
Nitrogen Vacancy center in diamond and its application to Quantum Information Processing.



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the degree of Master of Science*

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Declaration

I hereby declare that the work contained in this thesis is my own and has not been submitted for any degree or examination in any other institution of higher learning. Results highlighted and presented from other authors are duly acknowledged and referenced accordingly throughout this present text. This work is being submitted for the degree of Master of Science at the University of the Witwatersrand, Johannesburg.

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Abstract

In recent times the search for reliable quantum systems has gained momentum in the pursuit to establish quantum technologies that surpasses the operational power of their conventional counterparts. This has led to Solid-state based single photon systems to be at the heart of the second quantum revolution. There is great interest in research focusing on structurally embedded color centers in diamond, particularly NV^- centers. It has been shown that the excitation of these color centers generates non-classical states on demand, applicable in quantum information processes, i.e., processes that allow the exploitation of quantum mechanical properties. Due to the robustness of diamond as the host matrix, the reported emission is very stable while the centers exhibit non photo-bleaching effects even after several weeks of constant operation. Consequently, the emission properties of NV^- centers in diamond have been studied extensively over the years and show great promise in the ongoing pursuit of successfully manufacturing functional quantum based technological devices.

However, the proposed center still faces a few obstacles before it can be declared an ideal quantum system to be integrated in current communication systems. In this study, we engineered NV^- centers in well-defined isolated regions within a type IIa CVD diamond sample via ion implantation accompanied by thermal annealing. Photoluminescence spectroscopy was used to monitor the effect of the implanted ions in the diamond, with interest in the 637 nm emission line associated with NV^- centers. Fluorescence microscopy was employed to image the implanted regions to ascertain the positions of any created NV^- centers. The photon distribution of the fluorescence from a single NV^- center can be experimentally characterized to establish the non-classical attributes of the center. For this effect, a study on the HBT light intensity interferometer is largely referenced, which can provide the second-order correlation function ($g^{(2)}(\tau)$).

To my family...

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Contents

Declaration	i
Abstract	ii
Acknowledgements	iv
List of Figures	xv
List of Tables	xvi
1 General introduction	1
1.1 Single photon sources	2
1.2 Why nitrogen vacancy centers?	4
1.3 Outline	7
2 Theory	8
2.1 Nitrogen impurities in diamond	8
2.1.1 Physical properties of diamond	9
2.1.2 Charecterization of diamond types	12
2.1.3 Nitrogen-related point defects	14
2.2 Nitrogen vacancy centers	15
2.2.1 Crystallographic structure of NV centers	17
2.2.2 Photophysical properties of NV centers	18
2.2.3 Absorption and luminescence spectra	20
2.3 C_{3v} point group symmetry	26
2.3.1 Uniaxial stress measurements	26
2.3.2 Group theory	28
2.4 Electronic properties and spin manipulation	32
2.4.1 Optically detected magnetic resonance	34
2.4.2 The fine structure of the ground state of NV^-	35
3 Ion implantation in diamond	38
3.1 Introduction	38
3.2 Ion doping in diamond	38
3.3 Ion-solid interactions	40
3.3.1 Ion implantation	41
3.3.2 Energy-loss process	42
3.3.3 Projected ion range	45
3.3.4 Crystallographic channeling effects	46
3.4 Ion distribution and calculated damage	47
3.4.1 Damage recovery with thermal annealing	49

4	Experimental considerations: instrumentation and sample preparation	52
4.1	Introduction	52
4.2	Experimental equipments	52
4.2.1	The Ion implanter	52
4.2.2	Laboratory tube furnace	54
4.2.3	Photoluminescence spectroscopy	56
4.3	Sample preparation	59
4.3.1	Implantation process	60
4.3.2	PL intensity analysis after ion implantation	61
4.3.3	Annealing	62
4.3.4	PL intensity analysis after implantation and annealing	62
5	Results and discussions	64
5.1	SRIM simulation for N ion implantation	64
5.2	Analysis of the PL spectra of diamond samples	66
5.2.1	Room temperature PL analysis	69
5.2.2	Low temperature (77 K) PL analysis	71
5.3	Discussions	77
6	Optical beam manipulation studies	78
6.1	Introduction	78
6.2	Laguerre-Gaussian and Hermite Gaussian modes.	79
6.3	Experimental modulation of modes	80
6.3.1	Mode modulation using phase holograms	80
6.3.2	Mode modulation using complex amplitude modulation	82
6.4	Experimental Implementation	84
6.4.1	Experimental setup	84
6.4.2	Measurement of mode quality	84
6.5	Discussions	86
7	Optical imaging of NV⁻ color centers	88
7.1	Introduction	88
7.2	Confocal fluorescence microscopy	88
7.2.1	Description	89
7.2.2	Experimental setup	91
7.2.3	Results	95
7.2.4	Discussions	98
8	Summary, Conclusion and recommendations	99
8.1	Summary	99
8.2	Conclusion	100
8.3	Future recommendations	101
	Appendices	102
	A Publication	103
	B Conferences attended and Presentations	104

C	Simulated output for ion and target vacancy production	105
D	Optical characterization of NV^- centers with a $g^{(2)}(\tau)$ function	108

List of Figures

1.1	Optical state transition and photon distribution. (a) Schematic of a two-level state transition from ground ($ g\rangle$) to excited ($ e\rangle$) state, with transition rates t_{ij} (where $i,j = 1-3$). (b) State transition of a three-level system with metastable state in between the $ g\rangle$ and $ e\rangle$ states. (c) The types of photon distribution with antibunched photons in red representing SPSs, while the random and bunched photons are represented by coherent (green) and thermal (blue) sources, respectively. (d) Schematic of an interferometer with a beam splitter, two detectors and a coincidence counter, used to characterize the distribution of photons from a source of light.	3
1.2	Photon antibunching effect. The photon count ($n(\tau)$) as a function of the time delay ($\tau \rightarrow 0$) approaching zero indicates photon antibunching [4].	4
1.3	The photon count rate reported for each diamond based color center. The highest count rate recorded for each diamond based color center in last two decades. The current trend is represented by the dash line. The solid line on top represents the required single photon emission to bridge the gap between the conventional and quantum radiometry [10].	6
2.1	Diamond types due to defects. Different colored diamonds attributable to unique impurities. From left: type Ia pink, type Ia “cape” yellow, type IIa colorless, type IIb blue and type Ib “canary” yellow diamonds [39].	9
2.2	Carbon phase diagram. Regions of metastability of diamond and graphite are bounded by extensions of the diamond and graphite liquidus lines shown as dashed lines [40].	9
2.3	Diamond cubic structure. (a) The face centered cubic (FCC) crystal structure of diamond with 8 carbon atoms per unit cell, with lattice parameter ‘ a_0 ’ of length 3.57 Å. (b)-(d) Represents the diamond lattice structure oriented along the three commonly considered crystallographic planes for a cubic crystal. (b) The lattice structure is perpendicular to (111) plane, while at (b) and (c) the lattice structure is perpendicular to (001) and (110) planes, respectively.	11
2.4	Schematic of diamond atoms and impurities of diamond types. Diamond type classification based on the presence or absence of nitrogen and boron impurities and their configuration in the diamond lattice [39].	13

2.5	Schematic of point defects that are possibly available in diamond. Vacancy (V) and self-interstitials (I) are intrinsic point defects, while foreign atoms (H, Li, N, P, B) can exist either at interstitial or substitutional lattice sites. [52].	15
2.6	Photoluminescence and electronic structure of NV center. (a) Normalized emission spectra of NV center defect with NV^- and NV^0 charged states represented by 637 nm and 575 nm ZPLs, respectively [10]. (b) Electronic schematics of NV^- and NV^0 with the permitted energy transitions.	16
2.7	Crystallographic structure of NV centers. (a) A single NV center in the diamond lattice structure with [111] orientation [10]. (b) Four possible orientations of an NV^- in a diamond lattice with angle between the center's axis and the magnetic field direction represented by $\theta_{\text{NV-B}}$. The brown and green arrow lines represent the orientations of the NV^- axis the in magnetic field [31].	17
2.8	Change in absorption spectra. A comparison between the spectra of (a) and (b) [78]. Immediate change in the absorption spectra of the NV^- center with ZPL at 637 nm at (a), when the irradiation dose is double at (b).	19
2.9	Absorption and Luminescence bands of the NV^-. The comparison of the absorption (solid line) and luminescence spectra (dotted line). The absorption spectra is the mirror image of the luminescence spectra reflected in energy [56].	21
2.10	The Huang-Rhys model in Frank-Condon principle. Schematic of the Frank-Condon principle with harmonic potentials describing the electronic energies (E) of the ground and excited states separated by the nuclear displacement coordinate Q [90].	22
2.11	Jahn-Teller effects on the excited (3E) electronic state. (a) Adiabatic potential energy surface (APES) of the excited state with symmetric displacement coordinates (Q_x and Q_y) for the vibrational mode e . (b) Comparison of the calculated and measured linewidth of the ZPL of the NV^- center as a function of temperature [92]. The solid black line is the T^5 fitting which represents the temperature dependence associated with the optical linewidth [93].	25
2.12	A schematic of the ground state level configuration. (a) The a -orbital is completely filled. The wave function is denoted as $ e_x e_y\rangle$ with a total spin of $ m_s\rangle = -1\rangle$ for 3A_2 state symmetry. (b) Only one of the a -orbitals is completely filled. The wave function is denoted as $ a_1 e_y\rangle$ with a total spin of $ m_s\rangle = -1\rangle$ for 3E state symmetry.	31
2.13	Electronic scheme of the NV center in C_{3v} symmetry with a molecular model. (a) The electronic levels and the electron occupation of the molecular orbitals of the center together with their respective ZPL energy transitions. (b) Molecular orbitals (MOs) associated with the 6-electron model of the center.	33

2.14	Optically detected magnetic resonance measurements. (a) ODMR spectra of a single NV^- center with zero field splittings of spin sub-levels $ m_s\rangle = 0\rangle$ and $ m_s\rangle = \pm 1\rangle$ in between the energy states 3A_2 , 3E [116]. (b) The effect of the orientation axis of NV^- to the ODMR signal [31].	34
2.15	Energy level schematic for NV^- center. The allowed optical and magnetic transitions represented respectively by the radiative (solid arrows) and non-radiative (dashed arrows) transition lines.	36
2.16	The fine structure splittings of both energy levels. (a) and (b) Represents the effect of spin-spin, spin-orbit interactions on the ground (3A_2) and excited (3E) states in the presence and absence of strain [82]. (c) The effect of the transverse strain energy on the fine structure of the NV^- [115].	37
3.1	Band gap states in diamond. The energy states for n-type donors represented by Phosphorus (P 0.6 eV) and Nitrogen (N 1.7 eV) dopants below the conduction band, and a p-type donor represented by Boron (B 0.37 eV) dopant above the valence band.	40
3.2	Ion implantation interaction processes. Illustration of possible defects induced by ion implantation [144].	41
3.3	Dependence of the nuclear and electronic stopping power on the energy of the projected ion. At low energy implants (E_2) nuclear stopping power dominates in stopping the incident ion, while at higher energy implants (E_4) electronic stopping power dominates the stopping of the ion. At E_3 , the nuclear and electronic stopping power are comparable [144].	44
3.4	Gaussian range distribution of implanted ion. The Gaussian distribution of the implanted ion with $R_p = 2.25\Delta R_p$ and full width half maximum (FWHM) of ΔX_p [146].	46
3.5	Range distribution for an ion channeled along (100) axis. The solid line shows the range distribution for a channeled ion in comparison with a Gaussian distribution (dashed line) for an ion undergoing no channeling effects [146].	47
3.6	SRIM calculations for 7 keV nitrogen beam incident on a diamond crystal. Details from calculations with full damage cascades. (a) Depth profile of the N ions. (b) Vacancy distribution due to cascading of C atoms.	48
3.7	SRIM calculations for 7 keV nitrogen beam incident on a diamond crystal. (a) Ion distribution in red with collision cascades of the carbon recoils in green in the Y transverse coordinate. (b) Similar to (a), with only a change in the transverse coordinate to Z.	49
4.1	Photograph of the ion implanter at iThemba LABS. A Varian-Extrion model 200-20A2F.	53
4.2	Schematic diagram of an ion implantation system. A schematic of the ion implanter made up of 5 components: ion source, magnetic particle filter, electrostatic accelerator, beam manipulating system and the end station [162].	54

