistic annealing and defect interaction are not accounted for in these simulations [184]. A simulation that takes into account annealing of He ion implanted diamond was done by Federico Bosia as articulated in Bosia *et al* [128] to give a theoretical estimate of the depth variation of mass density upon annealing at 1200 °C is shown in figure 6.8.

By analyzing the density at a given depth, one can predict the material type within that local environment (for instance, $\rho_d = 3.515$ g/cm³ for diamond, $\rho_{ta-C} = 3.3$ g/cm³ for tetrahedral amorphous carbon and $\rho_{gr} = 2.2$ g/cm³ for graphitic carbon, a whole other range of densities of diamond like carbon (DLC) lie between

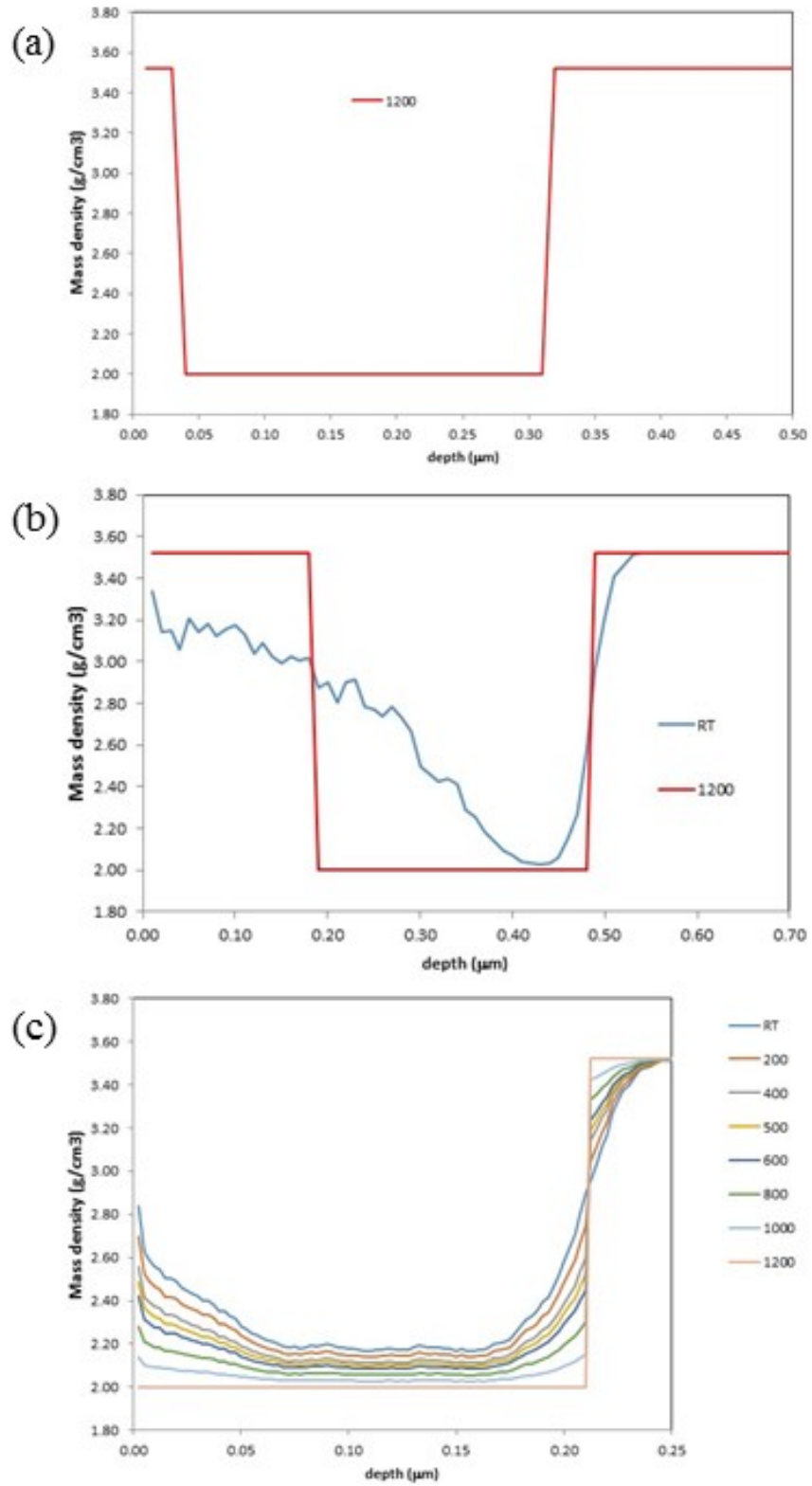


Figure 6.8: (a) FEM simulation of He ion implanted and annealed diamond at 1200 °C for implantation energies of (a) 80 keV and (b) 160 keV. (c) FEM simulation for step annealing of single energy C ion implanted diamond (sample 3).

that of the graphitic carbon and the ta-C). The technique has been shown to correlate well with experimental measurements (EELS and TEM) for low fluences of He ion implantation in diamond at MeV energies [184]; the same calculation principle has been applied for high C fluence at sub-MeV energies in this work.

The FEM simulations predict a top thin diamond layer of $0.04\ \mu\text{m}$ and $0.19\ \mu\text{m}$ thick for the 80 and 160 keV He ion implants, respectively. These thicknesses are not only smaller than those predicted by the TRIM simulations in figure 6.1 but also the geometric width of the probing wavelength calculated in section §6.2.3. This may in part explain the failure to observe any meaningful surface or bulk modes due to indirect scattering, the other reason could be interference effects as explained above. Thus the FEM results of annealed diamond provide a correlation to the earlier observations of the ‘wipe-out’ effect, in the sense that the thickness of the top diamond layer was much smaller than the geometric wavelength.

NB: The simulation spectrum in figure 6.8(c) is for sample 3 (fluence of 1.5×10^{16} ions/cm²). It shows that the entire layer from the surface became amorphized and the end of range forms a sharper boundary (better mirror) upon annealing. This fact has been proved in this work in the sense that the accumulation time is reduced extensively when measurements involving $\mathbf{k}_b^{(2)}$ are taken with light impinging from the back of the sample.

6.3 Conclusion

The work reported in this chapter has shown that it is possible to create a thin diamond film by implanting diamond with lighter ions and annealing at high temperature. It also sought to highlight an experimental approach in search of the elusive Rayleigh mode in transparent material, a journey unsuccessfully commenced

in chapter 5. However, due to a small scattering volume created, the Rayleigh wave which could aid in partially characterizing a diamond film was not observed. The technique employed also discovered interference effects as a hindrance to such measurements, a factor that has never been identified before by early researchers on transparent thin films. The observations made pave the way for further research using a much deeper ($\geq 0.5 - 1 \mu\text{m}$) implant, whose recrystallized diamond width is slightly $\geq$ the wavelength of the probing light. The recrystallized region above the reflective interface may then be ion implanted with carbon and studies conducted on the ion-damaged semi-transparent layer using Krüger geometry at the low temperature annealing regimes (below 500°C) before the sample becomes completely opaque.

Chapter 7

High temperature annealed diamond

7.1 Introduction

Ion implantation introduces stresses and strains in the implanted region of any crystal. There is therefore a need for annealing the stressed materials by allowing for target displaced atoms and implanted ion species to move and settle in local sites where the materials attain minimum energy [185]. This is accomplished through annealing where thermal energy sufficient to remove the defects created in the collision cascades within the implanted region is provided. Having a fluence that exceeded the critical damage density, annealing was therefore expected to bring about a material with different properties from the original pristine diamond. Diamond sp^3 tend to form sp^2 carbon during irradiation once a certain fluence is exceeded. Upon annealing, this remains as an amorphous sp^2/sp^3 matrix which is unlike other covalently bonded semiconductors Si and Ge, that recrystallize [183]. In this chapter the analytical observations after isochronal annealing cycles (200-1200 °C) of samples 2, 3 and 6 (see section §3.2) are reported. Emphasis is on the higher temperature anneals (600-1200 °C) where observable changes in SBS are

seen as the material transforms from amorphous/ diamond-like to graphitic amorphous carbon. Raman measurements using two different wavelengths show that the layer evolves to a more graphitic-like state with respect to annealing temperature. SBS results for annealing up to 1200 °C are reported. Data from these optical techniques were observed to depend on opacity of the sample determined from the light transmission results. The electronic techniques EELS and HRTEM which are independent of opacity were used to explain structural changes taking place in the sample as annealing temperatures increased even where data from the light dependence showed no significant changes. The observations from the optical techniques are explained by correlating with the structural changes shown by the electronic techniques. Finally the elastic constants of the final material after annealing at 1200 °C are determined by fitting the experimental values to the elastodynamic Green's functions.

7.2 Annealing of ion-implanted diamond

7.2.1 TRIM prediction of damage

Transport of ions in **m**atter (TRIM) simulations were used to predict the expected range and distribution of damage by ions in diamond after ion implantation. In all simulations, the atomic displacement energy E_{disp} was set at 45 eV [186]. Figure 7.1, shows the combined implantation profiles for samples 2 and 3.

The simulation for the single energy implant (sample 3) shows that the damage distribution displays a negative skew, asymmetrical shape with a long tail on the implantation (leading) side but falls fast towards end of range (trailing edge). The simulated damage density above D_c was high compared to the multiple energy implanted samples, 2 and 6 (total dose of 1.0×10^{16} vac/cm² each, see §3.2). The

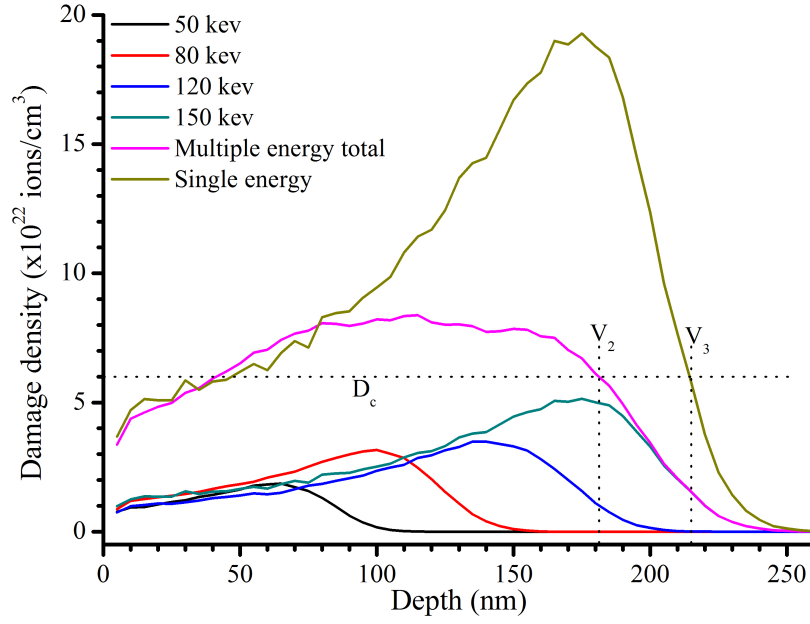


Figure 7.1: TRIM simulation for ion implantation of samples 2 and 3. The cumulative damage of sample 2 is ‘Multiple energy total’, while that of sample 3 is ‘Single energy’.

damage was also deeper ($V_3=215$ nm) compared to the multiple energy implanted sample. The other multiple energy implanted sample (sample 6) whose simulated TRIM profile is shown in figure 7.2 had a flatter distribution compared to sample 2 and had same damage depth ($V_2=V_6=181$ nm). The maximum simulated damage density of 8.3×10^{22} vac/cm³ for sample 2 was higher than that of 7.0×10^{22} vac/cm³ of sample 6. The simulation results imply that sample 6 had less local damage compared to other two samples 2 and 3. The simulations show that for the three samples (2, 3 and 6), there is ≈ 40 -50 nm width near the surface that lies below the D_c ; this thin layer ends up as strained diamond upon annealing.

7.3 Raman measurements of annealed samples

Raman data in this study provided insight in to the SBS results as a function of annealing temperature.

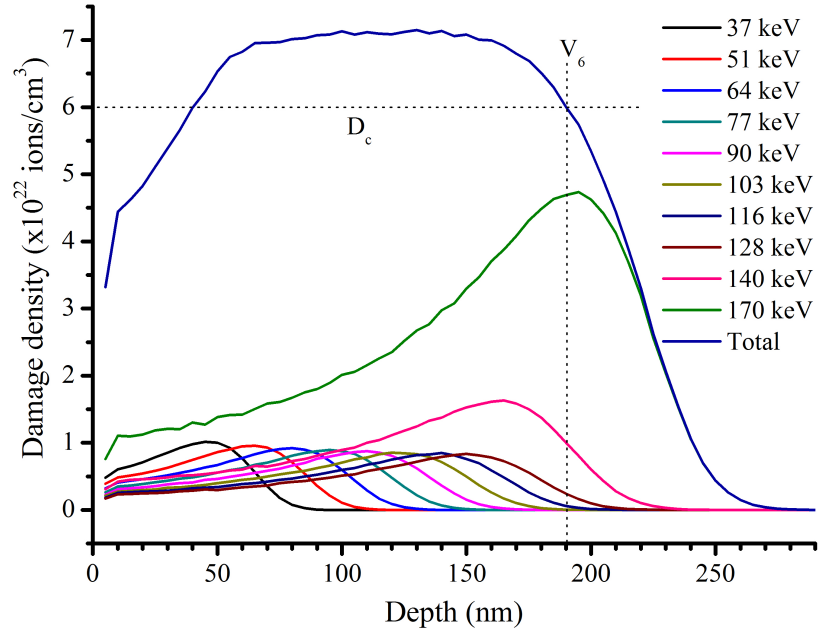


Figure 7.2: TRIM simulation representing ion implantation for sample 6. ‘Total’ is the cumulative

7.3.1 Raman measurements on single energy implanted diamond

Raman measurements were conducted on sample 3 after each annealing cycle. An Ar⁺ laser providing an excitation of 514.5 nm line operated in the backscattering mode was used. The spectra obtained from the different annealing cycles are shown in figure 7.3.

A Raman spectrum after ion implantation and at different annealing temperatures showed two prominent features (D and G peaks) which is consistent with amorphous carbons [187]. Each spectrum was fitted with a multiple Gaussian fit in order to identify the various inherent peaks and their evolution with change in annealing temperature. From the trend in the deconvoluted peaks (not shown) it was observed that one peak worth following was the G peak since it shows the evolution of the implanted layer towards graphitic ordering. This is shown by the shift in G peak position towards the 1600 cm⁻¹ wavenumber and narrowing of

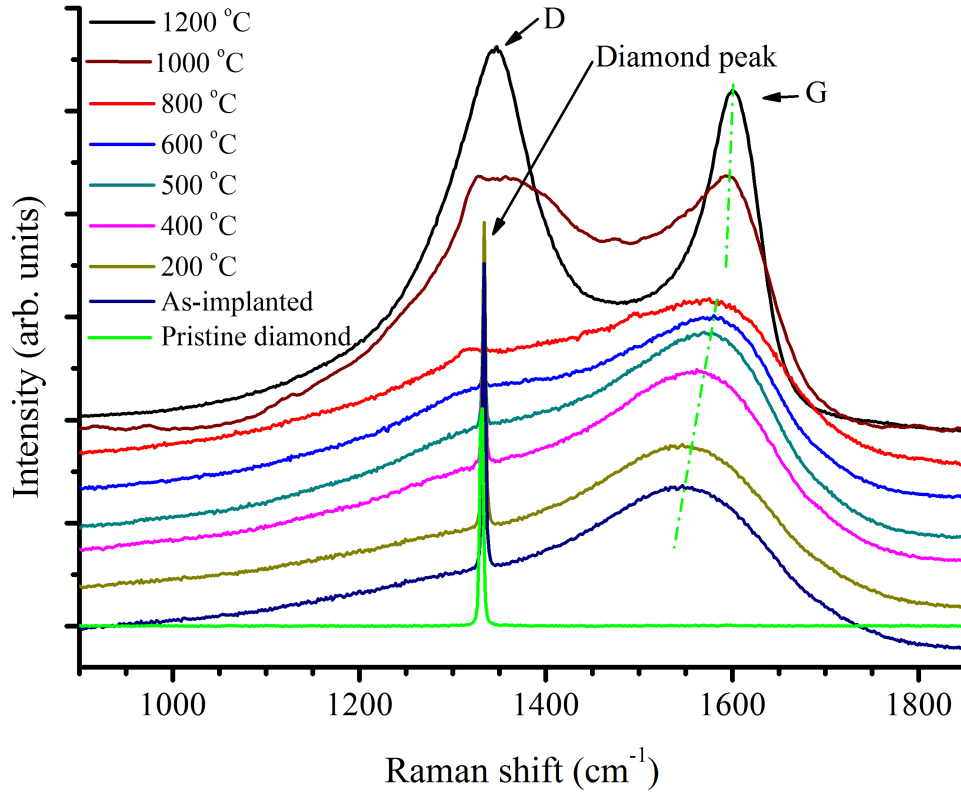


Figure 7.3: Raman measurements on single energy implanted diamond (sample 3) for annealing temperatures from as-implanted to 1000 °C using an excitation wavelength of 514.5 nm. It is seen that beneath the transition ($< 800^{\circ}\text{C}$) the finger print for the diamond peak is evident due to the transparency of the ion implanted diamond to the bulk single crystal. The decrease in transmission through the damage region leads to the decay in the single crystal Raman peak

the peak width [188] as the annealing temperature increases (see figure 7.4). Table 7.1 shows the G-peak position for three different excitation wavelengths for the sample upon annealing at 1200 °C. The G peak positions lay within a range of 7 cm^{-1} for the excitation wavelengths of 514.5 nm and 785 nm used. The closeness of these values imply that the structure attained may not change significantly even at higher temperature anneals. This is attested to by observation in figure 7.3 which shows a minor change in the G peak position after annealing at 1000 and 1200 °C as shown by the dotted green line in figure 7.3. This implies that annealing up to a maximum of 1200 °C was sufficient to study the material transformation and properties of the final product.