4.3	A photograph of a Carbolite high temperature horizontal thermal tube furnace. A wire wound tube furnace (CTF 17/300) with a 0°C – 1700°C temperature range.	55
4.4	Schematic of a typical horizontal furnace tube. A diamond sample annealed in a presence of Ar gas enclosed by an RCA high temperature tube [163].	55
4.5	Schematic diagram for band-to-band excitation process. A photon with incident energy (E_i) excites an electron from its ground state energy (E_0) to an excited state (E_e). For $E_i \geq E_g$, photoluminescence generation takes place, with electron and hole donor-acceptor (D→A) emission pair, and emits a photon.	56
4.6	The Horiba Jobin Yvon LabRam HR800 spectrometer. A photograph of an operational Raman/PL spectrometer hardware taking measurements.	58
4.7	Schematic of a Raman spectrometer. Laser light is directed into a specimen by optical components. The resulting fluorescence is dispersed and directed to a CCD detection system for imaging.	59
4.8	Ion implantation process. (a) A single commercially available laser marked diamond plate undergoes an ion implantation process. (b) A Varian-Extrion model 200-20A2F ion implanter. (c) Ion implanted diamond plate with regions A–D for N and 1–4 for C implants.	60
4.9	Photograph of mask used for ion implantation. The mask was made such that the small hole is directly above the center of the diamond, with the holes on the right used for C and N implantation.	62
4.10	A photograph of a Linkam THMS600 cryostat. The cryostat is placed on a lowered micrometer movement (x,y) stage for low temperature PL measurements.	63
5.1	SRIM simulation for the damage and ion depth profiles. The predicted damage on a diamond material caused by N ions with incident implant energy of 7 keV. The depth profile of the damage stretches ~ 21 nm into the material with a damage peak at ~ 7 nm from the surface while the ion depth profile is about ~ 24 nm in the width from the surface with an ion distribution peak at ~ 11 nm. The insert represents the linear relationship between the ion fluence and the vacancy concentration in the simulated damage at the peak of the damage density.	65
5.2	Raman spectra of the investigated diamond. A Raman spectra of an unimplanted region within the diamond sample with a Raman peak of 1332 cm^{-1} from a laser excitation wavelength of 458 nm and 514.5 nm at room temperature. The inset shows the 2nd order Raman ranging from 1950 cm^{-1} – 2750 cm^{-1}	66
5.3	PL intensity spectra of an unimplanted diamond sample. A typical PL spectra of the unimplanted sample with a Raman peak of 551.75 nm from a laser excitation wavelength of 514.5 nm at room temperature. The inset shows a zoomed in PL spectra of the sample in the range of 570 nm–640 nm.	67

5.4	PL spectra for the reference diamond. The z-stack PL spectra for NV^- at six different depths from one spot. The excitation beam is focused from $10\text{ }\mu\text{m}$ below the diamond surface to $5\text{ }\mu\text{m}$ above the surface in six steps.	68
5.5	PL spectra zoomed around NV^0. The PL spectra at room temperature, where the top halve shows the PL spectra for the implanted and annealed sample, while the bottom halve shows the spectra for implanted sample.	69
5.6	PL spectra zoomed around NV^-. The PL spectra at room temperature, where the top halve shows the PL spectra for the implanted and annealed sample, while the bottom halve shows the spectra for the implanted sample.	70
5.7	Low temp. PL spectra of implanted diamond. The PL spectra is normalized to the first-order Raman peak for N implanted regions A–D with increasing fluence. The inset shows a zoomed PL spectra of the sample in the range of 570–640 nm.	71
5.8	Low temp. PL spectra of annealed diamond. The PL spectra is normalized to the first-order Raman peak for N implanted regions A–D with increasing fluence. The inset shows a zoomed PL spectra of the sample in the range of 570 nm–640 nm.	72
5.9	Low temp. PL spectra of annealed diamond. The PL spectra is normalized to the first-order Raman peak for C implanted regions 1–4 with increasing fluence. The inset shows a zoomed PL spectra of the sample in the range of 570 nm–640 nm.	73
5.10	PL spectra of the unimplanted region 1. The PL spectra is normalized to the first-order Raman peak. The inset shows a zoomed PL spectra of the sample in the range of 570 nm–640 nm.	74
5.11	PL spectra of the unimplanted region 2. The PL spectra is normalized to the first-order Raman peak. The inset shows a zoomed PL spectra of the sample in the range of 570 nm–640 nm.	75
5.12	PL spectra of the unimplanted region 3. The PL spectra is normalized to the first-order Raman peak. The inset shows a zoomed PL spectra of the sample in the range of 570 nm–640 nm.	75
5.13	Intensity map (77 K) for NV^- centers after annealing. The intensity map of the $2000\text{ }\mu\text{m} \times 2000\text{ }\mu\text{m}$ sized diamond sample scanning over 51×51 grid points with $\sim 50\text{ }\mu\text{m}$ grid intervals. Relatively strong intensity signals for regions D, while regions C and B exhibit similar weak signals. No NV^- activity for region A. NV^- center activity ranging from weak to strong are also visible from unimplanted regions 1–3.	76
6.1	Theoretical 2D instensity profiles of LG_p^ℓ and HG_{nm} modes. Intensity distribution of (a) LG modes with $l = [0, 1, 2, 3, 4]$, $p = [0, 2, 3]$ and (b) HG modes with $n = [0, 1, 2, 3]$ $m = [0, 1, 2]$	80

6.2	Digital holograms, phase and amplitude for LG_p^ℓ and HG_{nm} modes. The first row shows the amplitude while the corresponding phase profiles are given in the second row. Phase only and complex-amplitude modulation (CAM) holograms shown in the third and fourth row, respectively were encoded on the SLM to generate (a) LG_p^ℓ and (b) HG_{nm} modes.	81
6.3	Mode modulation concept. (a) A laser beam impinges on an SLM screen encoded with a hologram where the modulated beam is reflected in the 1st diffraction order. (b) Holograms with unique carrier frequencies (grating) are separately encoded on to the SLM. (c) The unique carrier frequencies correspond to a specific spatial position, on the Fourier plane, of the encoded modes as shown in.	82
6.4	Schematic representation of a mode generation setup. A laser beam ($\lambda = 532$ nm) is expanded using a $10\times$ microscope objective (MO) and a collimating lens L_1 on to a reflective spatial light modulator (SLM) where a hologram generating LG_p^ℓ (2 & 3) and HG_{nm} (1 & 4) modes is displayed. The desired modes are generated in the focal plane of the Fourier lens L_2 (Screen) with unique spatial positions. . .	85
6.5	Mode purity measurements using correlation. Experimental and theoretical intensity profiles of LG_p^ℓ and HG_{nm} modes with corresponding correlations values C (top row). Cross-sectional intensity profile along the dashed line comparing theory and experiment (bottom row). Notice how the correlation values decrease as the mode complexity increases.	85
6.6	Comparison of beam geneation techniques. The top row shows the theoretical intensity profile of LG_p^ℓ (left) and HG_{nm} (right) modes. Second and third row show experimental intensity profiles of phase only and complex amplitude modulation (CAM), respectively. Notice that CAM allows for higher correlation values.	86
7.1	Schematic of a typical confocal microscope system. Excitation beam (purple) from a laser source enters a confocal system through an illumination pinhole and is reflected by a dichroic mirror onto an objective lens that focuses the beam onto a specimen. The scattered light is reflected back through the lens where only the excited light (green and pink) is allowed to pass through the mirror while the background light is reflected. The confocal pinhole blocks out of focus light (pink) and allows only light (green) from the focal plane to go through to a detector [230].	90
7.2	Schematic of conjugate planes. A combination of the focal point of the lens and a pinhole placed before the detector. The pinhole is dubbed as a “confocal” pinhole because it is conjugate to the focal point of the lens.	91

7.3	Schematic of a confocal fluorescence microscopy. A. A laser propagates and impinges onto a reflective SLM screen that can be modulated to modify the propagating angle of the laser beam. B. The generated modes are directed into a confocal imaging configuration system where the diamond sample is excited. C. The resultant fluorescence is detected by a CCD camera where the results are processed by a computer.	92
7.4	Confocal scanning process with SLM. (a) Schematic of a confocal scanning process. A modulated beam provides optical excitation in a small NV center active area of the sample at a time (NB. not multiplexing). (b)–(c) Horizontal and vertical cross-sections at $x \approx 98$ and $y \approx 98$, through maximum which are fitted with a Gaussian. The FWHMs (half width at $1/e^2$) are 9 pixels, respectively, which corresponds to a beam waist of $\sim 0.72 \mu\text{m}$. (d) Excitation beam focused through a microscope objective ($100\times$, $\text{NA}=1.3$). The beam size is about 9 pixel $\times$ 9 pixel on proximity to the diamond surface. . .	93
7.5	Wide-field fluorescence microscopy. A bright-field image overlapped with a fluorescence image of the reference diamond taken by a $10\times$ objective. The bottom scan clearly shows the mark from the bright-field image while the top scan shows the opposite side of the same position.	95
7.6	Confocal microscopy scan of NV center active region. RGB intensity plots of a NV center active region (38 pixel $\times$ 28 pixel). The scan is focused at $z = 4 \mu\text{m}$ above the diamond sample.	96
7.7	Confocal microscopy scan of NV center active region. RGB intensity plots of a NV center active region (38 pixel $\times$ 28 pixel). The scan is focused at $z = 0 \mu\text{m}$ in proximity to the diamond sample. . . .	96
7.8	Confocal microscopy scan of NV center active region. RGB intensity plots of a NV center active region (38 pixel $\times$ 28 pixel). The scan is focused at $z = -4 \mu\text{m}$ within the diamond sample.	96
7.9	Confocal microscopy scan of NV center active region. RGB intensity plots of a NV center active region (38 pixel $\times$ 28 pixel). The scan is focused at $z = -8 \mu\text{m}$ within the diamond sample.	97
7.10	Confocal microscopy scan of NV center active region. RGB intensity plots of a NV center active region (38 pixel $\times$ 28 pixel). The scan is focused at $z = -12 \mu\text{m}$ within the diamond sample.	97
7.11	Confocal microscopy scan of NV center active region. RGB intensity plots of a NV center active region (38 pixel $\times$ 28 pixel). The scan is focused at $z = -16 \mu\text{m}$ within the diamond sample.	97
D.1	Second order correlation function ($g^{(2)}(\tau)$). (a) Second-order correlation characteristic curves for classical, coherent and single photon sources. (b) $g^{(2)}(\tau)$ function depicted via a beam splitter with reflected and transmitted intensities describing the probability of a single event.	109

D.2	An emission and excitation three-level system. (a) A jablonski diagram with excitation and emission rates k_{ij} (where $i, j = 1 - 3$) for ground state $ 1\rangle$, excited state $ 2\rangle$ and a metastable state $ 3\rangle$. (b) $g^{(2)}(\tau)$ function with antibunching effect at $\tau = 0$ together with a bunching at finite time delay [235].	110
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List of Tables

1.1	The optical properties of known single photon sources in diamond [10].	4
2.1	The optical, mechanical and thermal properties of diamond [40]. . . .	10
2.2	Categorization of diamonds based on sample characteristics [35, 37]. .	12
2.3	Wave functions and the state symmetry for the electronic configurations e^2 and ae of the center [107].	30
2.4	Irreducible representations of the group C_{3v} . [107].	31
4.1	Initial dose and energy to be used for irradiation.	60

List of Symbols and Abbreviations

τ	Time delay	$n(\tau)$	Photon count
$g^{(2)}(\tau)$	Second-order correlation function	$\hat{a}$ & $\hat{a}^\dagger$	Annihilation & creation operators
ΔS	Stokes shifted excitation	ΔAS	Anti-Stokes shifted decay
H_{es}	Effective Hamiltonian	H_{gs}	Spin Hamiltonian
APES	Adiabatic Potential Energy Surface	LG	Laguerre Gaussian
BCA	Binary Collision Approximation	MO	Microscope Objective
CAM	Complex Amplitude Modulation	MOs	Molecular Orbitals
CCD	Charged Coupled Device	NA	Numerical Aperture
CIRA	Cold Implantation Rapid Annealing	NDs	Nanodiamonds
CTF	Carbon Tube Furnaces	NV	Nitrogen Vacancy
CVD	Chemical Vapor Deposition	N_s	Substitutional Nitrogen
CW	Continuous-Wave	OD	Optically Density
CCD	Charged Coupled Device	ODMR	Optically Detected Magnetic Resonance
CWL	Center Wavelength	OM	Optical Microscope
DMDs	Digital Micromirror Devices	PFO	Plan Fluorite Oil Immersion Objective
EPR	Electron Paramagnetic Resonance	PL	Photoluminescence
ESR	Electron Spin Resonance	PMT	Photon Multiplier Tube
FCC	Face Centered Cubic	PSBs	Phonon Sidebands
FM	Fluorescence Microscope	QIP	Quantum Information Processing
FWHM	Full Width at Half Maximum	RCA	Recrystallized Alumina
HBT	Hanbury-Brown & Twiss	RGB	Red Green Blue
HG	Hermite Gaussian	SLM	Spatial Light Modulator
HPHT	High-Pressure High-Temperature	SPDC	Spontaneous Parametric Down Conversion
IR	Infrared	SPS	Single Photon Source
IRs	Irreducible Representations	SRIM	Stopping and Range of Ions in Matter
LCAO	Linear Combination of Atomic Orbitals	TRIM	Transport Ions in Matter
LCD	Liquid Crystal Display	UV	Ultraviolet
LCoS	Liquid Crystal on Silicon	ZPL	Zero Phonon Line

Chapter 1

General introduction

From the 1600s through to the early 1900s, the nature of light intrigued philosophers and scientist alike. Beginning with the first generation of known scientists that dealt with the matter such as René Descartes Sabra [1] until the golden era of science led by many brilliant scientists such as the highly regarded physicist, Albert Einstein [2]. Separated only by a quarter of a millennia, the great mystery which light was before became scientifically elucidated and it birthed into science the modern theory of light with great discoveries to follow. And this timeless discussion would also become the epitome of the progressive nature of collaborative research. Debates of whether light is a wave or is made up of energy particles was quenched, but not without fundamental breakthroughs to modern optics and Physics in general. Young's double slit experiment described delicately the wave nature of light, while Max Planck's quantization of an electromagnetic field as a precursor to the photoelectric effect vindicated the particle nature of light, bringing into existence what would later be called the wave-particle duality of light [2, 3].

At this stage, there was a consensus to the existence of some form of energy carrying particles that also exhibit wave-like properties. This was due to the widely accepted postulation that electrons gained energy from electromagnetic radiation in the form of energy packets which would later be called photons. But there was no substantial physical evidence except for the effects due to light when in contact with matter. That was not until the 1970s, when photon bunching experiments began [4]. Consequently, the duality paradox, brought about immense progress in research and technological developments associated with modern optics. This was referred to as the *the first quantum revolution* [5]. The continuous advancement of Quantum Physics, brought about many significant inventions such as computer chips, information processors, solar cells, lasers, etc. Lasers in particular, together with the underlying principles of quantum mechanics incidentally introduced quantum optics. This stimulated scientific expectations within the science community in the form of engineering quantum based technologies which in principle surpasses the operational power of conventional technologies.

This batch of upcoming devices based on quantum processes is part and parcel of what is currently dubbed *the second quantum revolution*. The computation and processing of information via a two-level quantum system - qubit (basic unit for quantum communication), otherwise referred to as quantum information processing (QIP), is one of such technologies and is heavily reliant on spontaneous emitted light-photons. Such a process allows the exploitation of certain properties of quantum

mechanics such as the superposition and entanglement of arbitrary quantum states, with no possibility of perfectly cloning any of them if the states are unknown [6]. Collectively, this basically implies that a distinct and unknown quantum state can exist as a sum of two or more unique states that cannot be described independently nor duplicated. These unique properties were typically used to establish the science of quantum-based communication (i.e., Quantum Cryptography–QC), which is inherently secure as compared to conventional classical communication. The need for security in modern communication networks has been studied extensively over the years, consequently leading to the development of QC in the 1960s by Stephen Wiesner when he introduced the concept of conjugate coding [7]. However, the first experimental breakthrough came years later when Bennett et al. [8], realized that photon states do not store information but rather transmits it. They introduced and implemented a secure key distribution method for secure communication known as the **BB84** protocol. The BB84 quantum key distribution (QKD) scheme details how two parties (Alice and Bob) can share a private key via a single photon which a third party eavesdropper (Eve) cannot gain any information of without disturbing the transmission, and hence being noticed by Alice and Bob. Thus, the establishment of such secure communication links also relies on the generation of single photons (i.e., single photon sources–**SPSs**). This thesis covers the nature, properties and reliability of one of the few known available SPSs.

1.1 Single photon sources

A single photon source (SPS) is essentially a light source that emits a single photon state per excitation, resulting in spatially distributed photons with desirable time intervals between them [10]. The formulation of such a distribution can only be quantified within the framework of quantum mechanics. Intuitively, it is a two-level transition system, as seen in Fig. 1.1 (a), with ground ($|g\rangle$) and excited ($|e\rangle$) states. The system undergoes $|g\rangle \rightarrow |e\rangle$ state transitions upon optical excitation, and emits a photon at a time as it relaxes back to $|g\rangle$. And hence, such states inherently exhibit antibunching effects [4], as opposed to coherent and thermal sources where photons can arrive in bunches, depicted in Fig. 1.1 (c). The antibunching effect implies that in an interferometer experimental setting consisting of a 50/50 beam-splitter with two detectors, only one detector can register an event at a given time, resulting in no coincident events at both detectors [11], and it is this very process that affirms the physical potential of light being employed as the most crucial component to building secure communication systems. Realistically, most quantum emitters are three-level systems, depicted in Fig. 1.1 (b), and hence possesses additional levels with additional correlation in intensity of the fluorescence.

In the 1970s, the first photon antibunching effect was experimentally verified from the fluorescence of single atoms [4]. This resulted in an extended search for new and reliable SPSs. At present, there are numerous well-studied schemes that generate single photons. Kimble et al. [4], was the first scientist to demonstrate that the fluorescence of sodium atoms in an atomic laser is indicative of a two-level quantum system with antibunching effects, depicted in Fig. 1.2. Antibunching was also experimentally confirmed by Diedrich and Walther [12], who presented the non-classical nature of light from the fluorescence of single ions and showed how the antibunching signal decreases with an increase in ions. But the complexity

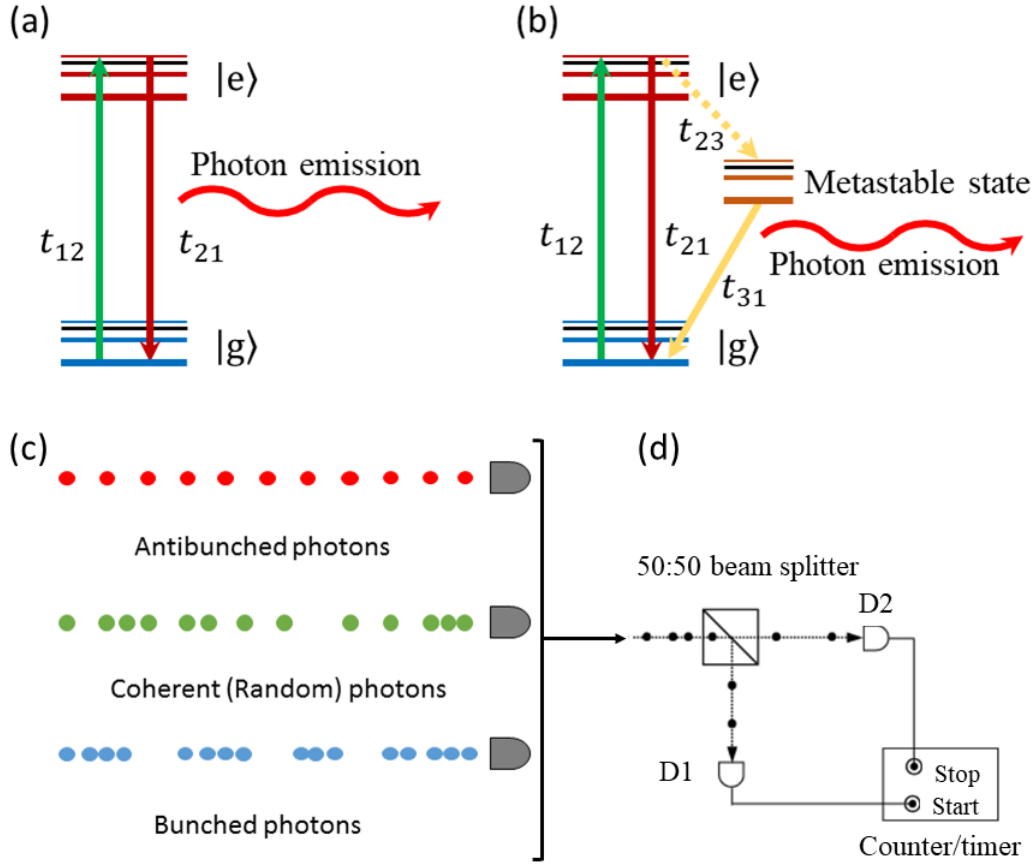


Figure 1.1: **Optical state transition and photon distribution.** (a) Schematic of a two-level state transition from ground ($|g\rangle$) to excited ($|e\rangle$) state, with transition rates t_{ij} (where $i, j = 1-3$). (b) State transition of a three-level system with metastable state in between the $|g\rangle$ and $|e\rangle$ states. (c) The types of photon distribution with antibunched photons in red representing SPSs, while the random and bunched photons are represented by coherent (green) and thermal (blue) sources, respectively. (d) Schematic of an interferometer with a beam splitter, two detectors and a coincidence counter, used to characterize the distribution of photons from a source of light.

of such experiments proved to be a challenge in terms of integrating into current communication systems. Experiments by Lounis and Moerner [13], showed that the excitation of highly fluorescent molecules, commonly known as dye molecules generate a high rate of single photons with just a simple experimental setup. But the emission events of the molecules degrade rapidly with time due to photo-bleaching [13, 14]. Another promising prospect for yielding single photons on demand is quantum dots (QDs). Santori et al. [15], studied and reported that QDs show strong antibunching with polarized emissions. But the low coherence times together with insufficient generation of indistinguishable photons seemed to be the leading obstacle for QDs. Fluorescence from carbon nanotubes was also investigated by Högele et al. [16], and showed antibunching under cryogenic conditions. Many more other promising schemes such as spontaneous parametric down conversion (SPDC) systems were also investigated with the use of nonlinear crystals [17]. However, the above mentioned schemes for SPSs are at present impractical for secure communication processes. But, there are alternative color centers which are easily accessible in diamond that currently show plenty of promise, operating even at room temperature [10].

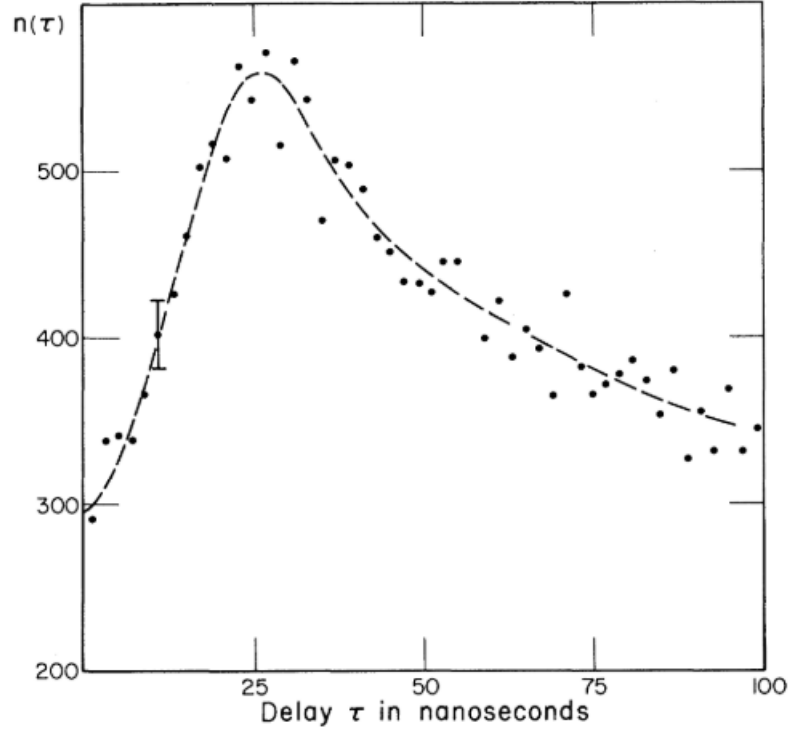


Figure 1.2: **Photon antibunching effect.** The photon count ($n(\tau)$) as a function of the time delay ($\tau \rightarrow 0$) approaching zero indicates photon antibunching [4].

1.2 Why nitrogen vacancy centers?

Diamond is home to a host of luminescent defects and to date, only a few can be characterized as single photon emitters, including nickel and chromium related complexes, silicon vacancy centers (SiV) and nitrogen vacancy centers (NV). The properties of each known diamond based color center is shown in Tab. 1.1 [10] below:

Table 1.1: The optical properties of known single photon sources in diamond [10].

Description	ZPL (nm)	FWHM (nm)	Lifetime (ns)	Count rate (count s ⁻¹)	Quantum efficiency
TR12 in bulk diamond	470	NA	~ 3.6	NA	NA
NV ⁻ in bulk diamond	637	~ 100	~ 11	1.7×10^5	0.7
NV ⁻ in nanodiamonds	637	~ 100	~ 20	3×10^5	NA
Unidentified center	734	4	~ 13.6	1.8×10^6	NA
SiV bulk diamonds	738	~ 10	~ 1.1	1×10^3	0.05
SiV nanodiamonds	738	~ 10	~ 1.1	4.8×10^6	NA
Cr in bulk diamond	749	~ 4	~ 1	0.5×10^6	0.29
Cr in nanodiamonds	756	~ 11	~ 3.5	3.2×10^6	>0.9
Ni/Si in bulk diamond	768	~ 5	~ 2	20×10^4	NA
Ni/Si in nanodiamonds	773	~ 3	~ 1.1	77×10^3	NA
NE8 in bulk diamond	803	~ 2	~ 1.1	75×10^3	0.7
NE8 in nanodiamonds	793	~ 2	~ 2	35×10^3	NA

Gaebel et al. [18], reported the generation of single photons from nickel nitrogen complex (NE8) centers in diamond with a narrow bandwidth of ~ 1.2 nm and quantum efficiency close to 70 %. The emission count rate of the center in bulk diamond was reported to be about 75×10^3 count/s, emitting light at near infrared (~ 800 nm), which is suitable for telecommunication fibers. However, the emission wavelength depends on the host matrix as seen in Tab. 1.1. Wang et al. [19], also reported single photon emission from the fluorescence of silicon vacancy (SiV) centers embedded in diamond via ion implantation. The SiV defect also possesses a narrow emission bandwidth of about ~ 5 nm with a zero phonon line (ZPL) at 738 nm. The investigated SiV center showed very weak photoluminescence intensities with low emission rates close to 1×10^3 counts/s for bulk diamond, possibly influenced by nonradiative transitions. The SiV defects in high-quality CVD nano-diamonds have shown significant improvement of the photon emission count rate to about 4.8×10^6 count/s [20].