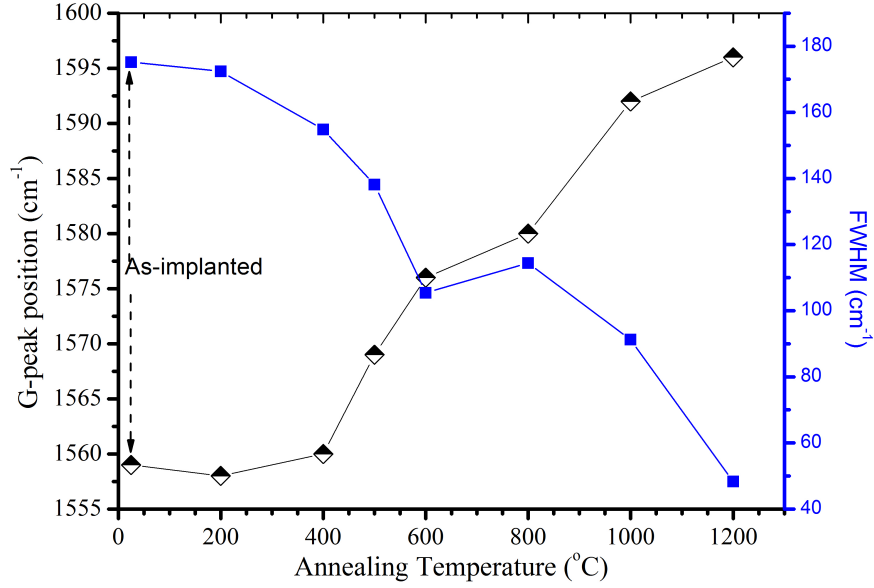


Figure 7.4: Change in G peak position (half shaded diamonds) and FWHM (filled squares) using Gaussian fit for single energy implanted diamond as a function of annealing temperature for 514.5 nm wavelength of light. The connecting line is a guide to the eye.

Table 7.1: Peak positions for single energy C ions implanted diamond upon annealing at 1200 °C.

Probing wavelength (nm)	D-peak (cm ⁻¹)	G-peak (cm ⁻¹)	Diamond peak (cm ⁻¹)
244	1509	1589	-
514.5	1342	1596	-
785	1309	1593	1332

7.3.2 Raman measurements on multiple energy implanted diamond

Taking it further from the comparison made in table 7.1, this section reports the Raman results of sample 6 (prepared as per table 3.3 in §3.2). Two excitation sources were used, 514.4 (green) and 785 nm (red). The deconvoluted peaks for each individual spectrum for all the annealing cycles are shown in figures 7.5 and appendix C.1 for green while figures 7.6 and appendix C.2 are for the red excitations, respectively. The measurements using the green light in this section complements those in §7.3.1. Table 7.2 gives a summary of the deconvoluted peak positions

measured by the two excitations following the colour coding and nomenclature in 7.6 (1200) and 7.5 (1200) for green and red lights, respectively. Figure 7.7 shows the evolution of the G peak and its width as a function of annealing temperature for the two wavelengths.

Table 7.2: Deconvoluted peak positions for C ion implanted diamond from the as-implanted to annealing at 1200 °C

λ (nm)	Anneal temp (°C)	Peak positions (cm ⁻¹)					
		I	II	III	IV	V	VI
514.5	As-impl		1222	1331	1356	1462	1549
	200		1142	1331	1382		1560
	400		1245	1334	1375	1457	1572
	500		1244	1332	1374	1463	1576
	600		1257	1333	1361	1464	1577
	800		1330	1333	1347	1465	1589
	1000	1046	1207	1323	1390	1485	1597
	1200	1058	1172	1324	1389	1520	1601
785	As-impl			1334	1376		1516
	200			1334	1379		1527
	400			1334	1365		1559
	500			1334	1354		1562
	600			1334	1355		1558
	800			1334	1345		1569
	1000	1060	1190	1447	1352	1506	1584
	1200	1055	1200	1453	1343	1508	1585

At least five deconvoluted peaks were observed in the Raman spectrum from the as-implanted state up to 800 °C for the green light, only 3 were observed for red light at these annealing temperatures. After annealing at 1000 °C six peaks were observed for both excitation wavelengths. It was observed using the green light, that the G peak, as for the case of the single energy implant, shows a shift towards the 1600 cm⁻¹ and as it also becomes narrow. The observations from the red line mode exhibits the same trend for the G peak position as that due to green light. The G peak positions observed from the two light excitations show near convergence as annealing temperature increases implying graphitic ordering of the material. There is a non-dispersive diamond mode positioned around 1331-1334

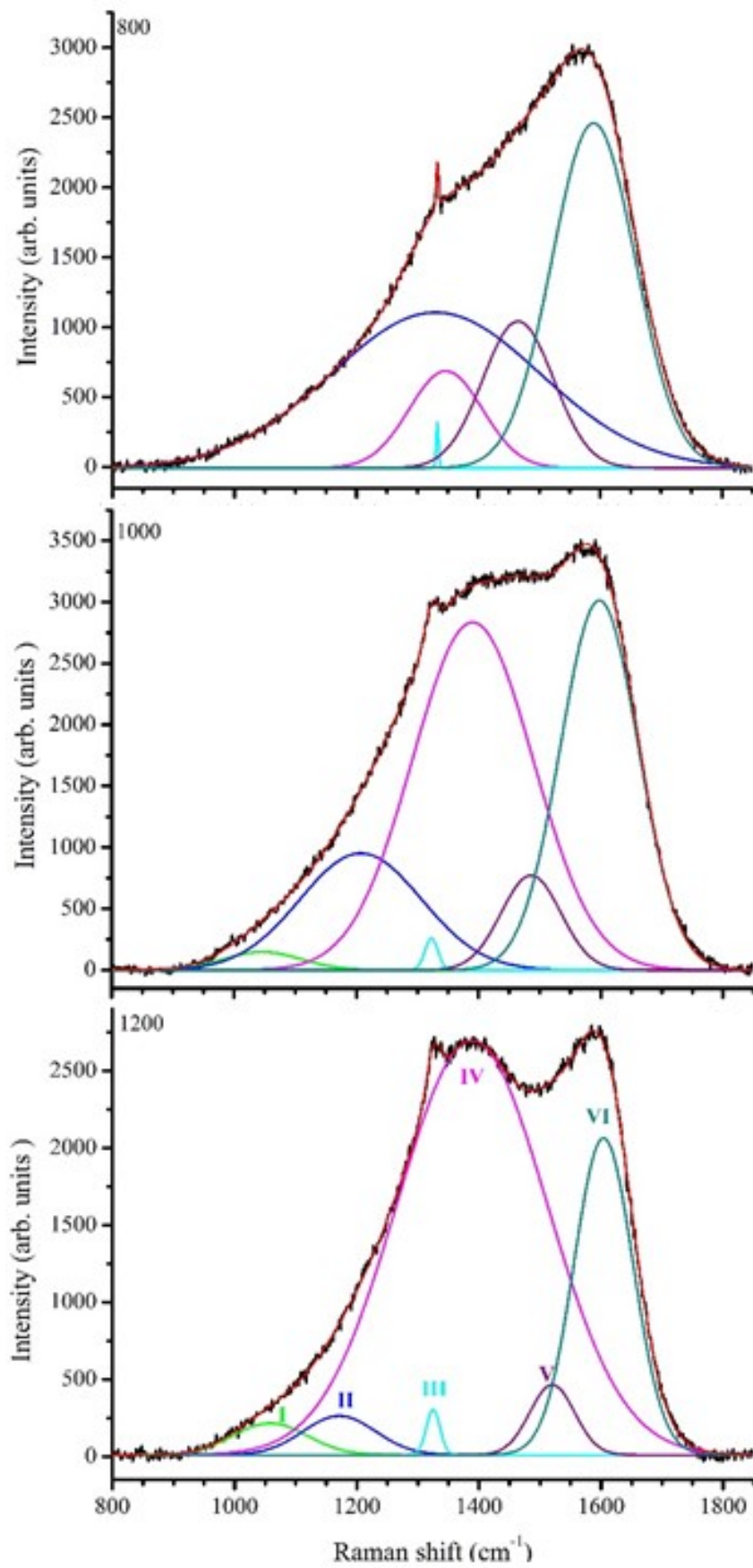


Figure 7.5: Raman measurements using single line mode at 514.5 nm upon annealing temperatures 800-1200 °C.

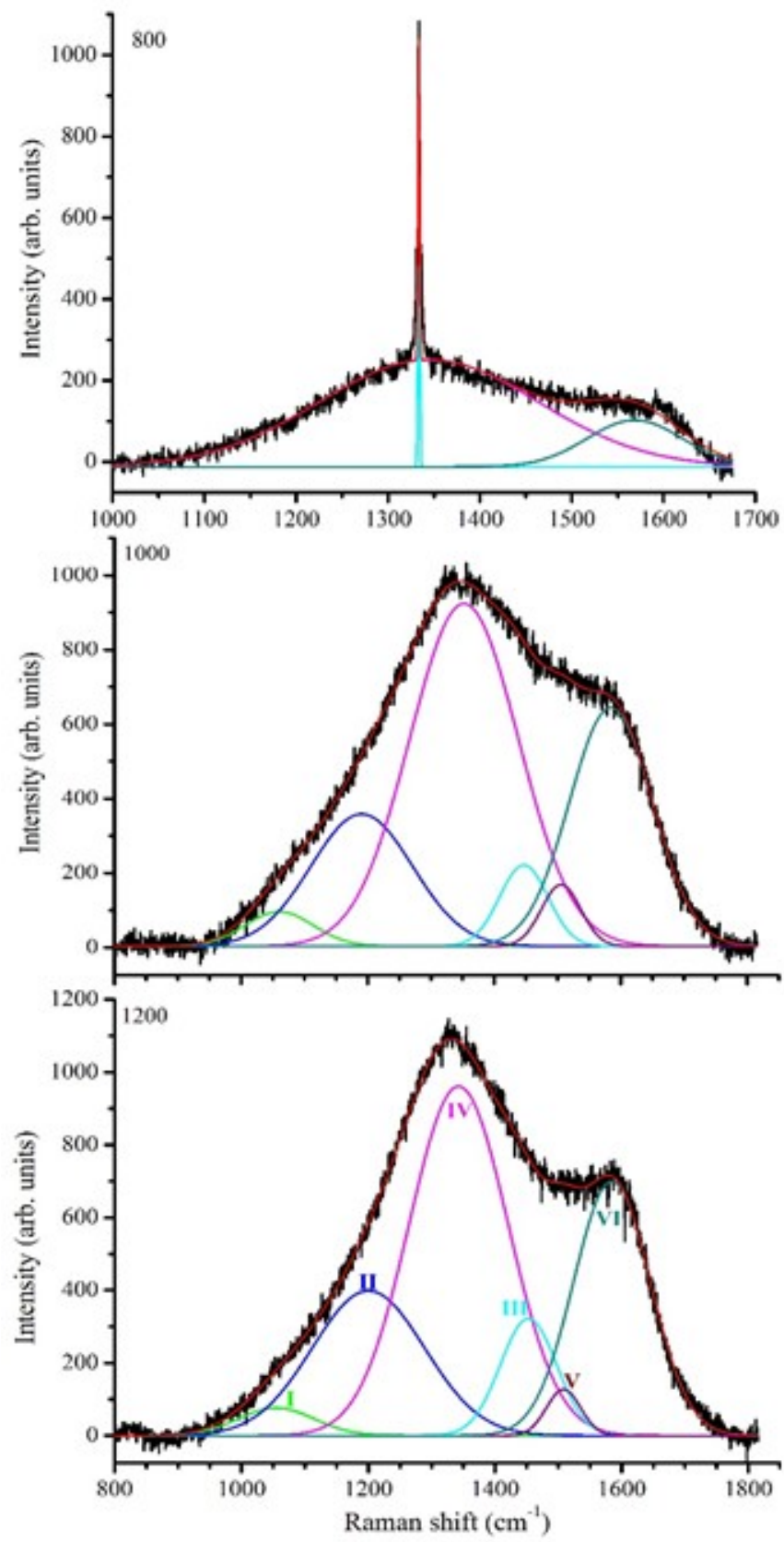


Figure 7.6: Raman measurements using single line mode at 785 nm at different annealing temperatures. The diamond peak for 800 °C was suppressed by a factor 3.2 in order to show the deconvoluted peaks.

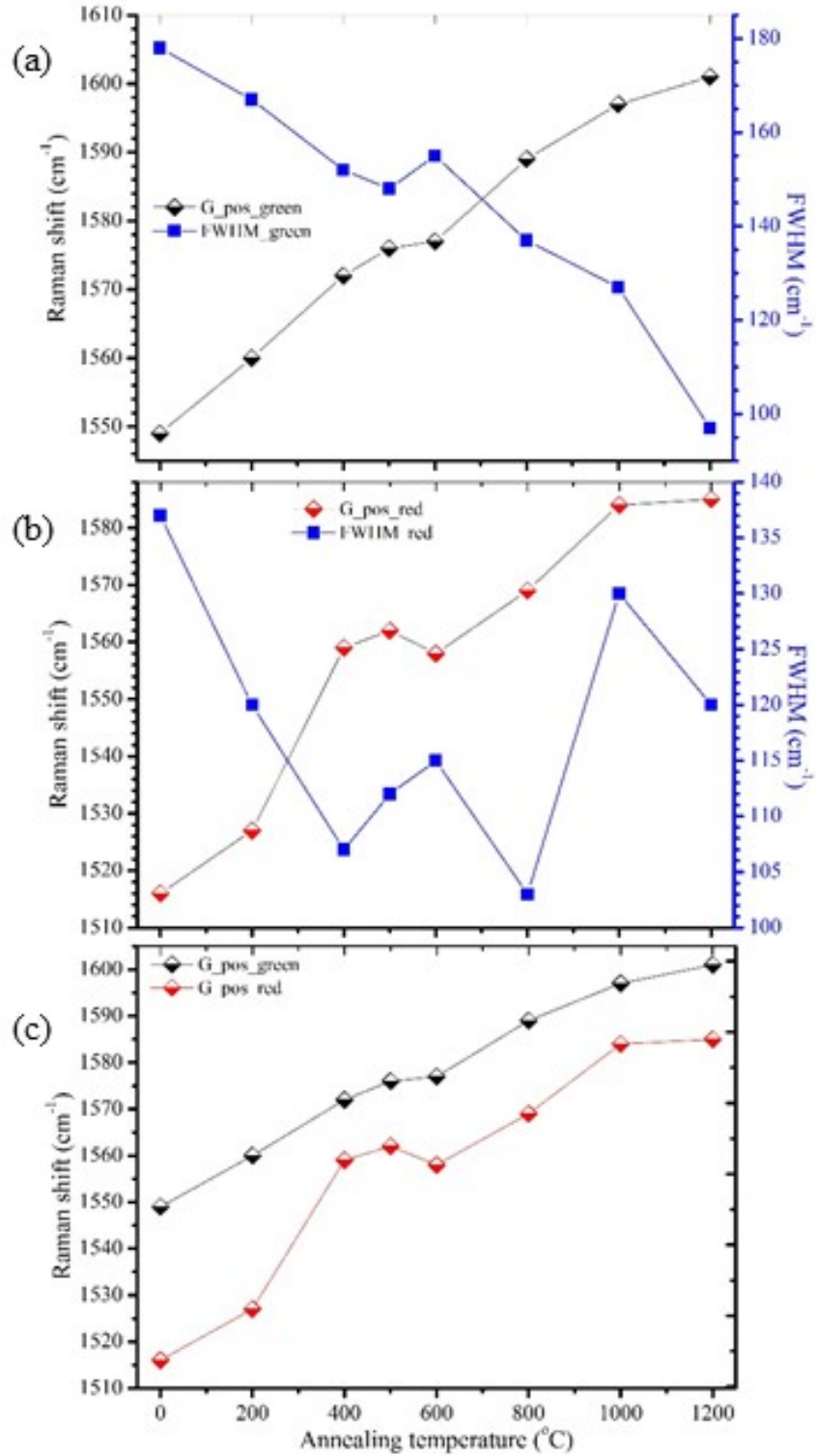


Figure 7.7: Change in G peak position (half shaded diamonds) and FWHM (filled squares) using Gaussian fit for multiple energy implanted diamond as a function of annealing temperature. The solid line is just a guide to the eye.

cm^{-1} (green) and 1334 cm^{-1} (red) for annealing cycles up to $800 \text{ }^{\circ}\text{C}$. The peak disappears for red light which is more sensitive to sp^2 bonding, however, it broadens and downshifts to 1323 and 1324 cm^{-1} upon annealing at 1000 and $1200 \text{ }^{\circ}\text{C}$, respectively for green light (see figure 7.5). This diamond peak is likely to have emanated from the thin strained diamond film ($\approx 40\text{-}50 \text{ nm}$ as predicted by TRIM simulation in section §7.2.1 above the graphitic amorphous region) that recrystallized upon high temperature annealing. Moreover, the transmission measurements showed $<1\%$ transmission after annealing at $800 \text{ }^{\circ}\text{C}$. The D peak that is observed from the as-implanted state up to the highest annealing temperature shows that the disorder created by ion implantation was not repaired by annealing.

There were also three other modes appearing at $\approx 1150, 1250 \text{ cm}^{-1}$ (labelled as peak II in table 7.2) and their companion at 1460 cm^{-1} (peak V) prominently observed using green (514.5 nm) light for all annealing temperatures. The same peaks were only observed after annealing at $1000 \text{ }^{\circ}\text{C}$ (peaks II and III in table 7.2) for red (785 nm) light. Normally one of the two peaks (at ≈ 1150 and 1250 cm^{-1}) is observed while the other may be obscured by the prominent tail of the D peak. These peaks have been identified as ν_1, ν_2 and ν_3 and these are a signature of trans-polyacetylene (trans-PA) [188]. They are as a result of vibrations within the grain boundaries of nanodiamond. A peak centred around 1050 cm^{-1} was observed using both green and red light, only after annealing at $1000 \text{ }^{\circ}\text{C}$ (peak I in figures 7.5 and 7.6). This peak is conventionally called the ‘T’ peak and corresponds to the CC sp^3 bonds vibration density of states (VDOS) [189, 190]. From all the peaks observed it can be noted that ion implantation and the subsequent annealing transformed the material from a crystalline diamond with the single Raman signature at 1332 cm^{-1} (sp^3) to one with different carbon bonding configurations distinguished by different

vibration modes. The different peaks observed suggest that the final material after annealing an ion-implanted diamond is composed of a mixture of disordered carbon, graphitic and nanodiamond clusters with CC bond configurations of (sp^n): $n=1, 2, 3$.

7.4 Surface Brillouin scattering in annealed diamond

The scattering mechanism explained in section §5.3.1 works for the transparent or semi opaque-samples. As the implanted region becomes opaque, the amorphous layer behaves like an opaque film hence photons scatter off phonons purely by elastic ripple mechanism shown as $\mathbf{k}_R$ in figure 4.9. Brillouin scattering study for pristine and as-implanted diamond was extensively covered in chapter §5. In essence, SBS spectra showed a single indirectly scattered $\mathbf{k}_b^{(2)}$ mode, corresponding to SHM of diamond. The same observations were made after annealing the samples up to 500 °C. This chapter therefore focussed on observations from higher temperature anneals (800-1200 °C). The FSR was restricted to ± 50 GHz in order to probe the modes mediated by a surface ripple mechanism from the opaque softer material that is a result of high temperature annealing of ion implanted diamond.

The implantation fluence in samples 2, 3 and 6 exceeded the critical level of 2.5×10^{15} atoms/cm² at which the diamond lattice does not recover from radiation damage after annealing at 500 °C [34]. Evidence of graphitization was elucidated by the Raman results in §7.3 after higher temperature annealing cycles. The material becomes visually dark after high temperature annealing though the surface remains shiny. SBS measurements become a long process compared to the time scales of measurements taken after low temperature anneals on the same sample, possibly

due to poor reflectivity on the leading edge and also enhanced absorption by the implanted region.

7.4.1 Surface Brillouin scattering in annealed single energy ion implanted diamond

Figures 7.8 and 7.9 show the SBS spectra obtained for annealing cycles on the single energy implanted diamond (sample 3) at incidence angles of 70° and 80° . A dispersive indirectly scattered SHM peak, ‘A’ was observed for anneals up to 500°C around 46 and 48.5 GHz for these angles, respectively. It diminished in intensity as a function of annealing temperature up to 500°C for both angles of incidence and was not visible after annealing at 600°C , an effect that is attributed to increased opacity of the implanted region, such that laser light no longer reflects off the back of the diamond. Two new peaks located around 26 GHz (C) and 34 GHz (B) that are non-dispersive appear after annealing at 500°C and remain for all the annealing cycles up to 1200°C . Within the limits of experimental error, peaks B and C were observed neither to change from their position at higher anneal temperatures (see dotted green line in figures 7.8 and 7.9) nor at different angles of incidence after the same anneal temperature.

From figures 7.8 and 7.9, there is a transition that occurs at 500°C anneal temperature if the local environment of damage is very high as happened in the single implanted diamond. This is shown by appearance of new peaks B and C that were not observed earlier. This phase transition of ion damaged diamond during annealing at 500°C has been observed in previous studies that were focusing on totally different aspects. Swanson [191] reported a change in both electrical and optical characteristics of natural diamond type IIa implanted with sodium ions to

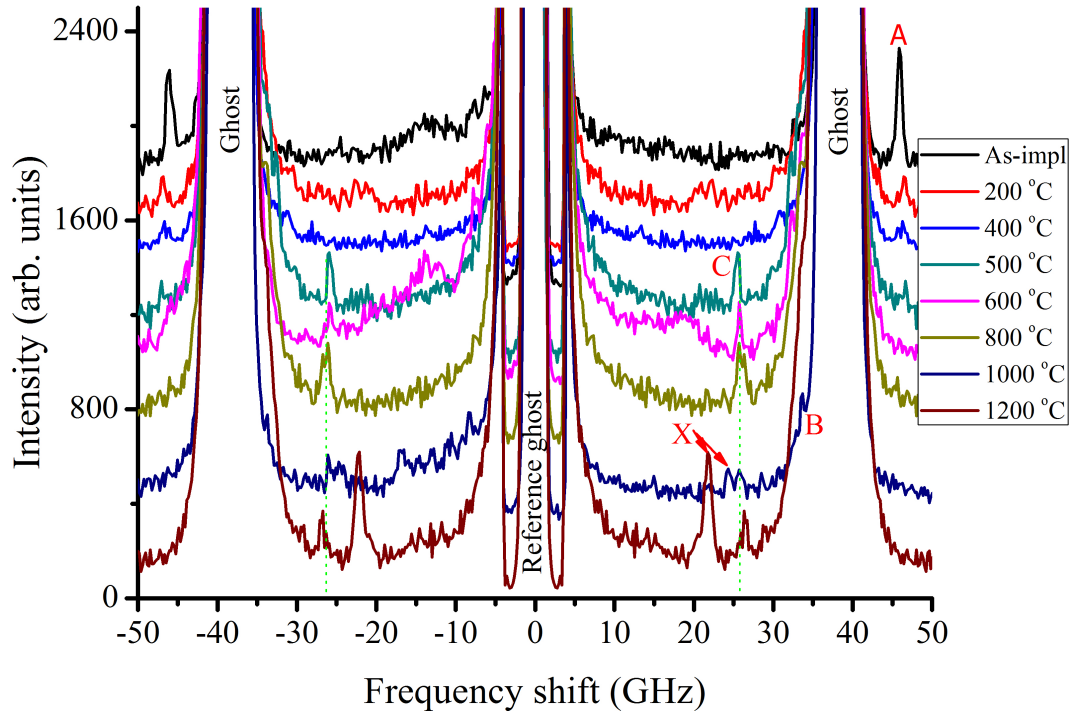


Figure 7.8: SBS spectra for single energy implant taken at angle of incidence 70° . The broad feature at ≈ 15 GHz on the Stokes side is an instrumental artefact also seen in subsequent SBS measurements for the instrument used in this study, hence had no significance in the analysis. Similarly, ghosts are instrumental features, the reference ghost is due to elastic scattering which not only acts as reference for frequency shift but also stabilizes measurements.

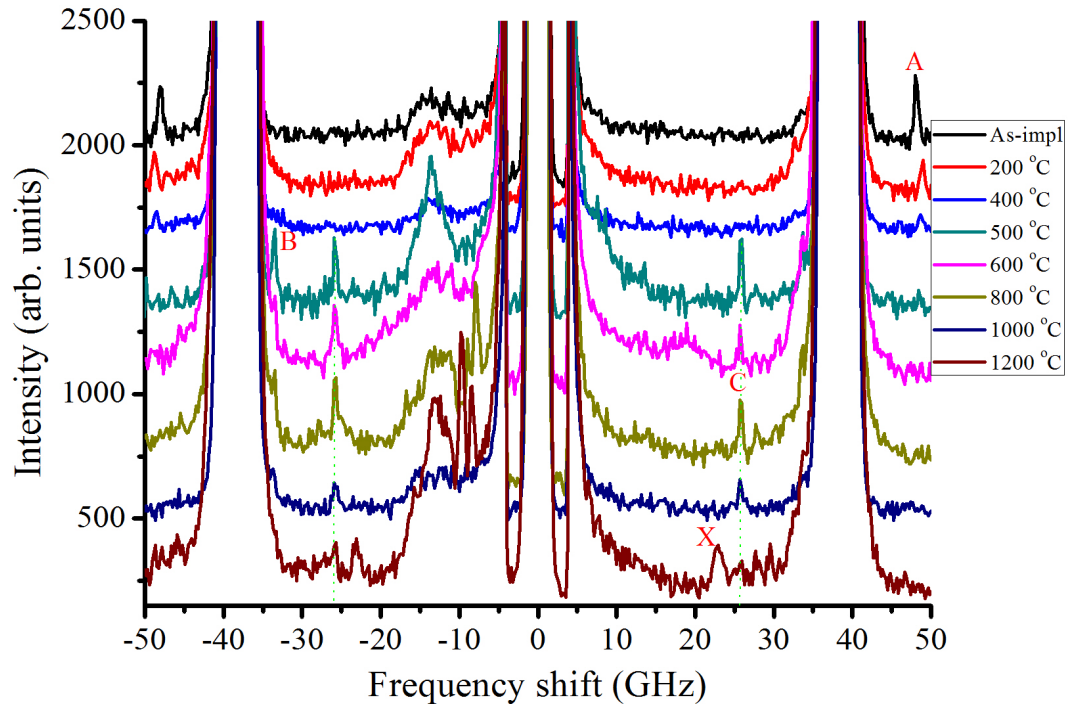


Figure 7.9: SBS spectra for single energy implant taken at angle of incidence 80° .

a high dose of 5×10^{19} ions/cm³, after annealing at 500 °C. He noted that a further anneal to 1000 °C only enhanced the observed change. In addition, the sudden darkening of diamond at about 800 °C can be associated with vacancies migration as they are more mobile at higher temperatures [123]; this leads to clustering of more defined graphitic-like structures as shown by EELS data in §7.5.

The non-dispersive peaks B and C that were observed after annealing at 500 °C may be related to bulk elastic modes of the damaged layer, whose scattering is thought to be mediated by the elasto-optic scattering mechanism of this layer in view of the 15.8% light transmission measured. At the same time, by considering the evolution of the damaged layer that sits on top of pristine diamond, there is a possibility of a thin layer supporting pseudo surface acoustic wave (pSAW) modes. Due to the related complexity of the scattering environment and the material property changes under the annealing conditions, peaks B and C which are reported for the first time for such a diamond system, will require further investigations to be fully understood. However, the fact that these peaks appear not to shift in position for increasing annealing temperatures could possibly indicate that the implanted diamond region has a fairly rigid phase which only changes drastically after annealing at 1000 °C, as shown by the formation of a new mode X in figures 7.8 and 7.9.

The presence of peaks B and C upon annealing at temperatures 600-800 °C without a corresponding surface peak in sample 3 is akin to what was observed when the sample was in the as-implanted state and annealing up to 500 °C state. At those lower annealing temperatures, transverse and longitudinal peaks were observed without a corresponding surface peak as was clearly shown in chapter 5 (for instance see figure 5.17). In this analogy therefore, peaks B and C were more

likely to be bulk peaks of the amorphous layer (opaque). The not-so-well defined interface between the opaque region and the thin recrystallized diamond at the top could not bring about measurable surface modes at annealing temperatures of 600-800 °C.

The dispersive peak X only appeared after annealing at 1000 °C and was also observed after a 1200 °C anneal, but at lower frequency shift for similar angles of incidence. It is arguable if what looks like a split peak of the 800 °C anneal spectrum for figure 7.8 is a degeneracy of peak C and X as it was not observed for an incidence angle of 80°. Peak X appeared under a totally different scattering environment from that which governed the earlier dispersive bulk peak A. Peak A was due to indirect scattering while peak X was explained by invoking the surface ripple mechanism. Peak X was therefore a SAW of the amorphous film sitting on pristine diamond due to its lower frequency shift compared to of peaks B and C. At the anneal temperatures ≥ 1000 °C, there was a strained diamond layer (40-60 nm whose density was not constant along its depth [180]) sitting on an amorphous material (170-190 nm) whose EELS data §7.5 show a material with constant density. The strained layer may have been responsible for the tensile stressed diamond peak observed in figure 7.5. The trailing edge had a ‘mirror’ finish that forms the boundary between the amorphous region and pristine diamond that lies beyond the end of range. The scattering volume of the strained diamond just below the surface was too small to cause any visible modes (a much bigger volume than this created using He ions in chapter §6 failed to produce observable peaks). At the annealing temperatures of 1000-1200 °C therefore, the film and substrate are optically distinct materials having an intimate contact at the interface.