An unidentified but highly efficient diamond based SPS has been documented by Simpson et al. [21]. The center has an exceptionally high photon count rate of $\sim 1.8 \times 10^6$ counts/s and a narrow spectral emission of 4 nm while also emitting light at near infrared (~ 734 nm) with a short excitation lifetime of ~ 13.6 ns. The color center behaves as a true two-level system, increasing the efficiency of the single quantum system. However, the atomic structure of the center is still unknown with suggestions that the center lies in the mixture of the constituents present in the diamond reactor during growth, i.e., N, Ni, Si and H atoms. Naydenov et al. [22], also reported on a single photon generating carbon interstitial-related (TR12) color center in diamond, emitting in the blue spectral region (470.5 nm). The center is created by high energy irradiation of type IIa and type IIb diamond. However, currently there is limited information regarding the photophysical properties of TR12 color centers to be considered as serious candidates for QIP applications.

Aharonovich et al. [23], recently reported photon-bunching effects from CVD grown chromium (Cr)-related diamond defects. Similar to NE8, the emission wavelength of these defects also depend on the host matrix, i.e., bulk diamonds (749 nm) and nanodiamonds (756 nm). The center exhibits a strong emission count rate of about $\sim 3.2 \times 10^6$ photons/s with quantum efficiency greater than 90 % in nanodiamonds and an excited lifetime close to 14 ns [24]. Kurtsiefer et al. [25], also reported a stable single photon emission from NV^- centers in diamond with emission wavelength at 637 nm. The emission lifetime of the center embedded in bulk diamond was found to be about ~ 11 ns with a relatively high emission count rate of 1.7×10^5 count/s and 3×10^5 count/s for bulk and nanodiamonds, respectively [26].

The controlled fabrication processes of most of these defects mentioned above coupled with either or both short excited lifetimes $\tau \rightarrow 1$ ns or low quantum efficiencies (<30 %), proves to be a challenge, and hence limits the practical application to QIP.

However, nitrogen vacancy centers appear to be at present the best candidate for QIP applications, owing to its overall photophysical properties presented in Tab. 1.1, with short excited lifetimes (>10 ns), suitable emission count rates, above average quantum efficiencies with well-studied malleable fabrication processes. Moreover, the properties of the NV center are well known and have been studied for well over 5 decades, of which most will be elucidated in the duration of this thesis. The wide bandwidth of over a 100 nm appear to be one of the few drawbacks associated

with the NV center. A narrow bandwidth is necessary to increase the spectral yield for applications. Considering the Purcell effect for emission enhancements, studies have shown encouraging results by coupling the center into fiber-based microcavities [27, 28]. During fabrication processes, the color centers can be localized and spatially distributed within the host matrix, which allows individual addressability with excitation lasers [29]. The structural integrity of the diamond matrix seemingly offers a photo stable environment for these defects, with optimum operation even at room temperature. Figure 1.3, shows the gap between the conventional and quantum radiometry that must be filled in order to fully achieve a functional solid-state based quantum emitter [10].

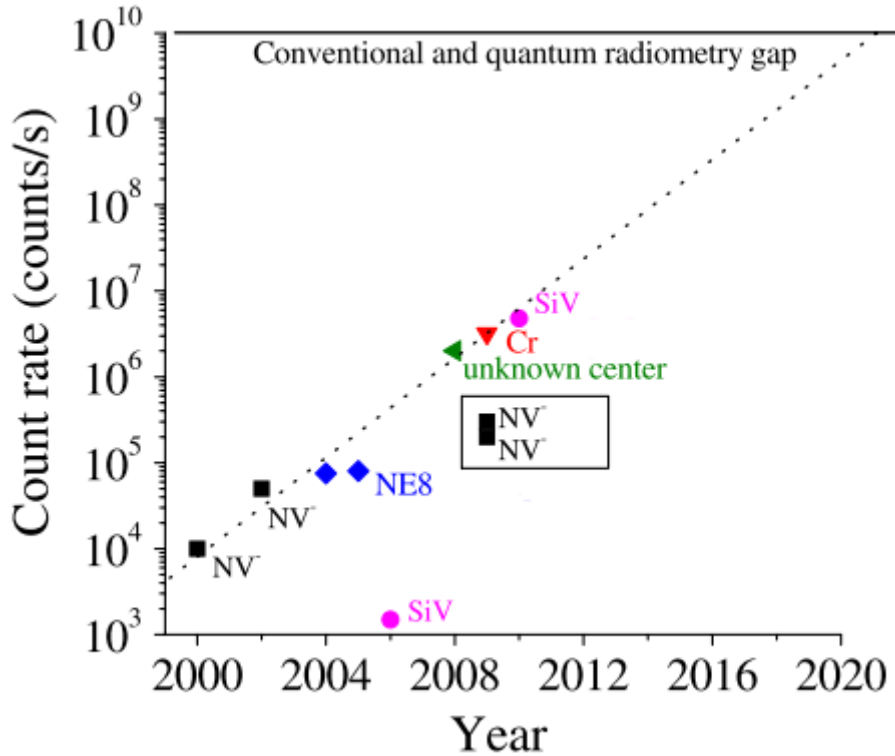


Figure 1.3: **The photon count rate reported for each diamond based color center.** The highest count rate recorded for each diamond based color center in last two decades. The current trend is represented by the dash line. The solid line on top represents the required single photon emission to bridge the gap between the conventional and quantum radiometry [10].

The electronic properties of NV centers indicate a three-level quantum system with suitable attributes for a qubit: a triplet ground state with long coherence spin states to manipulate the qubit with optical transitions in the visible [30]. To date, the realization of QIP via NV centers has seen much progress. Distinct fabrication techniques together with electron spin resonance measurements have established fourfold increase in the optical readout from a single NV center [31, 32]. The optical readout from a single center has been utilized to perform optical and microwave qubit gate operations [33]. Electron spin coherence times exceeding 1 ms at room temperature have been observed [34]. The coupling of NV centers to waveguides and microcavities has shown incredible enhancement to the emission count rate [27, 28]. It is apparent that with the diamond-based NV center, it is only a matter of time to

achieving a fully operational, stable and reliable SPS.

1.3 Outline

The aim of this thesis is to investigate if NV^- center active regions within a CVD grown synthetic type IIa diamond sample, created by ion implantation can be from spatially isolated NV^- centers. We will look at various independent processes: from ion implantation, spectral analysis for detection of NV centers to imaging of samples via a home-built confocal microscopy. This will lead to the establishment of procedures which will guarantee in house production of NV^- . This thesis follows the undermentioned structure:

- **Chapter 2**, Background study based on nitrogen related defects associated with the different types of diamonds. And we investigate the properties of NV centers, particularly the negatively charged NV center (NV^-): The techniques involved in fabrication of single NV^- centers together with the optical and electronic detection processes.
- **Chapter 3**, The ion doping technique suitable for this particular project. A thorough consideration will be given to the ion and solid interaction processes required to successfully fabricate a controlled concentration of NV centers in diamond, while also giving an overview of the SRIM simulation package used in this study.
- **Chapter 4**, Experimental techniques involved with the engineering of NV centers and photoluminescence of the centers. This include the ion implantation process and its suitability for a type IIa CVD diamond (Nitrogen concentration < 5 ppm). The effects of annealing of the diamond sample and the detection of the zero phonon lines (ZPLs) associated with both NV centers.
- **Chapter 5**, Results obtained for the fabrication of NV centers. This include the analysis of an ion implanted and thermally treated diamond sample by employing photoluminescence characterization techniques to substantiate the dynamic attribute of the defects involved in the formation of NV centers.
- **Chapter 6**, The study of optical techniques for scanning processes. Optical pumping involving computer controlled spatial light modulators (SLM) for the modulation of coherent laser beams with holograms will be discussed and demonstrated.
- **Chapter 7**, Fluorescence microscopy techniques that can be used to image NV color centers. A home-built confocal microscope is employed to demonstrate single scanning of the diamond sample with holographic techniques. The data processing of the image information gathered by a suitable detector is included.
- **Chapter 8**, Summary and conclusion of the results obtained. A brief discussion of the future work based on the enhancement of NV center detection in imaging techniques for applications in QIP.

Chapter 2

Theory

In this chapter we provide a theoretical background related to this study. Firstly, we discuss the physical and atomic structure of diamond, together with the characterization techniques used for all the diamond types. This includes a discourse on the optical properties of diamond with respect to the numerous well-studied impurities that are found in the diamond matrix, particularly nitrogen and vacancy defects leading up to a combination of the two defects, which is simply the formation of a nitrogen vacancy (NV) center defect. The second section, mainly focuses on the photo-physical properties specifically associated with NV centers, including the crystallographic structure of a NV center and its related optical properties. In the third section, we discuss the electronic properties and the point group symmetry of the NV center by making use of *ab initio* uniaxial stress and group theory studies. Lastly, we give a detailed discussion based on the magnetic properties of NV centers with the spin-Hamiltonian related to the electronic structure of the centers.

2.1 Nitrogen impurities in diamond

Adámas which in part means ‘invincible’ in ancient Greek, is one of several common translations for diamond which is befitting for a gemstone of its near indestructible and scenic physical properties. Diamond is renowned for its beauty and representation of wealth, showcasing its superlative nature with a variety of colors when viewed under a source of light. It has been well established that these colors are attributable to the presence of impurities or defects infused within the lattice structure of the diamond crystal [35]. In principle, a pure diamond should be optically isotropic (i.e., a clear colorless crystal) due to its 5.47 eV wide energy band-gap [36, 37]. But in reality we have more than 500 known color centers in diamond caused by the presence of extrinsic atoms including nitrogen, boron, nickel, cobalt, hydrogen, titanium, chromium, zinc, silicon, tungsten, silver and thallium atom impurities [38, 39], infused within the crystal lattice structure of diamond. Moreover, each color center gives diamond unique optical and physical properties, some of which are fundamental in several branches of Physics [39]. The centers emit radiation across the spectrum, from ultraviolet to far infrared. Unlike any other material, diamond is rich in optical centers such that even individual color centers can be detected and addressed at room temperature. These individual color centers are often referred to as artificial atoms and studied as an independent quantum system that is capable of generating single photons on demand.

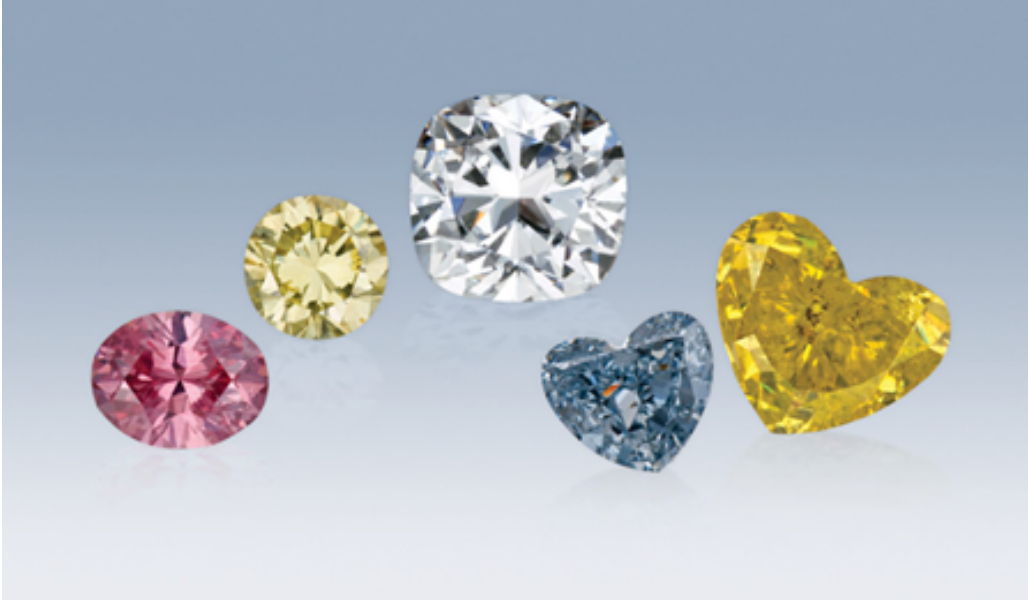


Figure 2.1: **Diamond types due to defects.** Different colored diamonds attributable to unique impurities. From left: type Ia pink, type Ia “cape” yellow, type IIa colorless, type IIb blue and type Ib “canary” yellow diamonds [39].

2.1.1 Physical properties of diamond

A diamond is a carbon-based material with atoms covalently bonded within its matrix structure and it is chemically inert. It is the hardest known bulk material on earth with a very high thermal conductivity of $\sim 25 \text{ W cm}^{-1} \text{ K}^{-1}$.