7.4.2 Surface Brillouin scattering in annealed multiple energy ion implanted diamond

Figures 7.10 and 7.11 show the SBS spectra obtained for annealing cycles on the multiple energy implanted diamond (sample 2) at the high incidence angles of 70° and 80°. Just as for the single energy implanted sample there was a dispersive SHM peak (A) observed around 42 GHz and 44 GHz respectively, up to 800 °C. Note that the difference in SHM peak positions is related to the azimuthal orientation of the individual sample during measurements as discussed in section §5.6.1 and not to the implantation profile or fluence. The non-dispersive peaks with similar characteristics as those observed for a single energy implant were also observed around 26 GHz (C) and 33 GHz (B) after annealing at 600 °C. Between 600-800 °C measurements, they have very low intensity but they exhibit high intensities after annealing at 1000 °C. The results of anneal at 1200 °C are not shown since the surface got attacked by oxygen during annealing, and could not give any clear peaks.

Following the debacle of annealing sample 2 at 1200 °C, further measurements were done on another multiple energy implanted diamond (sample 6). This sample was annealed in the RF furnace (§3.7.2) since it has more advantages than the “horizontal shoot-in furnace” (§3.7.1). Peak A was observed for all measurements conducted for annealing up to 600 °C. Peaks C and X were only clearly visible after annealing at 800 °C as shown in figure 7.12.

Peak X has the characteristic of a surface wave, scaling with the sine of the angle of incidence as shown for the representative spectra in figure 7.13 for sample 3 after 1200 °C anneal. The scaling behaviour of peak X for samples 2, 3 and 6 was summarized in table 7.3. Although it is difficult to conclude on the control of

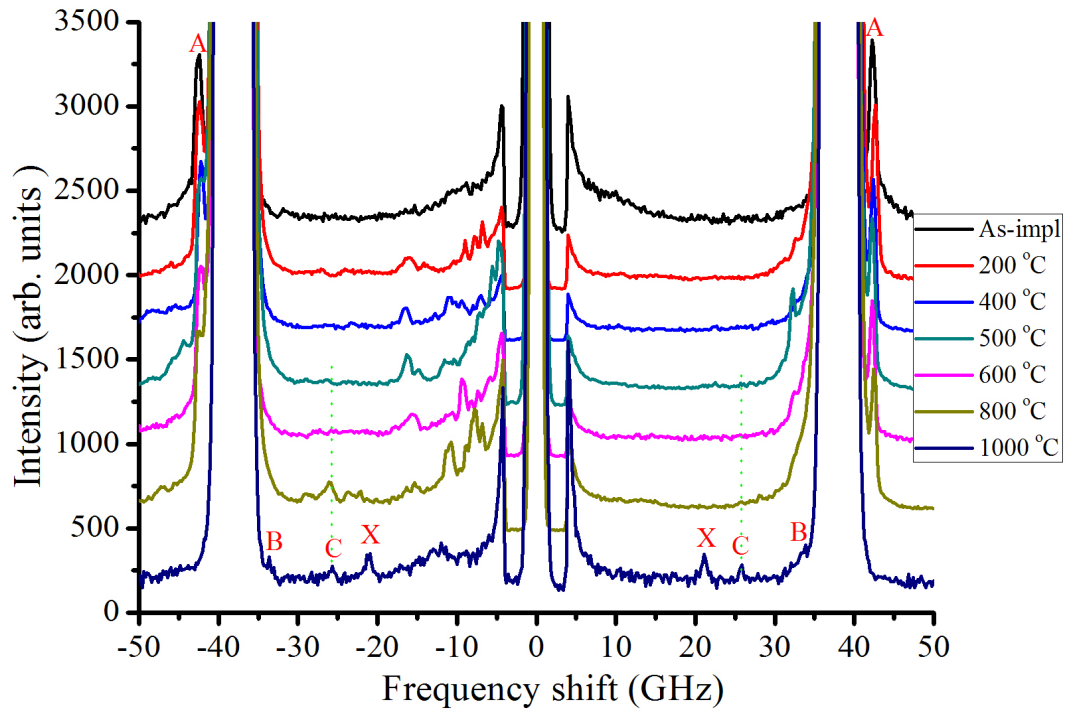


Figure 7.10: SBS spectra for multiple energy implant taken at angle of incidence 70° .

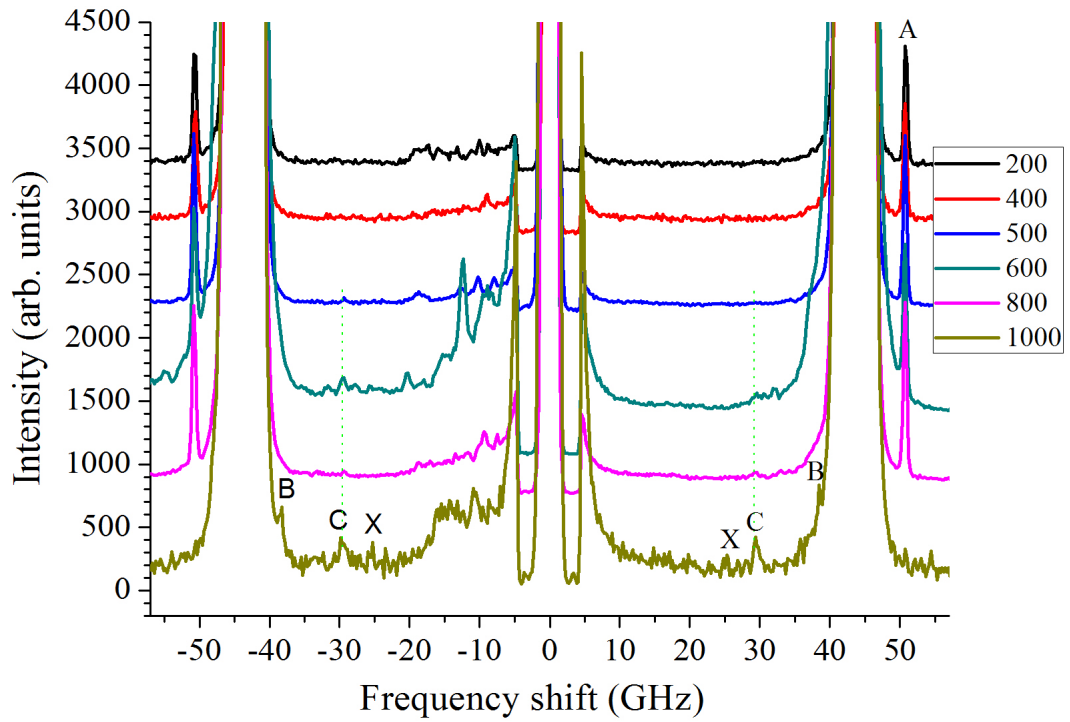


Figure 7.11: SBS spectra for multiple energy implant taken at angle of incidence 80° .

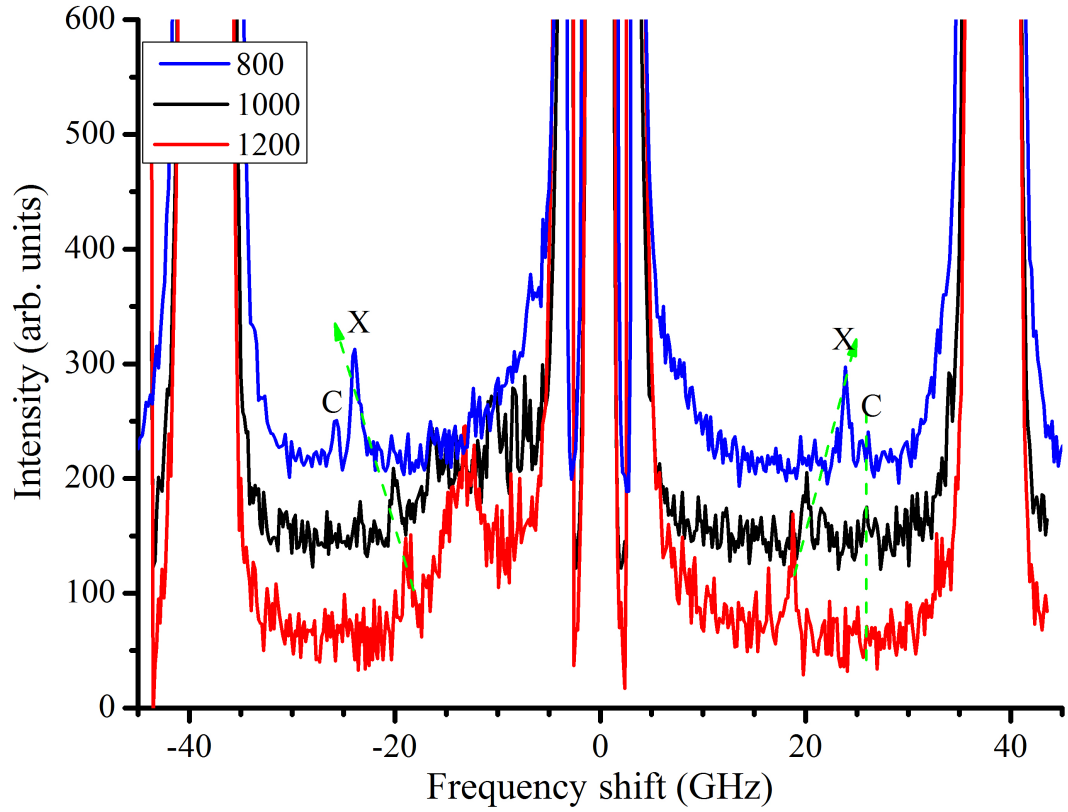


Figure 7.12: SBS spectra for sample 6 at incident angle of 70° after annealing cycles at 800-1200 $^\circ\text{C}$. Peak X position of just below 20 GHz after 1200 $^\circ\text{C}$ compared to its position after 800 and 1000 $^\circ\text{C}$ shows a softening material.

Rayleigh velocity in such complex stack, as it depends on the entire stacks and on the thickness of all layers, in this study peak X is take as the Rayleigh mode of the damaged annealed layer. The Rayleigh SAW velocity was calculated from a plot of the graph of frequency shift against the sine of angle of incidence (see figure 7.14) using equation (4.6.14).

Considering the results in table 7.3, the Rayleigh SAW velocities obtained after 1000 $^\circ\text{C}$ anneal for the three samples, it was observed that sample 3 had the highest Rayleigh velocity (6670 m/s) and sample 6 the least (5460 m/s). This difference seems to follow the pattern of the level of damage above D_c as estimated in figures 7.1 and 7.2. The differences in Rayleigh velocities due to dose differences, implantation profile and annealing temperatures, show that it is possible to vary the elastic constants of an ion implanted diamond by varying fluences in different

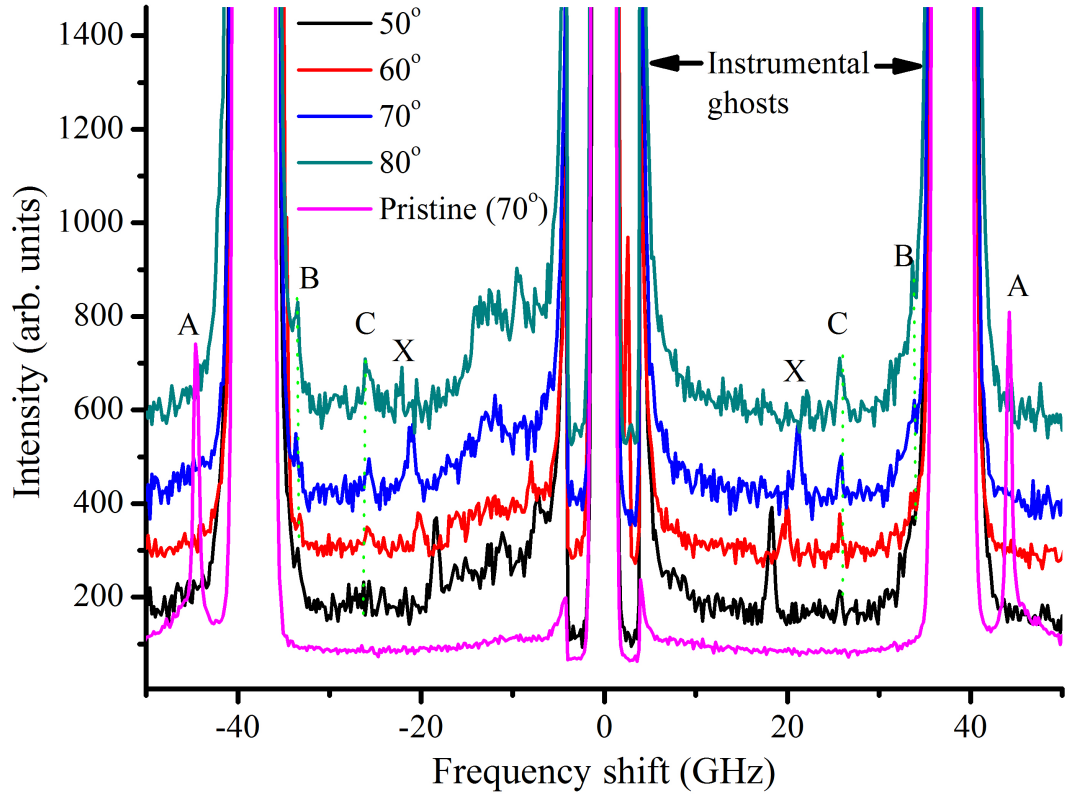


Figure 7.13: SBS spectra at incident angles 50-80° in the same azimuth orientation upon annealing at 1200 °C.

sections of the same sample. This property can therefore be utilized to tune the elastic constants within the same material by implanting different regions with different fluences and such a material could be applied in microelectronmechanical systems (MEMS).

The measured surface velocities of peak X (5100-6800 m/s), compares well with Rayleigh wave velocities of 5300-6800 m/s obtained for a homogeneous and layered 70 nm ta-C layer measured by Pastorelli *et al* [143] using SBS. Salas *et al* [189] reported a SAW velocity of 5440 m/s for 80 nm a-C films while Beghi *et al* [192] found average SAW velocities of 4950 m/s and 5100 m/s for ta-C films of thickness 4.5 and 8 nm, respectively. These velocities are however, far less than the Rayleigh velocity of diamond, an observation that supports the argument presented above that the radiation damaged and annealed layer transforms to a much softer material

Table 7.3: Frequency shift of peak X with respect to angle of incidence and its Rayleigh velocity upon annealing.

Sample	Annealing temperature	Angle of incidence	Peak X position (GHz)	Velocity (m/s)
2	1000 °C	50	18.3	5840
		60	20.1	
		70	21.1	
		80	22.1	
3	1000 °C	50	19.2	6670
		60	22.2	
		70	24.5	
		80	25.7	
	1200 °C	50	16.9	5960
		60	19.6	
		70	22.0	
		80	23.0	
	800 °C	30	13.3	6600
		50	19.1	
		60	22.3	
		70	24.1	
	1000 °C	30	10.8	5460
		50	16.0	
		60	18.4	
		70	20.1	
	1200 °C	30	10.2	5150
		50	15.5	
		60	17.4	
		70	18.7	

than diamond. The amorphized region is a therefore softer material characterized by slower surface mode velocities. It is however much harder than pure graphite which has a transverse velocity of 1507 m/s [189]. An assumption is however made that to obtain the Rayleigh velocities measured with respect to peak X, there was a need for non-varying density in the entire damaged layer from the surface to about 230-250 nm with a sharp interface. The damaged region became an amorphous/graphitic layer whose properties resemble that of ta-C, as evidenced by the studies reported in section 7.5.