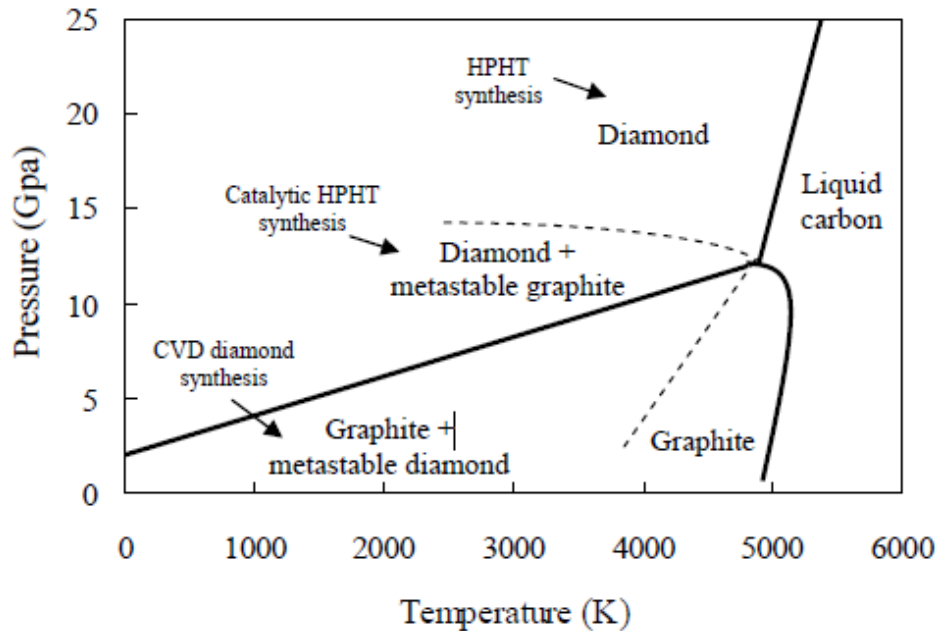


Figure 2.2: **Carbon phase diagram.** Regions of metastability of diamond and graphite are bounded by extensions of the diamond and graphite liquidus lines shown as dashed lines [40].

Diamond along with graphite are the most studied and well-known allotropes

of carbon (see Fig. 2.2). Allotropy is the structural rearrangement of a principal atom to form different materials with unique properties. Diamond is one of many revered semiconductor materials, mainly due to its excellent mechanical properties and extreme physical prowess in luster, hardness, high Debye temperatures and optical transparency amongst other properties, some of which are shown in Tab. 2.1, integral in various industrial applications and jewelry markets. Diamond owes its unique properties to the simple and regular arrangement of carbon atoms within its crystal lattice, i.e., the three-dimensional and highly symmetrical arrangement of atoms inside a material, influencing the underlying properties of that material. The diamond structure is sp^3 hybridized with each atom covalently bonded to four other carbon atoms via sigma ($\sigma = 1.54 \text{ \AA}$) bonds, with equal angles ($\beta = 109.4^\circ$) between them. The lattice structure of diamond is therefore crucial, in this case to fully investigate the properties of diamond.

Table 2.1: The optical, mechanical and thermal properties of diamond [40].

Properties of diamond	
Lattice structure	Cubic
Space group	$Fd\bar{3}m-O_h^7$
Lattice parameter (a_0)	$3.567 \text{ \AA}$
Density	3.515 g/cm^3
Thermal conductivity	$\sim 25 \text{ W cm}^{-1} \text{ K}^{-1}$
Debye temperature	1860 K
Melting point (12.4 GPa)	$4440 - 4773 \text{ }^\circ\text{C}$
Energy band gap (E_g)	5.47 eV
Raman frequency	1332 cm^{-1}
Index of refraction (visible)	2.4
Electron mobility (300 K)	$1800 \text{ cm}^2/(\text{V} \cdot \text{s})$
Hole mobility (300 K)	$1500 \text{ cm}^2/(\text{V} \cdot \text{s})$
Atomic density	$1.77 \times 10^{23} \text{ cm}^{-3}$
Bulk modulus	$45 - 5.5 \times 10^{11} \text{ Nm}^{-2}$
Dielectric constant (300 K, low frequency)	5.70
Thermal expansion coefficient (300 K)	$\sim 1 \times 10^{-6} \text{ K}^{-1}$
Velocity of sound	$\sim 1.96 \times 10^5 \text{ cm s}^{-1}$

The cubic lattice structure of diamond is formed by unit cells periodically arrayed and stacked together, described by a face centered cubic (FCC) point lattice structure in which each site has a two atom basis, with one located at $(0\hat{x}, 0\hat{y}, 0\hat{z})$ and the other at $(\frac{1}{4}\hat{x}, \frac{1}{4}\hat{y}, \frac{1}{4}\hat{z})$, where $\hat{x}$, $\hat{y}$ and $\hat{z}$ are orthogonal unit vectors [41]. The structure is depicted in Fig. 2.3 (a). The unit cells consist of lattice sites housing carbon atoms, with each carbon atom surrounded by four other carbon atoms to form a tetrahedral geometry. Each unit cell has 8 atoms from 18 lattice sites with 14 shared by other unit cells. Atoms located at the corner sites are shared by 8 unit cells each and hence make up 1 atom, while the 6 face-centered atoms are shared by 2 unit cells which then make up 3 atoms, and together with the 4 atoms inside make up 8

atoms per unit cell. The lattice parameter (a_0) or the edge length of the cubic unit cell is equal to $3.57 \text{ \AA}$ [41]. Figure 2.3 (b-d), shows the lattice structure of diamond viewed along three commonly considered crystallographic planes. The orientation of each atomic plane is represented by the reciprocals of a set of vector intercepts along the x , y and z axes known as Miller indices (hkl). Consider Fig. 2.3 (b), where the plane is parallel to axes y and z , the intercepts can be taken as $\hat{x} = 1$, $\hat{y} = \infty$ and $\hat{z} = \infty$. The reciprocal of these intercepts then gives us the Miller indices as $h = 1$, $k = 0$ and $l = 0$, representing the plane (100). Similarly, the planes in Fig. 2.3 (c) and (d) are referred to as (110) and (111), respectively. In general, each lattice point is represented in the form $\hat{r} = n_1\hat{x} + n_2\hat{y} + n_3\hat{z}$ and lies in the direction $[n_1n_2n_3]$ from the origin. The lattice crystal structure of diamond has a high degree of symmetry, where each plane can be rotated by 90° in each of the three dimensions. All the six faces of the cubic structure are identical and have entirely equivalent (100) planes referred to as $\{100\}$ set of planes. Similarly, there are sets $\{110\}$ and $\{111\}$ with equivalent planes (110) and (111), respectively. Furthermore, the particular direction of a plane is represented by square brackets $[hkl]$ and is perpendicular to the (hkl) plane. The differences in brackets is essential, and will be referred to throughout this thesis to describe both ion orientation and growth surfaces with respect to the diamond lattice structure. The lattice structure of diamond and many other materials has been expounded adequately in many texts over the years, hence the reader can refer to texts by Ashcroft and Mermin [41], and Kittel et al. [42], for further expatiation on the subject.

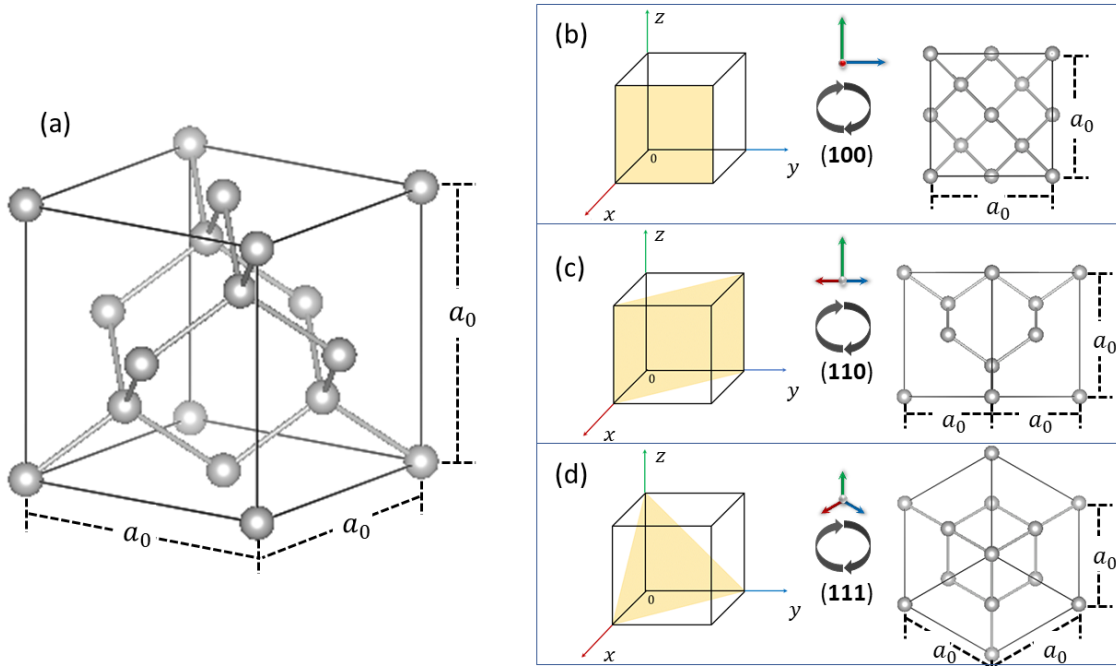


Figure 2.3: **Diamond cubic structure.** (a) The face centered cubic (FCC) crystal structure of diamond with 8 carbon atoms per unit cell, with lattice parameter ' a_0 ' of length $3.57 \text{ \AA}$. (b)-(d) Represents the diamond lattice structure oriented along the three commonly considered crystallographic planes for a cubic crystal. (b) The lattice structure is perpendicular to (111) plane, while at (b) and (c) the lattice structure is perpendicular to (001) and (110) planes, respectively.

2.1.2 Charecterization of diamond types

Natural diamonds are formed deep underground within the Earth's mantle (≈ 150 km). Most discovered diamonds were formed millions and billions of years ago under high pressure high temperature conditions, and transported over time to the Earth's surface via volcanic eruptions. Diamond deposits from the same region often possess similar chemical and physical traits which are somewhat different from other regions. The mechanical and physical properties of all discovered and manufactured diamonds are completely comparable, but vary over wide ranges depending on the internal structure and morphology of the crystal. The anisotropic nature of the crystal properties is due to different arrangement of carbon atoms in different planes as seen in Fig. 2.3 (*b-d*). Predictably, numerous characterization techniques of diamond were established by different authors over the last century.

Table 2.2: Categorization of diamonds based on sample characteristics [35, 37].

Type	Impurity	Visual properties	Feature	Optical absorption	
				Visible	Infrared
Ia	Aggregated nitrogen	Colorless, violet, green, brown, orange, yellow, pink	Opaque to short-wave UV; common	Secondary absorption edge at 300 nm, 415 nm	A-bands, B1 and B2 peaks
Ib	Isolated nitrogen	Brown, orange, yellow	Strong absorption increasing at higher photon energy; common	Strong absorption up to 450 nm	Peaks at 0.14 eV and 0.167 eV
IIa	None	Colorless, green, brown, pink	Transparent to short-wave UV; rare	Fundamental absorption edge, 5.5 eV	Lattice bands only
IIb	Boron	Gray, blue	Transparent to short-wave UV; electrically conductive; rare	Fundamental absorption edge, 5.5 eV, absorption at red end of spectrum	Acceptor bands, free carrier absorption

It was established by Robertson et al. [35], where their study introduced an optical categorization system for diamonds by studying the absorption spectra of various diamond samples. They were successful in categorizing diamond into two types:

type I and type II, determined by their transparency to infrared (IR) and ultraviolet (UV) light respectively. It turned out that type II diamonds often exhibited less to no birefringence from the UV light when viewed between two crossed polarizers as opposed to type I diamonds with IR, and hence led to the conclusion that the type II crystals must have a minimum amount of impurities or near to a faultless and pure crystal structure. Sutherland et al. [43] proposed that indeed the imperfectness of type I samples compared to that of type II is due to multiple chemical impurities clustered in and around the carbon lattice sites.

The availability of impurities in a carbon-based structure such as diamond has been studied extensively ever since, with intriguing optical absorption results. Research at the time focused on correlations between fluorescence from multiple samples and their absorption bands together with the physical appearance of each sample. Consequently, scientist began noticing methodical relations between the optical properties produced by type I and type II diamonds. The yellowish color and blueish fluorescence with unique absorption spectra (N3 defect-415 nm) are examples of some of the correlated characteristics of type I diamonds containing nitrogen impurities as reported by Lang et al. [44] and Thomaz et al. [45]. This all led to the sub-classification of these diamond types [37], as seen from Tab. 2.2 where researchers such as Dyer et al. [46] were able to separate clusters of nitrogen ions, otherwise known as aggregated nitrogen (type Ia) from isolated nitrogen (type Ib) in type I diamonds through IR spectroscopy. At the time it apparent that the presence and lack thereof of nitrogen in diamond was decisive in the identification of all diamond types since it is the most prevalent impurity in diamond [36].

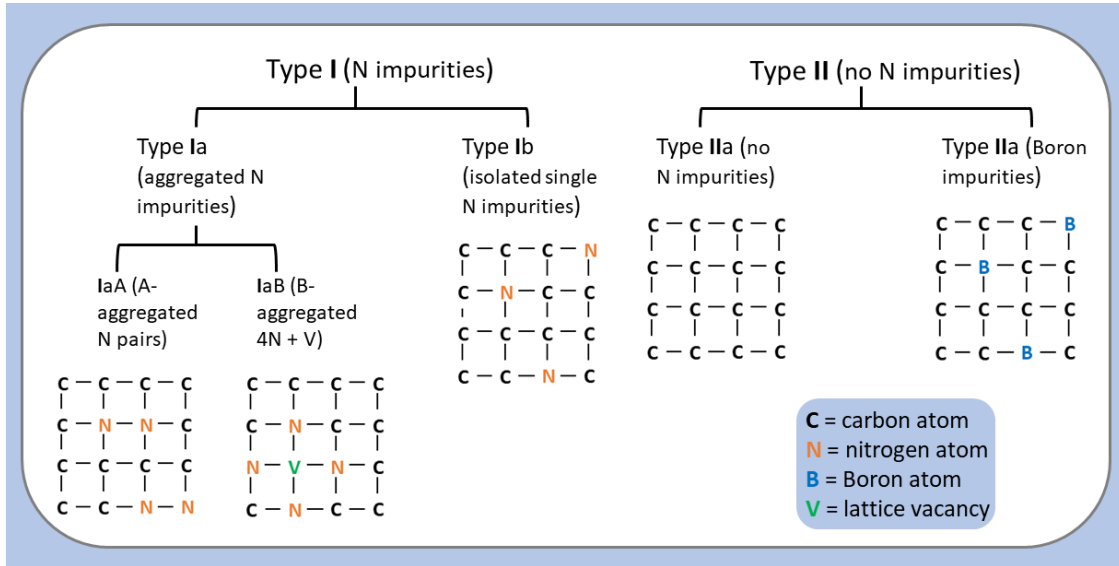


Figure 2.4: **Schematic of diamond atoms and impurities of diamond types.** Diamond type classification based on the presence or absence of nitrogen and boron impurities and their configuration in the diamond lattice [39].

Type Ia properties were found to be common in over 95 % of all natural diamonds, while type Ib were found to be rare in natural diamonds [37]. Others recognized the rarity of type II properties in natural diamonds as well and also recommended a splitting to type IIa and type IIb [47], due to certain disparities in physical and electric properties (again, see Tab. 2.2) where the former is mostly devoid of impurities and

the latter showing electrical conductivity due to the presence of boron. Figure 2.4, shows a schematic illustration in which nitrogen, boron and vacancies can replace carbon in the diamond lattice [48]. As a rare natural resource, diamond can also be engineered in a laboratory setting. The commonly used experimental techniques are the high-pressure and high-temperature (HPHT) [49], and chemical vapor deposition (CVD) [50, 51] growth methods for unique characteristics. Synthetically manufactured diamonds often exhibit optical properties of the naturally rare diamond types i.e., type Ib and type IIa, with HPHT and CVD processes respectively.

2.1.3 Nitrogen-related point defects

Many properties of diamond are influenced by the presence of point defects. Zhu [52], defines point defects as “zero-dimensional and thermodynamic equilibrium defects present within the diamond lattice”. Figure 2.5, shows a schematic of point defects that are possibly available in diamond. They include intrinsic vacancy (V) and self-interstitial (I) point defects and extrinsic (foreign atoms and impurities) substitutional or interstitial point defects. Nitrogen (N), along with a vacancy or a combination of both, are the most commonly studied point defects. Consequently, it is expedient to highlight the several configurations in which a N point defect and a vacancy point defect can exist within a diamond crystal lattice. As depicted in Fig. 2.4, the N impurity can exist either in simple configurations for isolated single nitrogen impurities in type Ib diamonds or in complex configurations for aggregated nitrogen impurities in type Ia diamonds. As such, a simple configuration can be a single nitrogen atom substituting a carbon atom from its lattice site or even occupying a usually unoccupied site within the diamond crystal lattice, with both such impurities commonly referred to as substitutional and interstitial impurities, respectively, as seen in Fig. 2.5. Complex configurations include a combination of nitrogen atoms adjacent to each other or other foreign atoms coupled with intrinsic vacancies inside the diamond crystal lattice. All the different configurations of nitrogen inside diamond induces unique physical and optical properties [37].

Since the classification of diamond types, several configurations of nitrogen-based defects were also established and characterized. Sutherland et al. [43] showed infrared absorption bands results from type Ia diamonds, identifying only two peaks at 1282 cm^{-1} and 1332 cm^{-1} falling into two groups, known as the A and B absorption bands respectively. The A and B centers are the most dominant form of nitrogen impurities clustered in diamond. By using uniaxial stress measurements (explained in detail in section 2.2.1), Davies [53], concluded that the A center has a trigonal symmetry consisting of a pair of adjacent nitrogen atoms, as seen in Fig. 2.4, for A-aggregated nitrogen pairs. The B center on the other hand, consists of a carbon vacancy surrounded by four substitutional nitrogen atoms, with a simplistic model given in Fig. 2.4 for B-aggregated nitrogen defects [54].

There’s also a small fraction of isolated single nitrogen impurities in most diamonds, typically found in the rare diamond type Ib. They’re commonly known as C centers with infrared absorption peaks at 1130 cm^{-1} [55]. A paramagnetic nitrogen defect was also found to be ever-present in natural diamonds. With an absorption and photoluminescence band at 415 nm, the center consists of a carbon vacancy surrounded by 3 nitrogen atoms [45]. An irradiation induced color center with an emission vibronic band of 1.945 eV was reported by Davies and Hamer [56] to be a

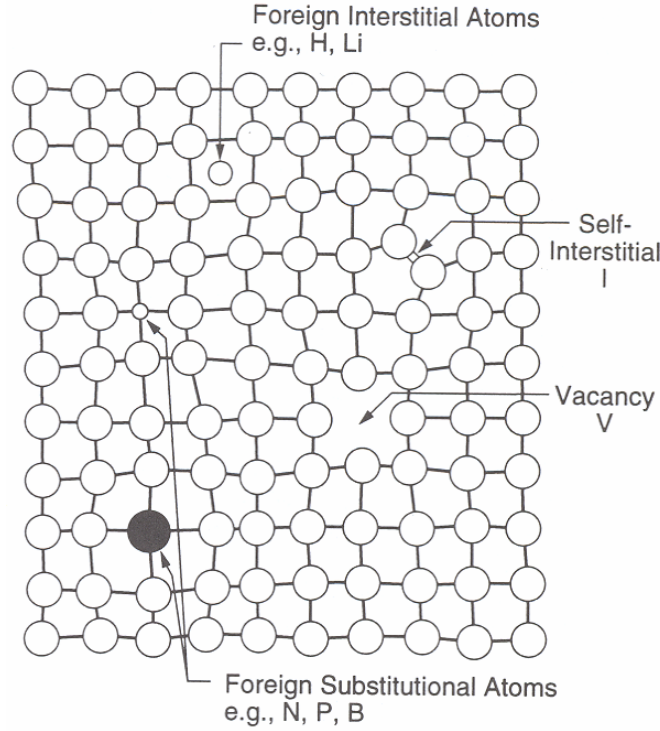


Figure 2.5: **Schematic of point defects that are possibly available in diamond.** Vacancy (V) and self-interstitials (I) are intrinsic point defects, while foreign atoms (H, Li, N, P, B) can exist either at interstitial or substitutional lattice sites. [52].

substitutional nitrogen atom coupled with a carbon vacancy, otherwise commonly known as an NV center. Throughout the scope of this thesis, focus will be on the properties related to this type of nitrogen configured defect.

2.2 Nitrogen vacancy centers

Introduction

The NV center is one of several impurities in diamond with research appealing photoluminescent properties. A single NV center consists of a substitutional nitrogen atom paired to a nearest-neighbor vacant lattice site in adjacent positions, and has a set of scientifically accepted orientations due to C_{3v} point group symmetry, as seen in Fig. 2.7. It has optical properties which are of interest in several emerging quantum and imaging technologies, including quantum information processing, quantum metrology and bio-imaging applications [10, 57]. NV centers exist in two charged states distinguished by the pairing of electrons: a neutral NV center, NV^0 with 5 unpaired electrons, and a negatively charged NV center, NV^- with 6 unpaired electrons [10]. It has been shown that the excitation of a single NV^- center emits single photons per excitation pulse, and this spatially extended array of photons is known as photon antibunching [4, 57, 58]; a crucial requirement for secure optical communication [59]. The neutral version of the center has so far limited known applications with some reported potential but no results associated with single photon generation [60], and at this stage, it is ordinarily exploited to better understand and

enhance the optical read-out from the NV^- center.

The optical spectra of the NV center provides with differing photo-luminescent features ascribed to both NV^- and NV^0 charged states which are invariably detected together in optical measurements [61]. Broadband illumination of about 532 nm induces zero phonon lines (ZPLs) at 637 nm (1.945 eV) and 575 nm (2.156 eV) for NV^- and NV^0 [56, 58], respectively, as shown in Fig. 2.6 (a). The ZPLs appear as a result of the electric dipole transition between the ground and the excited states depicted in Fig. 2.6 (b). The dipole transition associated with the NV^- exists between the triplet states, $^3A_2 \longleftrightarrow ^3E$ and has a paramagnetic ground state [62], with a metastable state transitioning between singlet energy states at near-infrared represented by $^1A_1 \longleftrightarrow ^1E$ [63, 64]. The NV^0 transition of its doublet energy states is denoted by $^2A \longleftrightarrow ^2E$, as shown in Fig. 2.6 (b) [65, 66]. The doublet ground state (2A) is non-paramagnetic, showing no signs of any detectable magnetic resonance credited to the presence of the dynamic Jahn-Teller effect [67].

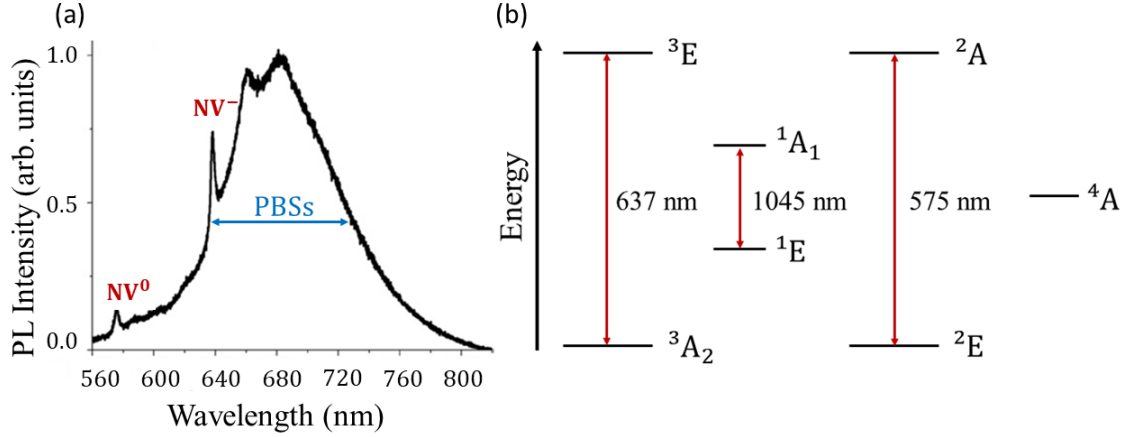


Figure 2.6: **Photoluminescence and electronic structure of NV center.** (a) Normalized emission spectra of NV center defect with NV^- and NV^0 charged states represented by 637 nm and 575 nm ZPLs, respectively [10]. (b) Electronic schematics of NV^- and NV^0 with the permitted energy transitions.

As mentioned before, NV centers are detected in natural diamonds, but it also turns out that they are commonly detected in untreated synthetic diamonds as ingrowth products of both HPHT and CVD processes. The centers are also readily fabricated in bulk or nanodiamonds (NDs) via irradiation damage of the diamond with electrons and via implantation of ions inside the diamond [61, 68]. The former is commonly used when a diamond sample already has a high concentration of nitrogen impurities embedded inside its crystal matrix while the latter is relied upon whenever the sample has a very low concentration of nitrogen. Irradiation damage is typically used in type Ib diamonds containing single substitutional nitrogens with nitrogen density of about a 100 to 3000 ppm ($n > 5$ ppm) to form NV centers [69]. The low density of nitrogen ($n < 5$ ppm) in type IIa diamond samples inevitably implies that nitrogen (N) ion implantation is a suitable processes to engineer NV centers with control over their concentration governed by the radiation dose and energy of the ions employed. After either one of these processes, it is common to anneal the prepared sample in high temperatures ($T > 600$ °C), which simply allows the trapped vacancies created to move within the diamond matrix. The migration energy of a

vacancy is ~ 2.3 eV, and often combines with other defects such as substitutional nitrogen to form complex defects such as nitrogen-vacancy centers [70].