Measurements conducted on sample 6 in different orientations show a total

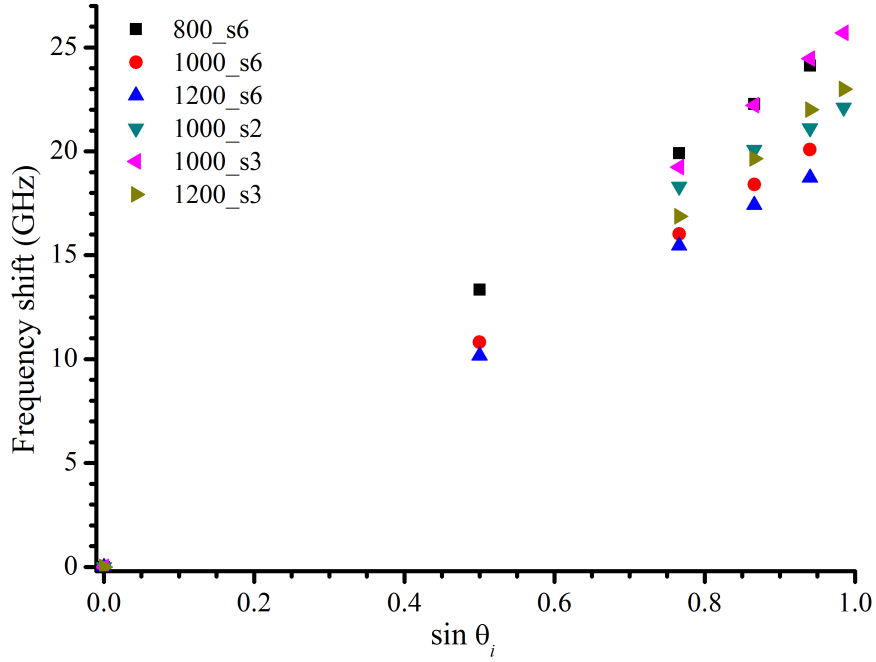


Figure 7.14: Frequency shift against incident angle plot used in determination of the Rayleigh velocities of peak X in samples 2 (s2), 3 (s3) and 6 (s6) upon annealing at temperatures 800, 1000 and 1200 °C.

loss of symmetry indicated by the loss of the four fold symmetry upon annealing at 800 °C. Figure 7.15 shows a comparison of the azimuthal spectra obtained for lower anneal values (as-implanted to 500 °C) and the higher anneal temperatures (800-1200 °C). The fourfold symmetry observed for lower annealing temperatures (as-implanted - 500 °C) was lacking after the high temperature annealing (800-1200 °C).

7.5 EELS and HRTEM results

A single crystal CVD diamond plate similar to sample 3 used earlier was implanted with C ions at a single energy of 150 keV and total fluence of 1.5×10^{16} ions/cm². It was then broken into smaller pieces. Different pieces were annealed at temperatures between 200 °C and 1000 °C for 20 min in a flowing argon environment. Though the annealing cycle was different from that used to acquire SBS and Raman data, the

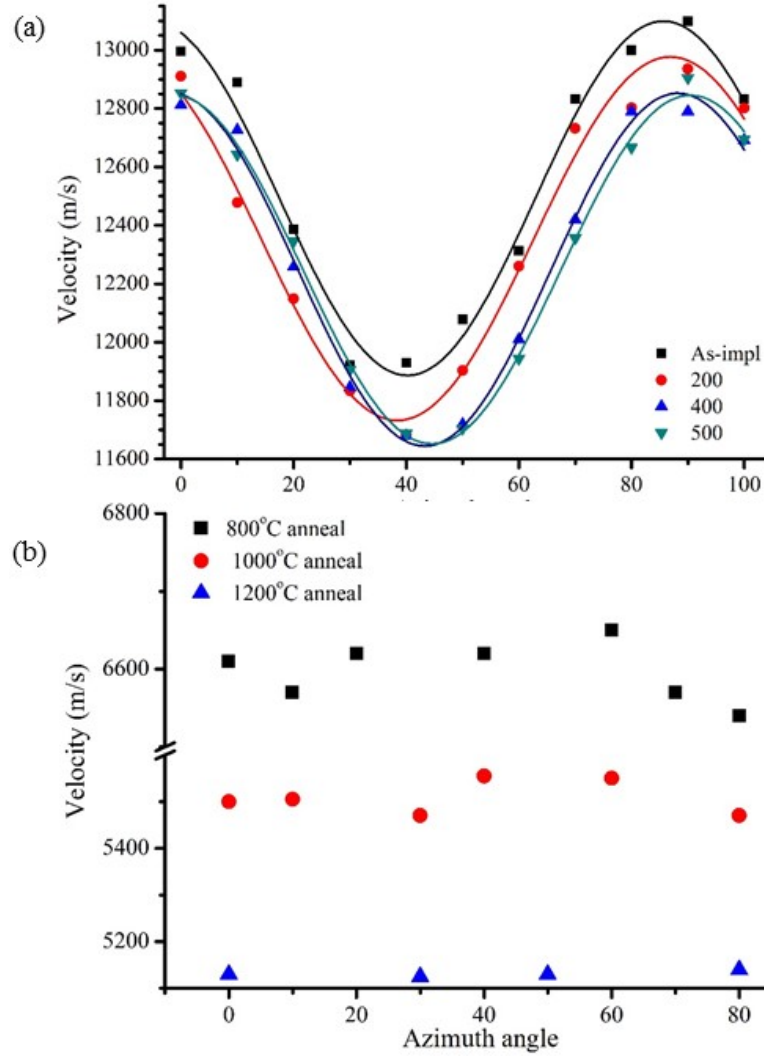


Figure 7.15: SBS spectra for different azimuth angle measurements (a) measurements at the ‘lower’ annealing temperatures while showing crystallinity (b) are similar measurements at ‘higher’ annealing temperatures showing the sample transformed to amorphous. All the measurements were taken at incidence angle 70° .

information obtained is useful in the overall interpretation and comparison of data.

In this case each piece was annealed once at a specific temperature (say one piece at 200 °C, another at 400 °C etc.), unlike previously where the sample was annealed at 200 °C, then after SBS and Raman measurements, the same sample was annealed at 400 °C, etc. From each annealed piece, FIB sections were prepared using a FEI Helios Nanolab 650. Then TEM analysis was done using a double aberration corrected JEOL ARM 200F fitted with a Gatan GIF Quantum ERS 965 with dual EELS capability as detailed in [2]. A beam current of 68 pA and probe size of

≈ 0.1 nm was used. The convergence and acceptance angles of 24-27 mrad and 70-100 mrad respectively were used. By using STEM-EELS spectrum imaging, the bonding environment of the as-implanted layer and the subsequent annealed profiles were mapped. The disordered carbon was mapped using the characteristic π bonding pre-edge for disordered carbon present at 284 eV energy loss for the C K-edge using an energy window of 4 eV. The diamond signal was mapped by using a multiple linear least squares (MLLS) fitting of the spectrum image area using a reference signal of diamond. The produced maps are shown in figure 7.16a. By scanning across the entire region of implanted range on each annealed piece, the percentages of disorder in carbon bonds and diamond bonding in the region were mapped. The selected area diffraction (SAD) pattern was taken over the width of the amorphous implanted zone so as to exclude as much as possible the diamond material at the near surface and the diamond substrate beyond the end of range, this is shown in figure 7.17.

It was observed that the implanted zone consists of largely an amorphous region of ≈ 240 nm in width. A very thin diamond layer occupies the top part of the ≈ 240 nm implantation zone. Just beneath this layer, an amorphous layer that was evolving due to heat treatment seems to saturate after annealing at 1000 °C. However, some diamond crystallinity was maintained at the near surface region after implantation. Annealing of the implanted zone beyond 600 °C led to a reduced width of the near surface diamond region and consequently an expansion in the amorphous-like carbon/ graphitic region. Sharpness of the boundary at the diamond-amorphous layer interface near the surface improved as the annealing temperature increased (figure 7.16a). Evidence for the alignment of graphitic basal planes were found with an increase in annealing temperature as determined

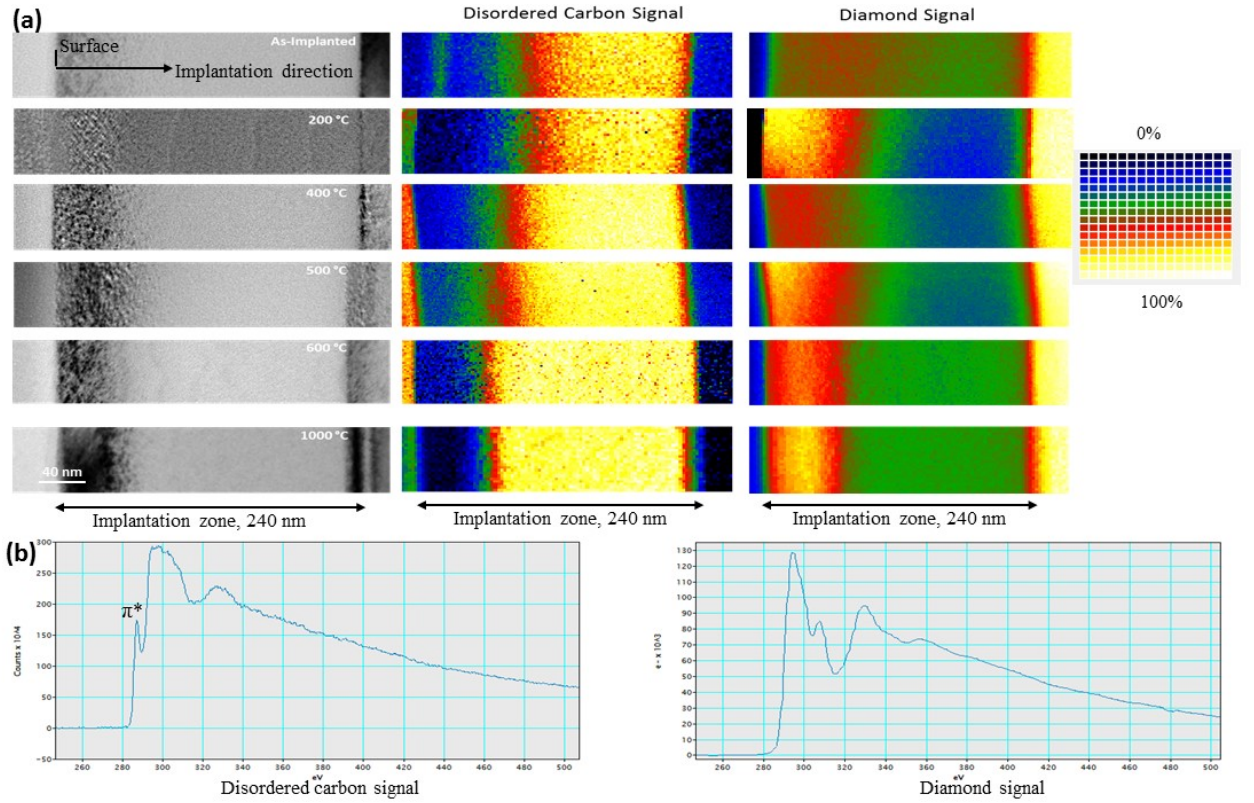


Figure 7.16: (a) Bright field micrographs of diamond C ion implanted and annealed at the temperatures shown with corresponding STEM-EELS spectrum images shown alongside. The grid to the right shows the percentage of disorder/diamond in the implantation zone. (b) Core loss EEL spectrum of the carbon k-edge used in mapping the middle and right column EELS spectrum of the implanted layer.

by SAD and HRTEM shown in figure 7.17. This can be seen due to the presence of the arcs in the SAD pattern and alignment of the basal planes in the HRTEM image. The lack of long range crystallinity in the graphitic carbon is also supported by the arcs observed in the SAD patterns which appear after annealing at 600 °C [2].

Density of the damaged layer may be estimated by calculating the sp^3 fraction in the diamond map in figure 7.16a and comparing it with the documented works of Ferrari *et al* [193, 194]. The percentage of sp^3 calculated from the colour map of diamond upon annealing at 1000 °C was ≈ 37.5 -46%. Fitting these values (red lines) in the graph of density of diamond-like carbon as a function of sp^3 fraction

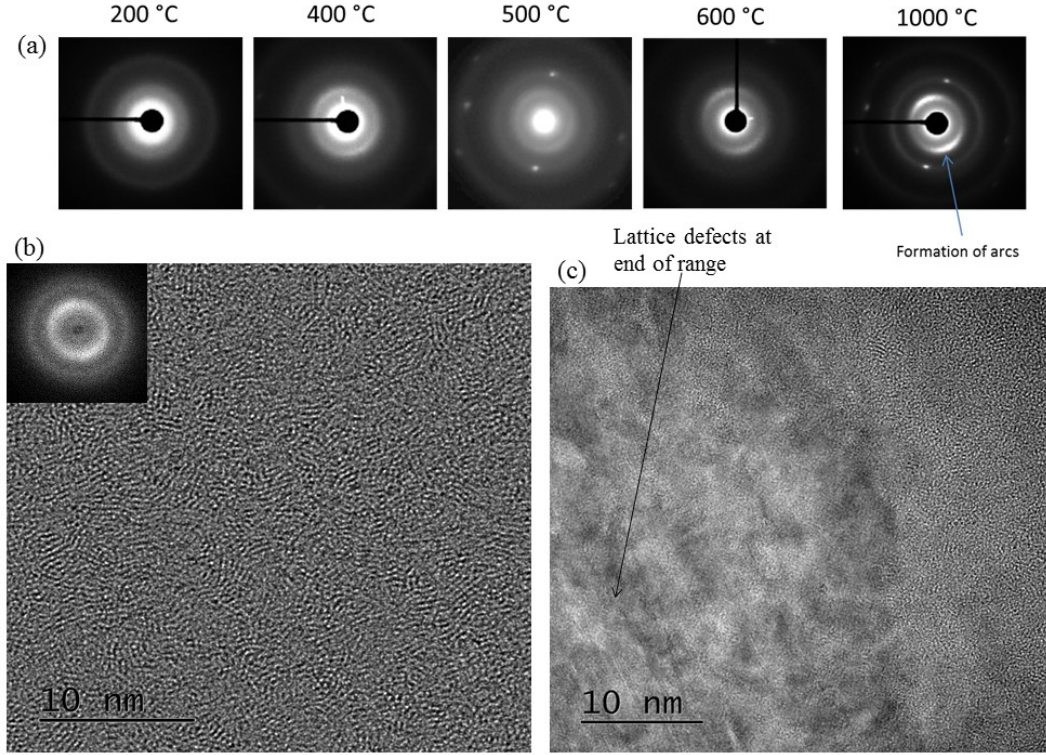


Figure 7.17: (a) SAD patterns from implanted zone at different annealing temperatures. (b) HRTEM image of the damaged zone after 1000 °C anneal.

shown in figure 7.18 gives a density of 2.4-2.6 g/cm³.

This value of density was in agreement with that obtained from the plasmon peak of low-loss EELS data (not shown), but calculation obtained from [195]. The bulk plasmon energy E_ρ corresponds to a high peak in a low-loss EELS graph, which according to free electron theory is given by,

$$E_\rho = \sqrt{\frac{n_c \hbar^2 e^2}{4\pi^2 m \epsilon_0}}, \quad (7.5.1)$$

where n_c is the number of valence electrons per unit volume (=4 for carbon), $\hbar$ (=1.0546×10⁻³⁴ Js) is the Planck's constant $h/2\pi$, ϵ_0 =8.8541×10⁻¹² m⁻³kg⁻¹s⁴A² is permittivity of free space, m =9.1094×10⁻³¹ kg and e =1.6022×10⁻¹⁹ coulombs are the effective electron mass and charge, respectively. The effective mass density ρ is proportional to charge density n_c :

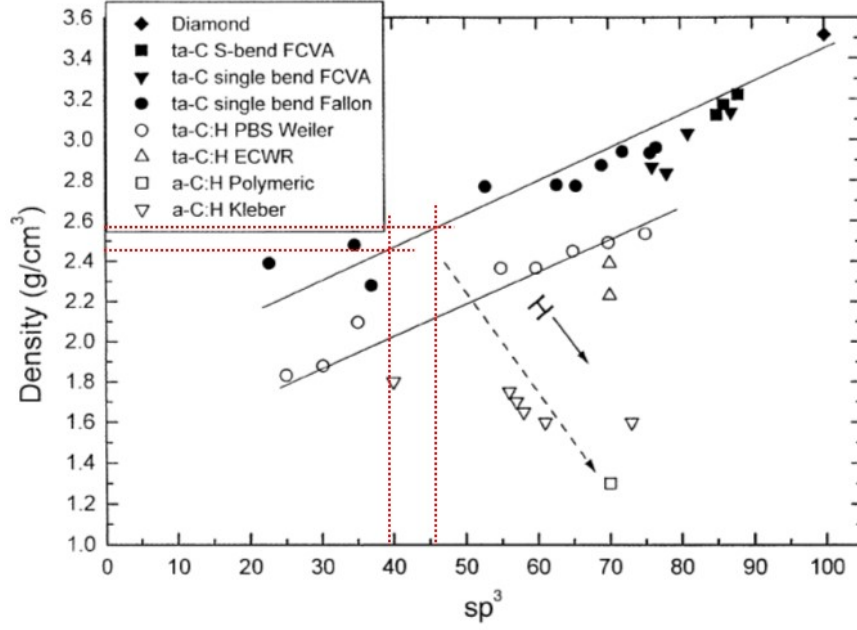


Figure 7.18: Graph used to estimate the density of the ion implanted and annealed at 1000 °C. Adapted from [194].

$$\rho = \frac{Mn_c}{n_v N_A} = \frac{3n_c}{N_A}, \quad (7.5.2)$$

where N_A ($=6.0221 \times 10^{23}$) is Avogadro's number, M is the atomic mass ($=12$ for carbon), n_v is the mean number of valence electrons per atom ($=4$ for carbon). The plasmon peak of diamond at 33 eV gives the density of diamond as 3.5 g/cm^3 while that of the damaged region was at 26.5 giving a density of 2.5 g/cm^3 , a result in good agreement with extrapolations deduced from figure 7.18 [194].

We compare the results summarized in the SBS spectra of figure 7.8 and the Raman spectra of figure 7.3, and corroborate them with the EELS and HRTEM measurements. It is observed that peak A, earlier identified as a bulk transverse wave of diamond, was only visible at annealing regimes that also showed an intense first order diamond signal in Raman measurements. This diamond signal could be due to the diamond near the surface as well as beyond the damaged region. There was a direct correlation between the SBS and Raman measurements linked to the

opacity of the damaged layer, as reported earlier in section 5.2.2 on transmission of the 514.5 nm light as a function of annealing. This correlation is shown by the decrease in the intensity of the SHM mode in SBS (figures 7.8 and 7.9) and decrease in intensity of the Raman diamond signal (figures C.1 as the layer became more opaque. As the disorder peak became more prominent after annealing at 500 °C as observed in Raman measurements, peaks B and C appeared in SBS measurements. These peaks appear after annealing at temperatures >500 °C when vacancies become mobile in diamond [123]. The annealing process associated with vacancy migration appears to be related to the clustering of the sp^2 . A process similar to Ostwald ripening takes place where materials with lower formation energy are preferred hence more clusters of sp^2 bonds form at the expense of sp^3 bonded ones in the damaged region. The alignment of the basal planes of graphitic carbon is seen as arcs in the SAD pattern taken over the implanted range and is more clearly visible after annealing at 600 °C (figure 7.16(a)). After the 200, 400 and 500 °C anneals, the SAD patterns which are rings indicate that the damaged region is amorphous. The SBS spectra only showed additional peaks after annealing at 500 °C which must be from direct backscattering from the phonons in the ion implanted and annealed layer. Annealing above 500 °C appears to be accompanied by the clustering and closer proximity of the graphitic carbon in the implanted region.

In SBS a new material in which sound propagates slower than in diamond was detected as peaks B and C and later as X when the reflectivity of the surface is good enough. The HRTEM image shown in figure 7.17(b) shows that the layer consists of bent carbon basal planes with no long range order and amorphous carbon which can consist of sp^2 and sp^3 bonded carbon. Reflectivity of the damaged layer improves

as the boundary at the diamond-damaged region becomes sharper. In EELS data, the boundary is observed to become sharper after higher annealing temperature of 600 °C, and greatly improved at 1000 °C. The EELS and HRTEM results show that for C implanted diamond beyond a critical threshold, the diamond is irreversibly damaged and solid epitaxial regrowth does not take place in diamond. This could be the reason why a sharp interface forms between the diamond and amorphous region. A thin strained diamond layer that remains intact at the surface was also observed in the EELS spectrum image map. This was not observed in the Raman spectra, and this could be due to the difference in the annealing cycle and possibly the shorter time that the diamond pieces were annealed for in the HRTEM/EELS study. It could also be that if there is a thin layer of diamond at the surface in the diamond used for the Raman study, that the diamond Raman line is overwhelmed under the D peak due to the large scattering cross-section for the D band in Raman scattering using visible light. In the SBS spectra after annealing above 500 °C, the peak due to indirect scattering labelled A reduces in intensity and is invisible after annealing above 600 °C. If it is considered that there is a diamond layer at the surface that remains, as the EELS spectrum image shows (figure 7.16), then it can be argued that the scattering path length of the light from the diamond structure at the surface (≈ 50 nm) reduces the number of elasto-optic scattering events that occur via the indirect scattering mechanism, hence the lack of signal observed. Evidence for lack of photon scattering off phonons from a thin transparent material sitting on an opaque layer was explained in section §6.2.3.

Peak X in the SBS spectra of figure 7.8, observed after annealing at 1000 °C, coincides with appearance of distinct peaks D and G in the Raman measurements. Notably, peak X reported in SBS measurements appears after the 1000 °C anneal,

which corresponds to the damage profile that has a sharp boundary on the surface side observed by electron microscopy. Basing on the trend at 600 °C and 1000 °C, the boundary would remain as it appears after 1000 °C or get sharper after annealing at 1200 °C, which explains the presence of peak X at that anneal temperature. From these observations, peak X is identified as a surface mode of the amorphized damaged region which consists of a network of carbon (sp^n , $n=1,2,3$) with some of the sp^2 in the form of nc -graphite.

7.6 The determination of elastic constants

Ion implantation and annealing at high temperatures (1200 °C in this section) produced a ‘film’ composed of (i) a top (40-60 nm) strained diamond of varying density sitting on (ii) an amorphous layer (170-190 nm), considered to have constant density and (iii) another very thin region of strained diamond (10-20 nm) with varying density which forms the interface between the amorphous layer and pristine diamond at trailing edge [2]. In order to smooth out the material and morphological complexities described above, the layer is modelled to a first approximation as a single homogeneous material with a sharp film-substrate interface, hereafter called amorphous film. The amorphous film is optically distinct from the diamond substrate. The approximate elastic constants of the film in this two layer system can be extracted by fitting experimental data into elastodynamic Green’s functions simulations.

Amorphous carbon/ diamond like carbon (DLC) systems like the implanted annealed layer in this study have a wide range of properties such as density, refractive index and hardness. To reduce the complexity of the problem at hand, a two system approach was employed; a 20 nm film of Pt was deposited on silicon

and on the amorphous film simultaneously. Pt was chosen for use because it has a metallic reflective finish and its heavy loading on the amorphous layer would stay longer as a coating for the long SBS measurements unlike Al which had been observed to peel off easily. Since the elastic properties of Si are known, only the elastic constants of the Pt film would be obtained by fitting experimental values into elastodynamic Green's functions. The elastic constants obtained for the Pt film would then be applied to find out those of the amorphous film now forming the substrate/ intermediate region above the pristine diamond. Therefore a 20 nm Pt film was deposited simultaneously on a (100) Si plate, pristine diamond, as-implanted diamond and on the amorphous film of sample 3 annealed at 1200 °C. SBS measurements were then conducted on the Pt on Si system at different angles of incidence in order to obtain sufficient data that would enable plotting of dispersion curves. A representative SBS spectrum showing the anti-Stokes side for Pt on Si is shown in figure 7.19 while that of Pt on pristine diamond, Pt on C ion as-implanted diamond and Pt on an implanted layer after annealing at 1200 °C are shown in figure 7.20.

It can be noted that transverse T_{KB2} and longitudinal L_{KB2} peaks due to indirect scattering $\mathbf{k}_b^{(2)}$ were observed for the Pt on pristine case, figure 7.20(a). This was clearly the case when light transmission was >15.8% as observed previously in this study. Light transmission for Pt on diamond was 28.3% as discussed in §5.2.2. In figure 7.20(b), the Pt on as-implanted diamond system had a 10.9% transmission, it shows the two bulk indirectly scattered peaks with a third peak at lower frequency shift, possibly a modified Rayleigh mode of the Pt film when light impinged on the Pt. When the same system was flipped over and light impinged directly on pristine diamond, only the two bulk peaks were observed as

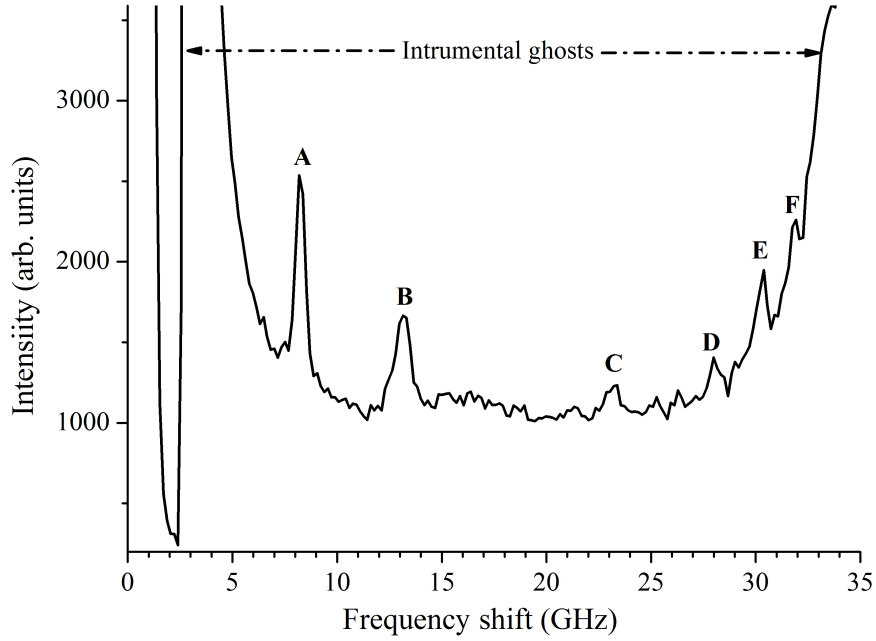


Figure 7.19: SBS spectrum of Pt on Si (100) surface for angle of incidence 40° .

expected. However, it is worth noting that the thin Pt layer affected the intensity of the longitudinal peak. When light impinged on Pt, the longitudinal peak was smaller compared to the transverse peak. Figure 7.20(a)-(b) seem to suggest that metallization enhances the transverse mode even for p-polarized light used in obtaining those spectra. This is attributed to the fact that the Pt layer was very thin, the incident laser light penetrated and reflected off the rear side of the sample, and because the transverse mode travels parallel to the surface, the thin Pt layer enhanced the scattering events of these modes. The Rayleigh and the transverse modes have similar scattering cross-section [135]. Figure 7.20(c) shows the Pt on the opaque amorphous film case where transmission was less than 1% showing a spectrum with many peaks (K-L) typical of a thin film on opaque medium [168]. Note that ideally, there was a strained diamond layer just below the surface on which Pt was directly deposited to which seemed not to have any obvious effects, hence could be ignored in the modelling. Therefore the substrate properties have an effect on what is observed despite keeping the film properties constant hence it

is possible to study the substrate once the film properties are known.

Preliminary work involved fitting the experimental values into the theoretical Green's function formalism of these systems. For the Pt on Si system, the literature values of elastic constants of Si, $C_{11}=165.78$ GPa, $C_{44}=76.62$ GPa and $C_{12}=63.94$ GPa and density of 2.332 g/cm³ were used [196]. The literature parameters used in fitting Pt were ($C_{11}=346.7$ GPa, $C_{44}=76.5$ GPa and $C_{12}=250.7$ GPa and $\rho=21.45$ g/cm³ [197]. The fitting process was conducted by keeping the substrate parameters constant and varying the film parameters (ρ and C_{ij} values) such that the best dispersion curve produced $\pm 2\%$ of the known velocities of Si as read at $k_{\parallel}d=0$. The velocities of Si are $v_R=4780$ m/s, $v_T=5648$ m/s, and $v_L=8344$ m/s reported by Zhang *et al* [198, 73]. The film elastic constants and density are however expected to be lower than that of its bulk due to the presence of the surface, surface roughness and interface layers [199]. Figure 7.21 show the best fit obtained at film parameters of thickness= 18.3 nm, $\rho=5.015$ g/cm³, $C_{11}=165$ GPa and $C_{44}=76.5$ GPa; the two elastic constants were enough for fitting an isotropic film such as Pt on Si. This reduction in mass density and elastic constants for such a thin amorphous Pt film (20 nm) compared to the bulk values was expected. Zhang *et al* [73] reported a reduction in density by 0.95 of that of crystalline Si and elastic constants ($C_{11}=83\%$ and $C_{44}=60\%$ of the bulk) of amorphous Si (200 nm on the (001) crystalline Si surface).

The Pt film parameters obtained from the Pt on Si were then used to model the layer on amorphous carbon. The film parameters were kept constant while the substrate parameters were adjusted to get a good fit of the Pt on amorphous carbon as shown in figure 7.22.

Owing to the complexity of sample preparation and time required for these

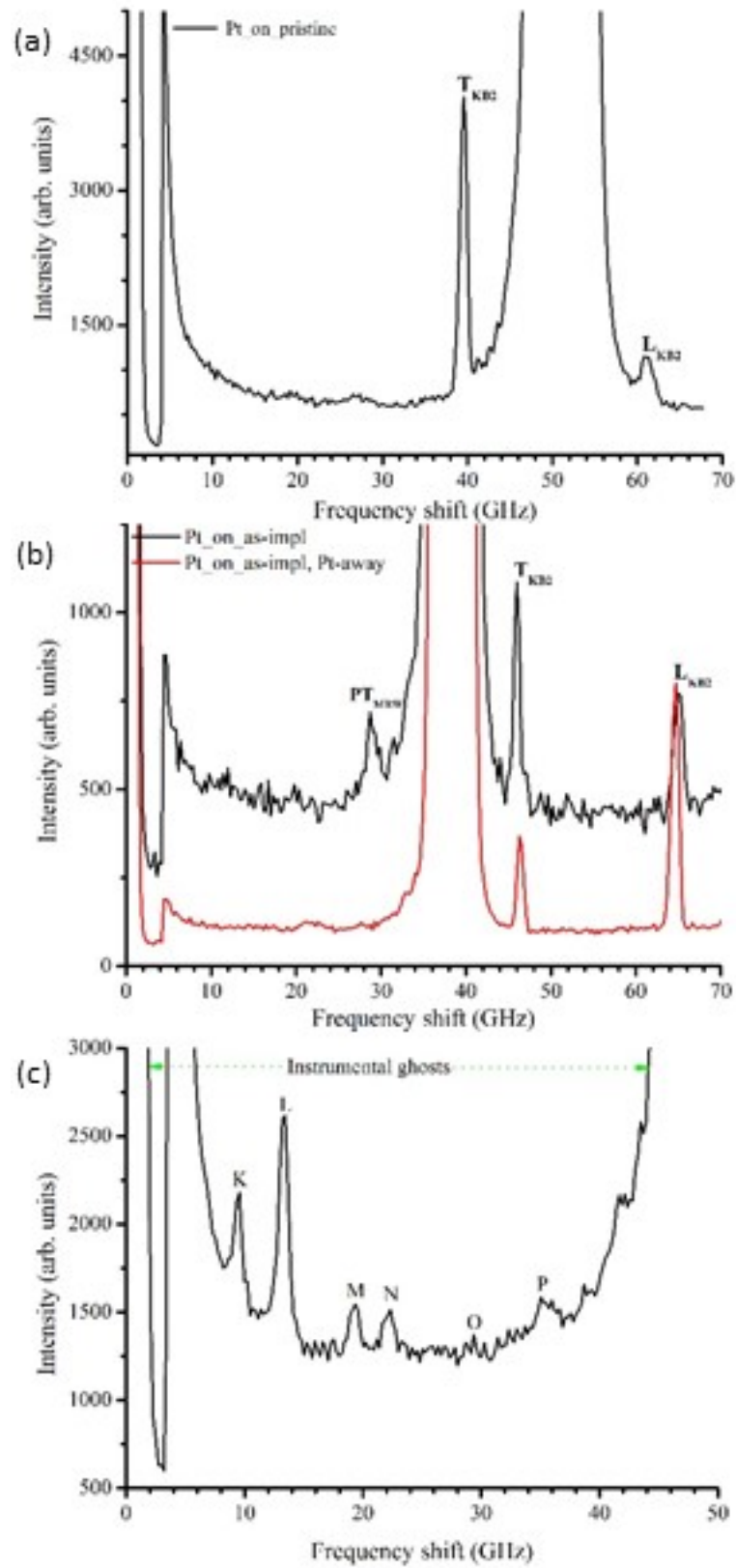


Figure 7.20: (a) SBS spectrum of Pt on: (a) pristine diamond surface at incidence angle of 60° , (b) as-implanted diamond with Pt film facing to and away from the impinging light at incidence 70° and (c) C ion implanted and annealed at 1200°C at incidence angle 70° .