2.2.1 Crystallographic structure of NV centers

The crystallographic structure of an NV center in a diamond cubic lattice is shown in Fig. 2.7 (a), in a $[111]$ orientation which is commonly used to depict an NV center. It consists of a substitutional Nitrogen atom adjacent to a vacant lattice site. It is this very specific atomic composition and arrangement that has attracted significant effort with a batch of studies in biomedicine, metrology and quantum optics; due to the electron spin and excellent optical properties that the center demonstrates. Furthermore, in order to induce excellent spin and optical response from NV centers we look at all the possible orientations for a single NV center, and how to manipulate the optical readout along an orientation axis. NV centers are always found to be in four possible crystallographic axis determined by the point group symmetry: $[111]$, $[\bar{1}\bar{1}\bar{1}]$, $[\bar{1}1\bar{1}]$ and $[1\bar{1}\bar{1}]$, as seen from Fig. 2.7(b) [31], where the negative sign above the index refers to a plane cutting an axis on the negative side of the origin (the reader can refer back to subsection 2.1.1). The probability of the centers being aligned equally along each axes is true if the centers are considered to be statistically oriented, while centers that are not aligned equally in all directional axes are known to be preferentially oriented. By studying the growth processes of synthetic diamond samples, scientists were able to ascertain control over preferred orientation of NV centers in diamond. Edmonds et al. [71] recently showed that in synthetic CVD diamonds grown on (110) substrates, NV centers can be preferentially oriented in the lattice in only two of the four possible orientations, $[111]$ and $[\bar{1}\bar{1}\bar{1}]$. They reported that by halving the number of the center's possible orientations, the sample showed greater contrast in magnetic resonance and better magnetic field sensitivity.

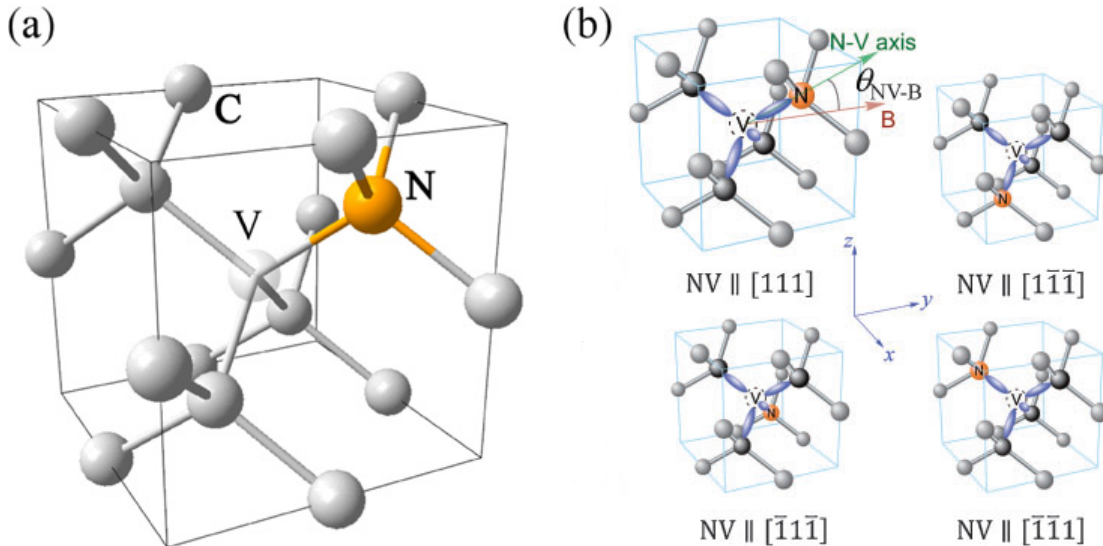


Figure 2.7: **Crystallographic structure of NV centers.** (a) A single NV center in the diamond lattice structure with $[111]$ orientation [10]. (b) Four possible orientations of an NV^- in a diamond lattice with angle between the center's axis and the magnetic field direction represented by $\theta_{\text{NV-B}}$. The brown and green arrow lines represent the orientations of the NV^- axis the in magnetic field [31].

It was also shown by Pham et al. [72], how synthetic CVD diamonds grown on (100) substrates can also yield preferentially oriented NV centers grown via a step flow mode where the surface morphology comprises of horizontal terraces and vertical risers corresponding to (100) and (110) surfaces, respectively. Both Edmonds et al. [71] and Pham et al. [72] reported a two-fold enhancement of the read-out contrast and magnetometry sensitivity, where the optimal magnetic field sensitivity for a single electronic spin is represented by [72, 73]:

$$\eta \approx \frac{\pi \hbar}{2g\mu_\beta} \frac{1}{C(T)\sqrt{\tau_{ac}n_{NV}}}, \quad (2.1)$$

where g is the Landé g-factor, $\hbar$ is the reduced Planck constant, μ_β is the Bohr's magneton, $C(T)$ is the parameter that accounts for the collection efficiency and contrast, and τ_{ac} and n_{NV} are the measurement time and the number of NV spins for the measurement, respectively. Most recently, Fukui et al. [31] and Lesik et al. [32] reported a near to perfect alignment of NV centers along the [111] orientation axis in high purity CVD grown diamond samples on (111) substrate, with the orientation probability of 99% and 97% respectively. They both showed a four-fold improvement of the read-out contrast and magnetometry sensitivity.

2.2.2 Photophysical properties of NV centers

From the previous section, we now know that diamonds possesses a considerable number of crystallographic imperfections in its crystal lattice that absorb visible light; and through light absorption experiments with ultraviolet and infrared light, it is possible to characterize the different types of defects embedded in diamond, in this case, the detection of nitrogen vacancy (NV) centers. The first optical observation of a single NV center at room temperature was reported by Gruber et al. [29]. Earlier on, Du Preez [70], showed that through annealing of type Ib electron irradiated diamond sample, the 1.945 eV vibronic band from a visible vibration spectrum is attributed to nitrogen related defects. It was suggested by Davies and Hamer [56], that the 1.945 eV center which is created via irradiation damage came from the coupling of the 1.673 eV band (GR1) or the 3.105 eV band (ND1) to a single substitutional nitrogen (N) atom, diffusing together at adjacent lattice sites during annealing to form the 1.945 eV center.

Moreover, due to observation of the correlated optical decrease of the intensity associated with the GR1 (1.673 eV) band with increase in intensity of the 1.945 eV band, it was notably speculated that the 1.945 eV band is a combination of a substitutional N_s atom and a vacant lattice site [70], and would later be referred to as a nitrogen vacancy (NV) center. Du Preez [70], based his assumption on the significant number of isolated substitutional nitrogen atoms present in a type Ib diamond and the fabrication processes of irradiation and annealing (> 600 °C) which produces mobile vacancies. The GR1 and ND1 bands were thought to be vacancies with differing charged states. They are prevalent in diamond after irradiation damage and also show a reversible bleaching behavior between them, under heating and illumination treatments, which was credited to the exchange of charges between the centers [74]. Electron acceptor and donor properties of the vacancies were taken into consideration to identify the state of the charges associated with each vacancy [75]. Neutral (V⁰) and the negatively (V⁻) charged vacancies seemed the more likely

with calculated stable energy levels by means of the linear combination of atomic orbitals (LCAO) by Coulson and Kearsley [76]. The non-paramagnetic GR1 and paramagnetic ND1 centers have been shown to represent the V^0 and V^- charge states, respectively [61, 68].

Charge states of NV centers

Aside from the 1.945 eV band, there exists another vibronic band at 2.156 eV which is present after fabrication processes, observed in cathodoluminescence due to the weak absorption spectra [77]. A detailed study on the above mentioned band was conducted by Davies [77], in which he noticed the presence of Jahn-Teller effects relatable to the neutral (V^0) vacancy. Under uniaxial stress measurements, the band also showed a $A_1 \longleftrightarrow E$ electric-dipole transition having a trigonal symmetry. Consequently, the band was identified as the neutral vacancy center. But it was not until Mita [78], reported a conclusive relationship between the 1.945 eV and 2.156 eV bands. He observed correlated changes in absorption spectra of the bands during high dosage of neutron irradiation, as seen in Fig. 2.8. This hinted on the photochromic nature of the center due to charges, and subsequently confirmed that the 2.156 eV band was the neutral charge state of the NV center (NV^0).

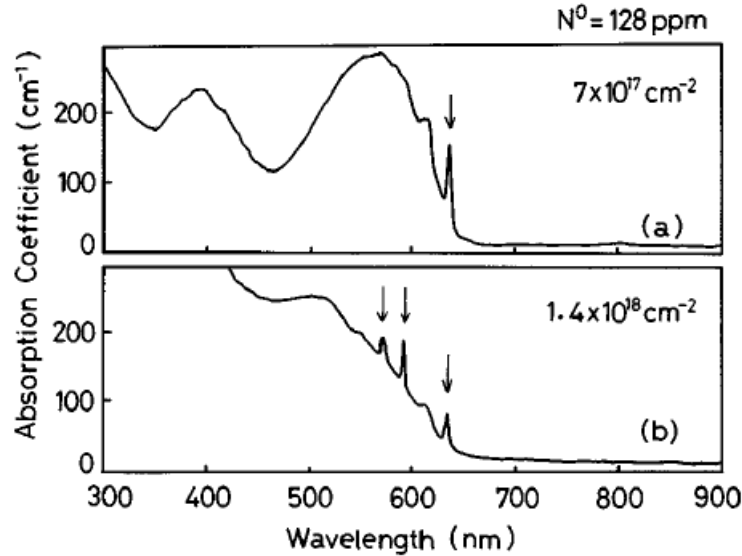


Figure 2.8: **Change in absorption spectra.** A comparison between the spectra of (a) and (b) [78]. Immediate change in the absorption spectra of the NV^- center with ZPL at 637 nm at (a), when the irradiation dose is double at (b).

The distribution of electron acceptors and donors in proximity of any defect often plays a significant role in determining the charge state of that defect, in our case, the NV center defect [79]. In type Ib diamonds, with high concentration of isolated substitutional nitrogens, deep electron donors with ionization energy of about 1.7 eV below the conduction band [80], the negative charge state of the NV center tend to be the more dominant charge state [81]. While, the more pure type IIa diamond with a low concentration of substitutional nitrogens, shows no clear dominant charge state [79]. This depends on the fabrication parameters for a type IIa diamond, including the ion fluence for the ion implantation process and the heat treatment employed on the sample through annealing [82]. In addition, it has also been established that

both charge states of the NV center can coexist in the same defect center, while exhibiting photo-conversion properties, i.e., photochromic effects [83]. Photochromic effect is essentially the photo-induced switching between the charge states of the NV center.

Due to the wide band gap of diamond, it has been established thus far that an NV center is a deep center with varying optical transitions for different charge states [84]. And, hence the charge states of the NV center are not photochemically stable under optical excitation and seemingly exhibit photochromic behavior. Scientists over the past 2 decades have evidently reported the photochromic effect with optical experiments. Iakoubovskii et al. [85], reported that the coexistence of the two charge states induces the charge states of other centers in diamond via optical excitation. Furthermore, Dumeige et al. [86] showed an irreversible photo-ionization of the NV^- charge state to create the NV^0 charge state, under intense pulse illumination of the NV center with femtosecond lasers. Manson and Harrison [81] reported similar effects with intense continuous-wave (CW) laser excitation of an ensemble of NV centers. Moreover, Gaebel et al. [83] reported reversible ($NV^0 \longleftrightarrow NV^-$) photochromism in a single NV center under intense laser excitation from a 514 nm laser source; the NV^0 ionizes to form the NV^- charge state and also relaxes back to the NV^0 charge state under dark conditions. All these observations are ascribed to the electron acceptor and donor dynamics, as discussed above.

2.2.3 Absorption and luminescence spectra

Davies and Hamer [56], while investigating the bandshapes of the absorption and luminescence spectra, were able to compare the bands by looking at the reflected mirror image of the absorption band, as seen in Fig. 2.9. This is true if we consider the linear coupling of the two modes in question, with small quadratic terms [87]. The associated equation is given by,

$$I(v_0 - v) = \frac{\varrho(v_0 + v)(v_0 - v)^3}{v_0 + v}, \quad (2.2)$$

where v and v_0 are the frequency and the zero phonon frequency, respectively, with luminescence intensity $I(v_0 - v)$ calculated from the absorption term $\varrho(v_0 + v)$. The minor differences in the bands is merely a signature of the Jahn-Teller effects, signifying the vibronic splitting of the one-phonon peak in the absorption band [88].

Both absorption and luminescent spectra of a NV center possess a common feature, i.e., a wide bandwidth about ~ 100 nm due to the host material. The rigid and stable qualities provided by the diamond matrix, also means that the photo-induced center couples with vibrational modes known as phonons, influential in the decoherence of the spin state and the transition of energy within the system. Hence, the wide bandwidth is referred to as phonon sidebands (PSBs), depicted in Fig. 2.6 (a). The interactions of the electronic (electronic excitation) and vibrational (vibrational effects) degrees of freedom can be explained with the vibrational structure of the center [89].