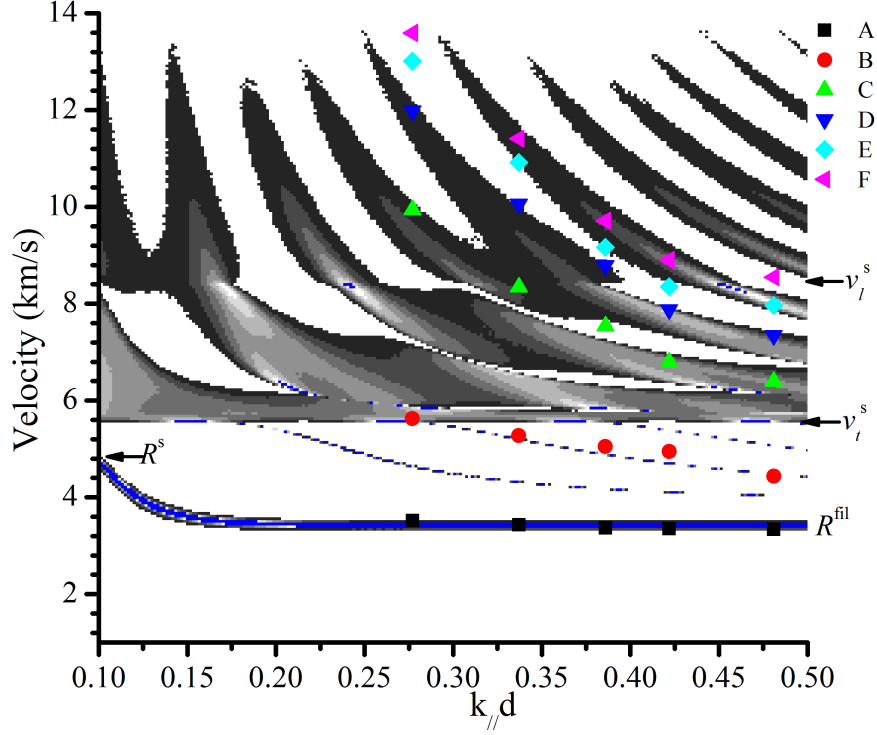


Figure 7.21: Experimental data of Pt on Si fitted using the Green's function formalism. A-F are experimental peak positions at different angles of incidence. The imaginary lines along v_l^s , v_t^s are the longitudinal and transverse wave velocities of the substrate while R^s and R^{fil} are the Rayleigh SAW velocities of the substrate and Pt film, respectively

experiments, only data from sample 3 is reported in this work. To obtain the best fit, the Rayleigh velocity had to be equal to ≈ 6.0 km/s as obtained in table 7.3 upon annealing the said sample at 1200 °C. The fitting parameters for the graphitic carbon substrate were $\rho = 2.5$ g/cm³, $C_{11} = 250$ GPa and $C_{44} = 110$ GPa. The two elastic constants are sufficient to describe the ion implanted and annealed layer since it is essentially an isotropic medium. Hence the engineering constants of the graphitic layer calculated from equations 2.1.30-2.1.32 are $E = 244$ GPa, $B = 100$ GPa, $G = 110$ GPa and $\nu = 0.107$. These are very close to those measured by Ferrari *et al* [64], where for a DLC film of $\rho = 2.7$ g/cm³ they obtained $E = 200$ -300 GPa, $G = 70$ -150 GPa and $\nu = 0.12$. It is therefore worth adopting the explanation of Hauser *et al* [200] who argued that diamond ion-implanted with C at a high fluence of 3×10^{16} / cm² attained graphite-like conductivity but with a hardness

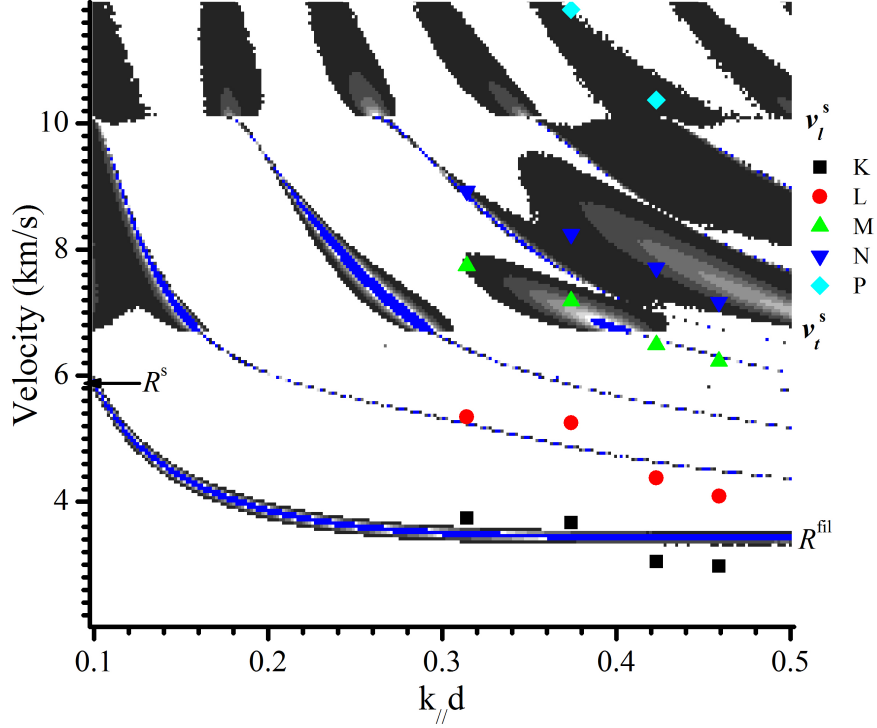


Figure 7.22: Experimental data of Pt on sample 3 after annealing at 1200 °C fitted using the Green's function formalism. K-P are experimental peak positions at different angles of incidence.

intermediate between graphite and diamond. This they concluded was consistent with the model for a-C in which had $\approx 10^{20}$ graphite bonds leading to metal-like conductivity and still about 10^{22} diamond-like bonds that caused the high mechanical strength.

From figure 7.22, the value of the transverse threshold is ≈ 6.67 km/s while that of the longitudinal mode is 10.09 km/s. Assessing the elastic constants due to these velocities ($C_{44} = \rho v_t^2$ and $C_{11} = \rho v_l^2$), then $C_{44}=111.22$ GPa while $C_{11}=254.52$ GPa. Generally, the elastic constants due to bulk elasto-optic scattering is given by $C_{ij} = \rho v_k^2/n$ where $\rho=2.5$ g/cm³, n is the refractive index of the graphitic layer, subscript k is either a longitudinal (l) or transverse (t) mode and $v_k = \nu_k \lambda$, where ν_k is frequency shift and $\lambda=514.5$ nm. Considering the two peaks in figure 7.8 observed after annealing beyond 500 °C: peak C at 26 GHz would be closer to the transverse mode, yielding $C_{44}=111.84$ GPa and peak B at 34 GHz would be near

the longitudinal mode of this layer yielding $C_{11}=191.25$ GPa, for $n=2$ a refractive index value close to 2.1-2.4 of amorphous carbon obtained by Stagg *et al* [201].

The expected transverse velocities for the other samples whose SAWs are shown in table 7.3 would easily be calculated using equation 7.6.1 [189]:

$$v_{\text{SAW}} = v_t \frac{0.87C_{11} + 2C_{12}}{C_{11} + 2C_{12}}, \quad (7.6.1)$$

since for an isotropic medium $C_{12} = C_{11} - 2C_{44}$, v_t can then be obtained. However, the samples in this study were unique since the position of the transverse peak (C) remains constant despite the differences in the SAW velocities due to heat treatment, dose difference and implantation profile differences.

EELS showed that there is ≈ 50 nm layer of diamond under stress and strain that recrystallized just below the surface. The effect of this diamond layer on the ≈ 180 nm of graphitic carbon was negligible in surface Brillouin scattering measurements. However, when Pt film was deposited directly on this thin strained diamond layer to aid in simulations and fitting experiment to theory, there was a discrepancy between the measured (real) and calculated (ideal) data. The ideal situation was Pt film on 240 nm graphitic carbon while in reality it was Pt on strained diamond sitting on graphitic carbon. The discrepancy as observed in the experimental Rayleigh mode velocities at $k_{\parallel}d \approx 0.42, 0.46$ which do not yield a good fit to the simulated graph of figure 7.22, may be attributed to the presence of the thin strained diamond layer between the Pt film and the graphitic carbon substrate which was not incorporated in the Green's function model parameters.

7.7 Conclusion

This chapter, using SBS, reports for the first time the transition in elastic properties that occur as C^+ implanted CVD diamond is annealed between 500-600 °C. The SBS results were corroborated by Raman, EELS and HRTEM measurements, which have shown a correlation between the structural changes and elastic properties that occur in ion-implanted and annealed diamond. SBS did not show a reduction in the velocity of the indirectly scattered bulk diamond transverse peak (SHM) as annealing temperature increases, it rather showed a transition from a hard to a softer material shown by appearance of slower acoustic modes B, C and X. The velocity of the Rayleigh mode obtained after annealing at 1000°C is within the range of reported Rayleigh velocities of the ta-C. The final product obtained from the annealing process of radiation damaged diamond beyond D_c was an amorphous material with a mixture of ta-C, nanocrystalline diamond and clusters of graphitic-like carbon.

Chapter 8

Conclusions and recommendations for future work

A conclusion of observations and findings was provided at the end of each chapter. From the conclusions reported in the results and discussion chapters 5-7, the following recommendations for future work are made:

1. Obtaining a sufficiently large scattering volume of recrystallized diamond layer will open up further work on the Rayleigh mode of CVD diamond and ability to study the change in stiffness as diamond heals itself when implanted with fluences that are below the amorphisation threshold.
2. Theory and experiment complement each other in physics, the FEM simulations (figure 6.8) show that there is a mass density change around $0.6 \mu\text{m}$ for annealing up 1000°C that is in agreement with low loss EELS data (not shown in this work) and the core loss EELS (figure 7.16). However, the calculated density and measured density differ, hence more study will be done to bring the two observations closer together.
3. Isochronal annealing at longer durations can be tried to find out the optimal durations when the stiffness threshold is reached for a given annealing temperature regime.

4. Studies on metallized samples need to be taken further. Figure 7.20(a) and (b) seem to suggest that metallization enhances the transverse mode even for p-polarized light. Although this study did not observe a SAW mode of the transparent substrate as a result of metallization, it is worth studying since other researchers have reported having observed SAW modes on transparent materials after metallization.

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Appendix A

Working with the thermal deposition evaporator

With the evaporation chamber dismantled, Al was loaded on a tungsten solenoid that closes the variac circuit. Place a clean glass dome onto the O-ring inserted into the metal base. The torus on the base and top metallic cover fits well with the circumference of the glass. Vacuum oil was lightly applied on the O-ring to prevent air leaks into the chamber. The chamber and its contents is shown on the LHS in figure A.1.

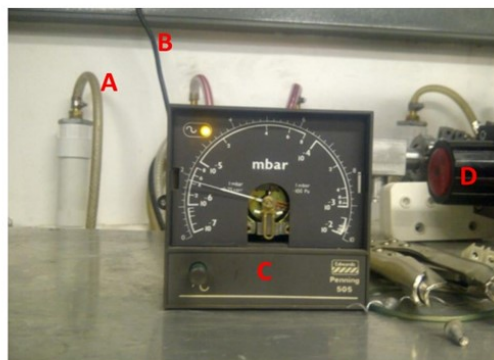
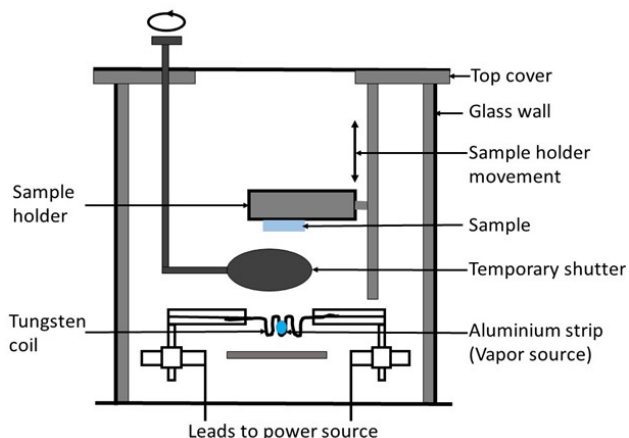


Figure A.1: (left) The evaporation chamber where the Al and diamond substrate were placed for deposition. The temporary shutter was only opened after heating the Al for some time to melt it completely and expel any impurities present. (right) A snapshot of pressure gauge just before deposition process is commenced.

Table A.1 shows summary of valve operations (figure 3.12), approximate time and approximate final pressure attained in the chamber as done in this study. The open circles imply an open valve while the filled ones imply a closed valve. Closure of any valve precedes opening for another e.g., in operation 4 close the Hi-Vac while the foreline is still open. Where time is not indicated it means that the time is

conditional/ determined by the user. The pressure column shows the pressure in the evaporation chamber after the operation on the said pumps.

Table A.1: Valve operation summary.

Procedure	Chamber Vent	Roughing	Foreline	Hi-Vac	Pump Vent	Time (min)	Pressure (mbar)
0	⊗	⊗	⊗	⊗	⊗		atm
1		⊗				40	$\leq 10^{-3}$
2		⊗	⊗			30	10^{-3}
3				⊗			10^{-5}
4				⊗		30	$\leq 10^{-6}$
5			⊗		⊗	0.5-2	10^{-6}
6	⊗				⊗		atm
7	⊗						atm
8	⊗	⊗	⊗	⊗	⊗		atm

All valves closed, switch on the mechanical pump and open water to flow through the diffusion pump. The rotary pump evacuates the tubes between the roughing and foreline valves. After about 5-10 minutes, when the sound of the pump is constant, open the roughing valve to start evacuating the chamber. Turn on the diffusion pump, this warms the silicone oil, a process that takes ≈ 40 minutes. Meanwhile the vacuum pressure in the chamber becomes better than 10^{-2} mbar. Close the roughing valve, open the foreline valve then keep pumping for another 30 minutes. The two pumps operating in tandem ensure that pressure in the region below the Hi-Vac valve is $< 10^{-3}$ mbar, that is in the chamber. Air molecules are removed from the diffusion pump and tubes between the roughing and foreline valves. A pressure difference is created with the chamber being higher than the one in the tubes and diffusion pump.

Open the Hi-Vac valve to continue evacuating the chamber through diffusion pump backed up by the rotary pump. The diffusion pump lowers the vacuum in the chamber to a pressure lower than 10^{-5} mbar. The pressure gauge on the RHS of figure A.1 show that a pressure better than 10^{-6} mbar was normally attained. Obstruct the sample-source path using the temporary shutter. Slowly ramp up the heating power to about 30 KVA to melt the Al. Al melts to a spherical jelly-like mass that rotates very fast around a point on the tungsten wire. Wait for the dark patches on the molten ‘ball’ to clear. Also wait for the disturbance of

pressure in the chamber due to melting Al and any outgassing effect to stabilize. Ramp up power to about 40 KVA to evaporate. Turn away the shutter from the source-sample path and simultaneously measure deposition time, close it at end of deposition. Save the sample from any contamination by first closing the Hi-Vac valve before turning off the variac.

Turn off the heater to cool the oil in the diffusion pump. Leave the foreline valve open to maintain the vacuum in the diffusion pump for about 30 minutes then close it. Shut down the water. Open the pump vent to allow the rotary pump and the metal tubes between the foreline and roughing valves to return to atmospheric pressure, then turn the rotary pump off. At this point all the valves are closed, open the Chamber Vent valve to break the 'vacuum' in the chamber and enable access to and removal of the sample(s) then close it after extracting the samples. In this state all valves are closed, the diffusion pump, baffle and cold trap are left in high vacuum which assures a clean start the next time the system is used.

Appendix B

Reflection from diamond surface and buried graphitic layer

Helium implantation at single high energy results damaged layer buried deep beneath a diamond layer that presumably recrystallizes on annealing at 1200°C. The buried thin film of graphitic carbon has reflective and absorptive properties. Thus it is a reflecting and also an absorbing medium. The intensity of reflected beam can thus be calculated from Fresnel's equations.

Reflecting power or reflection coefficient (R) is the ratio of the reflected to incident intensity [202]. The complex refractive index $n = n_r(1 - i\chi)$ for $\chi=1$

$$R = \frac{(n_r - 1)^2 + n_r^2}{(n_r + 1)^2 + n_r^2} = \frac{2n_r^2 - 2n_r + 1}{2n_r^2 + 2n_r + 1} = \frac{1 - 1/n_r}{1 + 1/n_r} \approx 1 - \frac{2}{n_r} \quad (\text{B.0.1})$$

For a non transmitting medium, absorption (A)= $1-R$

$$A = 1 - R = \frac{4n_r}{2n_r^2 + 2n_r + 1} \approx \frac{2}{n_r} \quad (\text{B.0.2})$$

If the He implanted layer is more graphitic after annealing then from [201], the refractive index for 500 nm light at room temperature is ≈ 2.6 , hence; $R=0.23$ and $A=0.77$.

A fraction of light incident on the diamond film reflects from the top while some refracts onto the 'top' surface of the graphitic carbon. The refracted light is reflected back to the free surface of diamond where some is transmitted and some fraction reflected back to the 'top' surface of the graphitic carbon again, and the

process is repeated leading to multiple reflections. This process goes on until the light reaches the edge of the diamond film.

The top diamond layer reflects and transmits fractions of the incident light.

$$R = \frac{(n-1)^2}{(n+1)^2} \Rightarrow \frac{(\frac{n_2}{n_1} - 1)^2}{(\frac{n_2}{n_1} + 1)^2} = \frac{(n_2 - n_1)^2}{(n_2 + n_1)^2} \quad (\text{B.0.3})$$

For light incident from air or vacuum, $n_2 \rightarrow 1$, and letting $n_1 \rightarrow n$, the refractive index of diamond.

$$R = \left(\frac{1-n}{1+n} \right)^2 \quad (\text{B.0.4})$$

$$R_{1 \rightarrow n} = R_{n \rightarrow 1}, \text{ similarly } T_{1 \rightarrow n} = T_{n \rightarrow 1}$$

Supposing the medium does ‘not absorb’ any light then $T = (1 - R)$. A schematic diagram of the multiple reflections is shown in figure (B.1),

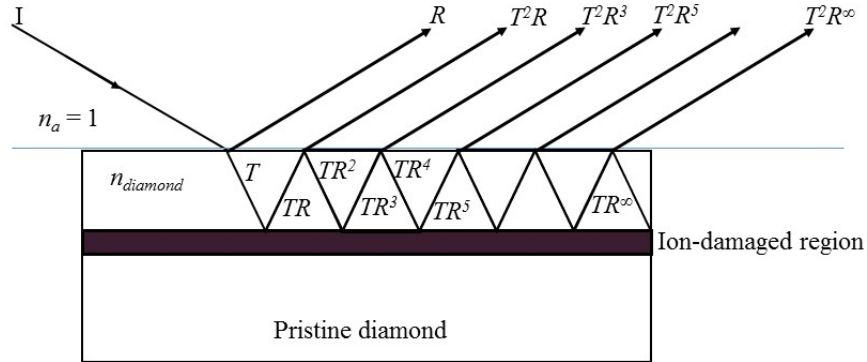


Figure B.1: Multiple reflection of light on the thin diamond film sitting on He ion damaged region

The total reflectance is therefore,

$$\begin{aligned} R_{Total} &= R + T^2R + T^2R^3 + T^2R^5 + \dots + T^2R^\infty \\ &= R + T^2R \{1 + R^2 + R^4 \dots + R^{\infty-1}\} \\ &= R + (1 - R)^2 R \{1 + R^2 + R^4 \dots + R^\infty\} \end{aligned}$$

Expanding the series in $\{\}$ brackets we obtain the total reflectivity.

$$R_{Total} = R + \frac{(1-R)^2 R}{1-R^2} = \frac{2R - 2R^2}{1-R^2} = \frac{2R(1-R)}{(1-R)(1+R)} = \frac{2R}{1+R} \quad (\text{B.0.5})$$

For $R = 0.23$, then $R_{Total} = 0.37$ of the intensity of incident beam.

Appendix C

Deconvoluted Raman graphs

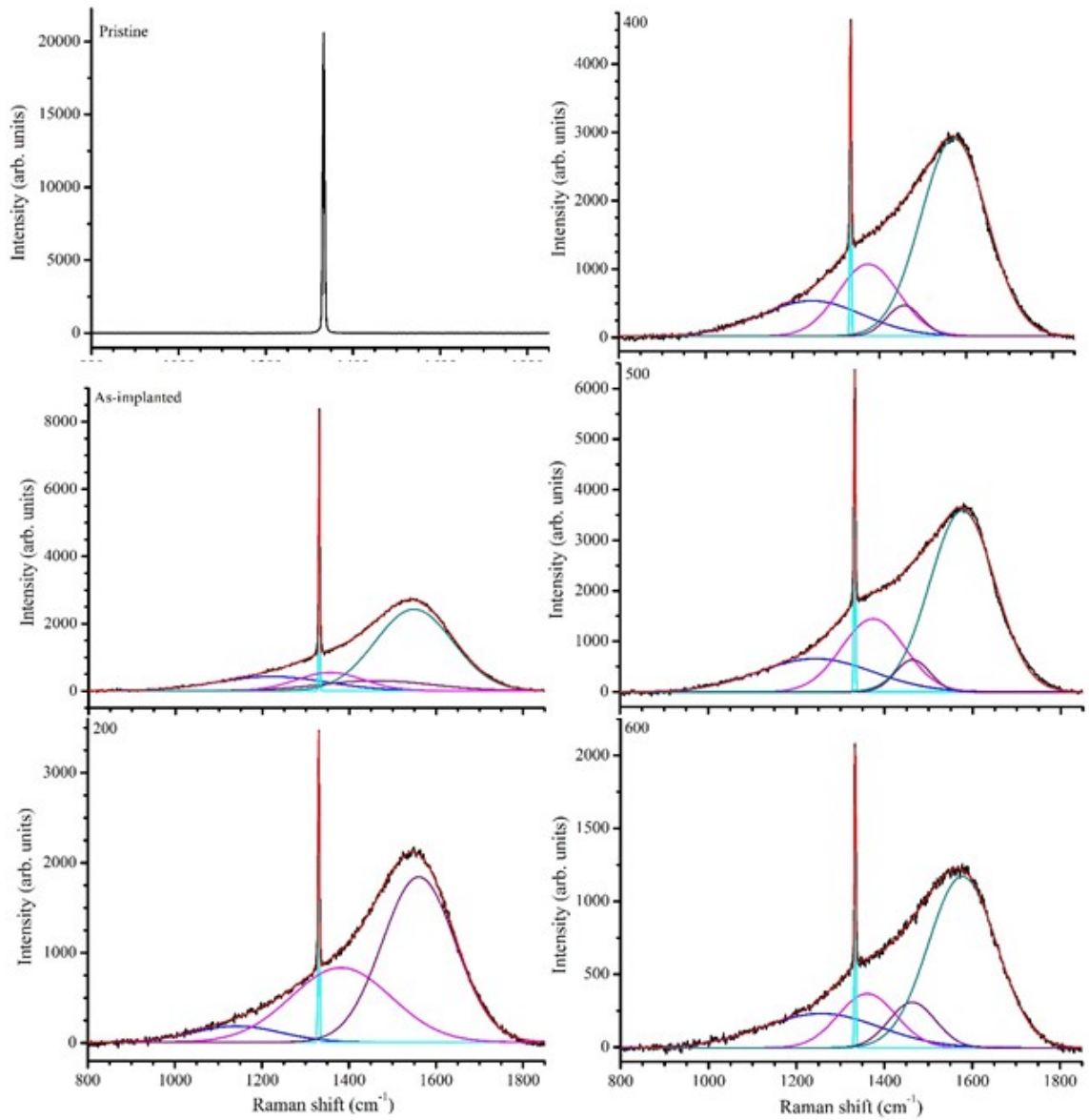


Figure C.1: Raman measurements using single line mode at 514.5 nm from as-implanted to annealing at 600 °C. Pristine diamond shows only one peak at 1332 cm⁻¹

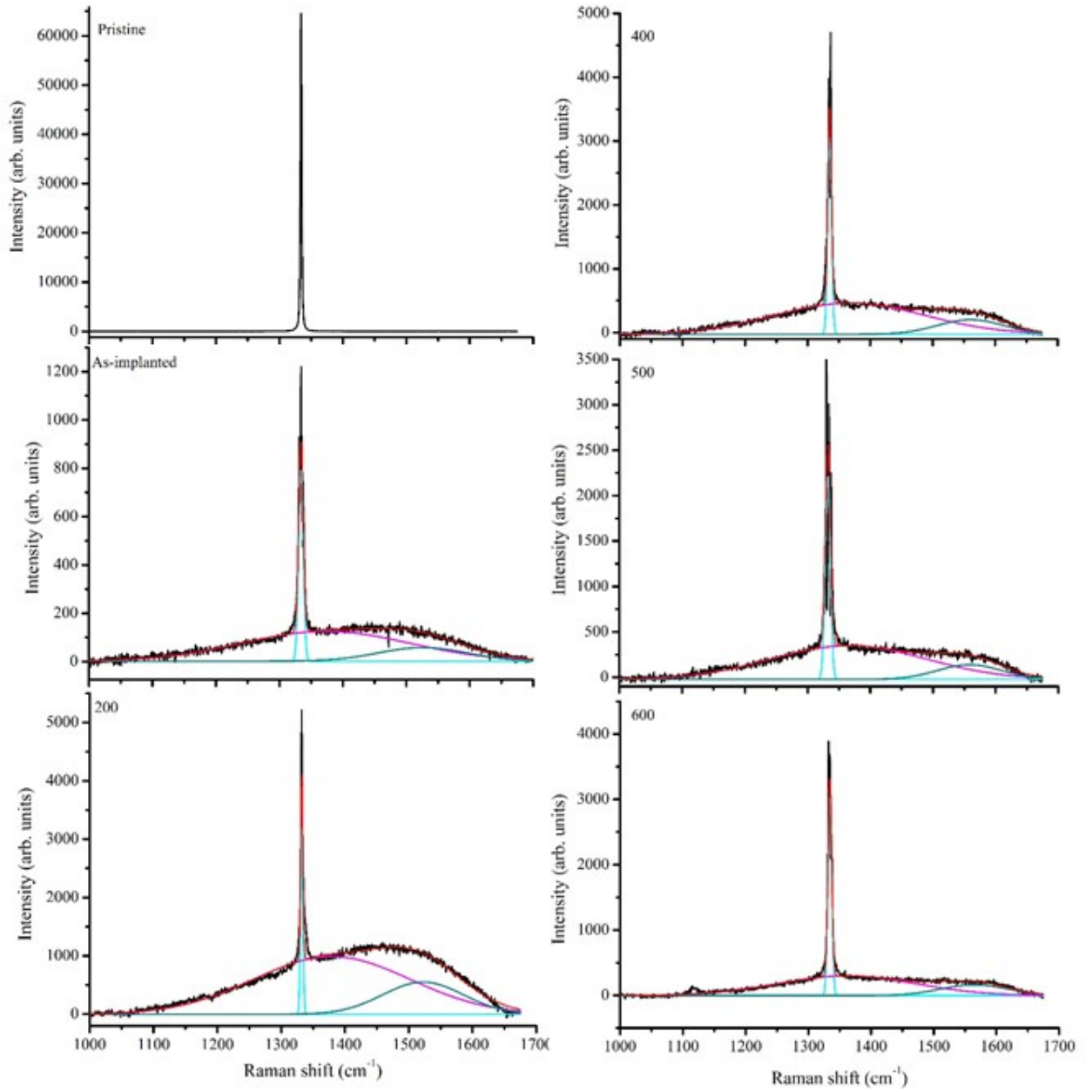


Figure C.2: Raman measurements using single line mode at 785 nm from as-implanted to annealing at 600 °C. Pristine diamond shows only one peak at 1332 cm^{-1} which was suppressed by a factor 8 so as to show the deconvoluted peaks.

Appendix D

Publications and Conference Presentations

D.1 Publications

1. I. Motochi, N. W. Makau, G. O Amolo, B. A. Mathe and S.R. Naidoo, *Ab initio* structural and electronic study of metals on diamond (111)-(1×1)surface, 207-211. *56th Annual Conference of the South African Institute of Physics*, 12-15 July 2011, Pretoria, South Africa.
2. E. Aradi, S.R. Naidoo, D. G. Billing, D. Wamwangi, I. Motochi, and T. E. Derry, Ion beam modification of the structure and properties of hexagonal boron nitride: An infrared and X-ray diffraction study, 140-143. *Nucl. Instr. and Meth. in Phys. Res. B* **331** (2014).
3. I. Motochi, S.R. Naidoo, B. A. Mathe, R. Erasmus, E. Aradi T. E. Derry and E.J. Olivier, Surface Brillouin scattering on annealed ion-implanted CVD diamond *Diam. Relat. Mater* (2015), doi:10.1016/j.diamond.2015.03.022.
4. I. Motochi, B. A. Mathe, S.R. Naidoo, and T. E. Derry, Surface Brillouin scattering in ion-implanted chemical vapor deposited diamond *Materials Today Proceedings* (2015), Submitted.

D.2 Conferences and Conference's Presentations

1. I. Motochi, N. W. Makau, G. O Amolo, B. A. Mathe and S. R. Naidoo, *Ab initio* structural and electronic study of metals on diamond (111)-(1×1)surface.

- 56th Annual Conference of the South African Institute of Physics*, 12-15 July 2011, University of South Africa, Pretoria, South Africa.
2. I. Motochi, *2nd African School on 'Electronic Structure Methods and Applications' (ASESMA 2012)*, 28 May - 8 June 2012, Eldoret, Kenya.
 3. I. Motochi, B. A. Mathe, S. R. Naidoo and T. E. Derry, Brillouin scattering study of ion-implanted chemical vapour deposited diamond. *57th Annual Conference of the South African Institute of Physics*, 9-13 July 2012, University of Pretoria, Pretoria, South Africa.
 4. I. Motochi, *4th CROSS-FACULTY POPSTGRADUATE SYMPOSIUM: Showcasing postgraduate research at Wits*, 19-22 October 2012, Johannesburg, South Africa.
 5. I. Motochi, B. A. Mathe, S. R. Naidoo and T. E. Derry, Back surface influence on surface Brillouin scattering in ion-implanted chemical vapor deposited diamond. *58th Annual Conference of the South African Institute of Physics*, 8-12 July 2013, University of Zululand, Richards Bay, South Africa.
 6. I. Motochi, *5th CROSS FACULTY GRADUATE SYMPOSIUM: Showcasing graduate research at Wits*, 1-2 August 2013, Johannesburg, South Africa.
 7. I. Motochi, B. A. Mathe, S. R. Naidoo and T. E. Derry*, Back surface influence on Brillouin scattering in ion-implanted chemical vapour deposited diamond. *International Conference on Diamond and Carbon Materials*, 2-5 September 2013, Riva del Garda, Italy.
 8. I. Motochi, *9th International Workshop on Adaptive Optics for Industry and Medicine*, 2-6 September 2013, Stellenbosch, South Africa.
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