Vibronic band structure

The simplest form to approximate the vibrational structure of the NV center is detailed rather expertly using the Huang-Rhys [90]. This implies a quasi-continuum

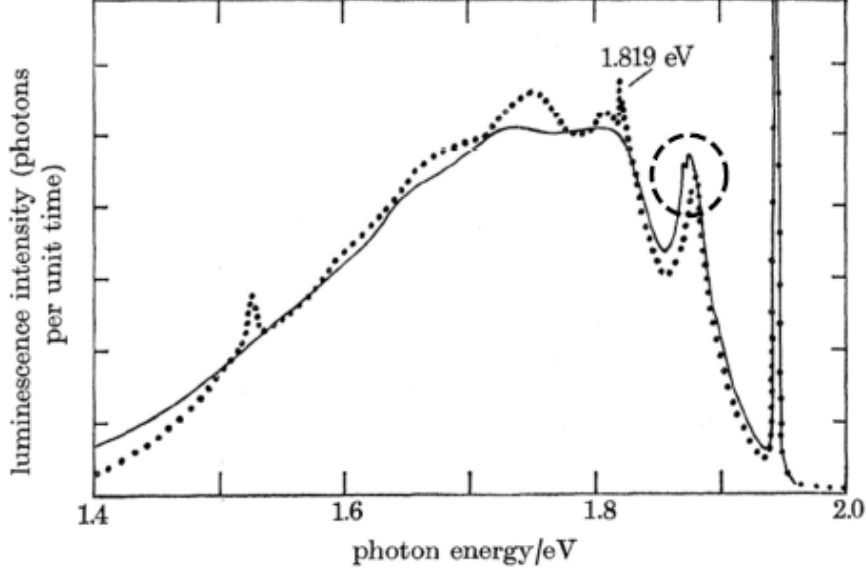


Figure 2.9: **Absorption and Luminescence bands of the NV^- .** The comparison of the absorption (solid line) and luminescence spectra (dotted line). The absorption spectra is the mirror image of the luminescence spectra reflected in energy [56].

system of phonons representing a single vibrational mode within the diamond lattice, with coordinates corresponding to the nuclei displacement due to transitions within the electronic states of the NV^- center. By making use of the Born-Oppenheimer approximation, Fig. 2.10, depicts the potential curves of the 3A_2 and 3E electronic states of the NV^- center, δQ apart in the normal coordinate space. The potentials have different electronic energies (E) with vibrational levels ($n = 0, 1, 2, 3$) associated with the 3A_2 and 3E states of the NV^- center. In this case, the Frank-Condon principle is also employed in order to account for the differences between the optical spectra of the electronic states. The Frank-Condon principle states that the highly probable transitions are at the same nuclear configuration, i.e., the vertical transitions depicted in Fig. 2.10. However, due to the overlap of the vibrational wave functions being non-zero where the probability is given by the Frank-Condon factors, other electronic transitions are also allowed with Stokes (ΔS) shifted excitation and anti-Stokes (ΔAS) shifted decay [90].

The vertical transitions implies an overlap between the two vibrational states, indicating a broader bandwidth as the excitation is most likely to be the PSBs (640 nm – 760 nm) than to the narrow ZPL (637 nm). The approximation of the potentials is described by the following quadratic function of the nuclear coordinates for the 3A_2 and 3E states [87],

$$\begin{aligned}
 E_{^3A_2}^{HR} &= \frac{1}{2}m\omega^2Q^2, \\
 E_{^3E}^{HR} &= E_{^3E} + \frac{1}{2}m\omega^2Q^2 + aQ + bQ^2, \\
 &= E_{^3E} - E_R + \left(\frac{1}{2}m\omega^2 + b\right)(Q - \delta(Q))^2,
 \end{aligned} \tag{2.3}$$

where $E_{^3E}$ represents the electronic energy of the 3E state at the nuclear equilibrium coordinate for the 3A_2 state ($Q = 0$), m is the mass of the mode, ω and $\sqrt{\omega^2 + b}$

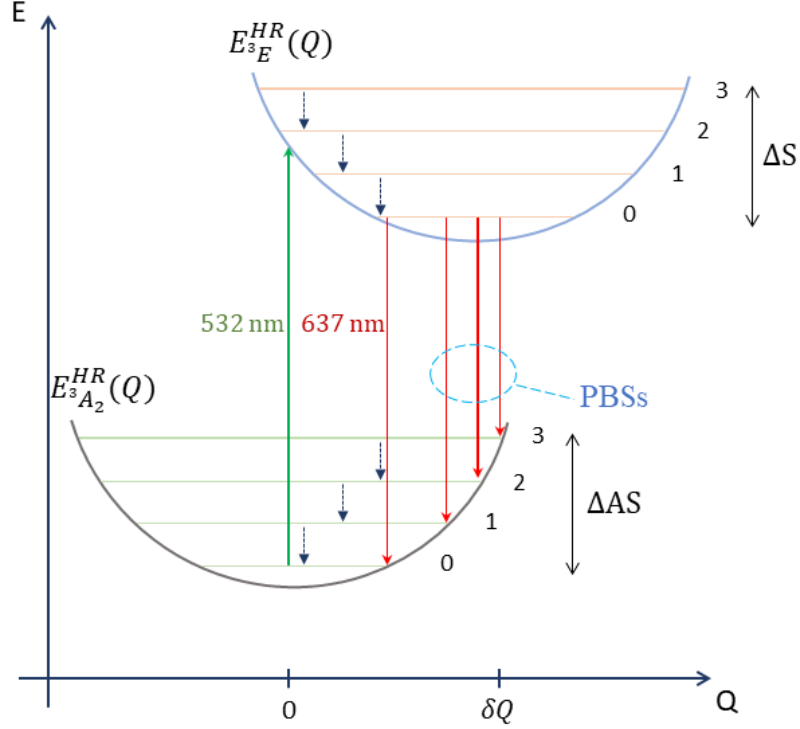


Figure 2.10: **The Huang-Rhys model in Frank-Condon principle.** Schematic of the Frank-Condon principle with harmonic potentials describing the electronic energies (E) of the ground and excited states separated by the nuclear displacement coordinate Q [90].

are the frequency of the vibrational modes in the 3A_2 and 3E states, respectively. The linear and quadratic electron-vibration coupling parameters to the 3E state are represented by a and b , respectively. The equilibrium displacement of the 3E state is given by $\delta Q = -a/(\omega^2 + 2b)$, while its relaxation energy is given by $E_R = a^2/2(\omega^2 + 2b)$. Davies [87], also expressed the probability integral for the optical transition for a single vibrational frequency as follows,

$$\iint dr dQ \phi_e^*(r) \chi_n^*(Q - Q_0) D \phi_g(r) \chi_0(Q), \quad (2.4)$$

where D is the electric-dipole operator, while the wavefunction is the product of the nuclear and electric components for both states (e.g., $\psi(r, Q) = \phi_g(r) \chi_0(Q)$ for the ground state). The Franck-Condon principle approximates that the electronic coordinate is independent of the vibrational coordinate, and hence Eq. 2.4, can be factorized,

$$\int dr \phi_e^*(r) D \phi_g(r) \int dQ \chi_n^*(Q - Q_0) \chi_0(Q) \quad (2.5)$$

The Franck-Condon factors are defined as,

$$M_{0n} = \int dQ \chi_n^*(Q - Q_0) \chi_0(Q) \quad (2.6)$$

for the harmonic states,

$$|M_{0n}|^2 = \frac{e^{-S} S^n}{n!}, \quad (2.7)$$

where $S = a^2/2m\hbar\omega^3 \equiv E_R/\hbar\omega$, is the Huang-Rhys factor measured from the fraction of the optical transition which lies in the ZPL,

$$S = \ln \left(\sum_{n=0}^{\infty} |M_{0n}|^2 / |M_{00}|^2 \right) \quad (2.8)$$

The model also accounts for the similarity between the absorption and luminescence transitions whenever the respective frequencies are equal ($\omega = \Omega$), resulting in the mirror images of the bands.

The treatment of Huang-Rhys model for multiple modes N is also given [88]. The harmonic nuclear potentials of the electronic states now takes the form,

$$\begin{aligned} E_{3A_2}^{HR} &= \frac{1}{2} \sum_{i=1}^N m_i \omega_i^2 Q_i^2, \\ E_{3E}^{HR} &= E_{3E} + \frac{1}{2} m_i \omega_i^2 Q_i^2 + \sum_{i=1}^2 a_i Q_i, \\ &= E_{3E} + \frac{1}{2} m_i \omega_i^2 (Q_i + a_i/(m_i \omega_i^2))^2 - \frac{1}{2} \sum_{i=1}^N a_i/(m_i \omega_i^2), \end{aligned} \quad (2.9)$$

The Huang-Rhys factor is now defined as,

$$S = \sum_{i=1}^N S_i \text{ where } S_i = \frac{a_i^2}{2\hbar\omega_i^3 m_i} \quad (2.10)$$

Now, considering the one-phonon sideband, one vibrational mode is excited. For a single excited mode, the Franck-Condon factor is given by,

$$\begin{aligned} M_{01}^i &= \int dQ_1 \chi_1^{0*}(Q_1) \chi_1^0(Q_1 - Q_1^0) \dots \int dQ_i \chi_i^{0*}(Q_i) \chi_i^1(Q_i - Q_i^0) \\ &\quad \times \dots \int dQ_N \chi_N^{0*}(Q_N) \chi_N^0(Q_N - Q_N^0), \end{aligned} \quad (2.11)$$

$$|M_{01}^i|^2 = S_i \exp(-S_i) \prod_{j \neq i} \exp(-S_j) = S_i e^{-S} \quad (2.12)$$

Giving total relative intensity on the one-phonon band to be,

$$|M_{01}|^2 = \sum_i |M_{01}^i|^2 = S e^{-S} \quad (2.13)$$

and likewise for the n -phonon band, the total relative intensity is ,

$$|M_{0n}|^2 = \frac{S^n e^{-S}}{n!} \quad (2.14)$$

If the independent spectral shape of one-phonon band is known, the function for the spectral shape of the n -phonon band at frequency ν can be determined as follows,

$$I_n(\nu) = \int_0^{\omega_m} dx I_1(x) I_{n-1}(\nu - x), \quad (2.15)$$

where ω_m is the frequency of the vibrational modes within the crystal defect, I_1 and I_{n-1} are the spectral form for the one-phonon band and the $(n-1)$ -phonon band, respectively. The absorption frequency of $(n-1)$ is given by $(\nu - x)$. The shape of the one-phonon band for the NV center was determined by Davies [87], and it peaked ~ 65 meV.

ZPL line broadening

The orbital degeneracy of the excited state has been established in subsection 2.4. Consequently, the degeneracy implies that the state will experience dynamic Jahn-Teller effects [91], leading to the coupling between the degenerate E electronic state with a doubly degenerate e vibrational mode, resulting in an $E \otimes e$ Jahn-Teller system. This leads to the homogeneous energy broadening of the optical transition, observed in the ZPL via a process referred to as dephasing of the excited state [92, 93]. The Hamiltonian to describe the interaction between the state and vibrational mode is given as,

$$\begin{aligned} H^{el}(Q_x, Q_y) = E_0 + \frac{K}{2}(Q_x^2 - Q_y^2)\sigma_z + F(Q_x\sigma_z - Q_y\sigma_x) \\ + G[(Q_x^2 - Q_y^2)\sigma_z + 2Q_xQ_y\sigma_x], \end{aligned} \quad (2.16)$$

where Q_x and Q_y are the displacement coordinates for the vibrational mode e in C_{3v} symmetry, E_0 is the energy of the state at the nuclear equilibrium coordinate ($Q_x=Q_y=0$), σ_x and σ_z are the Pauli matrices. K is the elastic force constant, while F and G are constants pertaining to the linear and quadratic vibronic components of the system, respectively. If the system has no quadratic coupling ($G = 0$), the energy potential then takes the form,

$$V = \frac{1}{2}K(Q_x^2 + Q_y^2) - F(Q_x^2 + Q_y^2)^{\frac{1}{2}}. \quad (2.17)$$

The potential has its minima whenever the radius is given by,

$$\rho_0 = (Q_x^2 + Q_y^2)^{\frac{1}{2}} = F/K. \quad (2.18)$$

where it yields a sheet of an adiabatic potential energy surface (APES), often referred to as the “Mexican hat” due to its shape. Whenever the energy is lowered by $E_{JT} = F^2/2K$ as compared to $Q_x=Q_y=0$, the system can evolve rapidly between the nuclear configurations, with the processes known as dynamic Jahn-Teller effect. For nonzero quadratic coupling ($G \neq 0$), the energy potential becomes,

$$V = \frac{1}{2}K\rho^2 - \rho[F^2 + G^2\rho^2 + 2FG\rho^{\frac{1}{2}}\cos(3\phi)]^{\frac{1}{2}}, \quad (2.19)$$

where the coordinates are given by $\rho = (Q_x^2 + Q_y^2)^{\frac{1}{2}}$ and $\phi = \arctan(Q_y/Q_x)$. In this case, three minima form lying in the energy potential surface with a radius

of $\rho_0 = F/(K - 2G)$, as shown in Fig. 2.11 (a). Whenever the barrier is much larger than the vibrational energy, the system stops evolving and gets trapped in one of the minima in a process known as static Jahn-Teller effect. The relation between Eq. (2.16) and the Jahn-Teller parameters i.e., radius of the potential energy surface (p_0), the Jahn-Teller stabilization energy (E_{JT}) and the barrier between the local minima (δ), is given as follows: $p_0 = F/(K - 2G)$, $E_{JT} = F^2/2(K - 2G)$ and $\delta = 4E_{JT}G/(K + 2G)$. The first-principle calculations were done by Abtew et al. [92], who came up with the following values for the case of the NV center: $E_{JT} = 25$ meV, $\delta = 10$ meV, and $\rho_0 = 0.068 \text{ \AA}$ finding $F = -0.74 \text{ eV \AA}^{-1}$, $G = 1.76 \text{ eV/\AA}^2$ and $K = 14.5 \text{ eV/\AA}^2$. The estimated energy of the e vibration mode is ~ 71 meV close to the energy for the ground state determined by Davies [87] to be ~ 65 meV. The energy is much larger than the barrier energy, and hence tunneling will be frequent, leading to the dynamic Jahn-Teller effect.

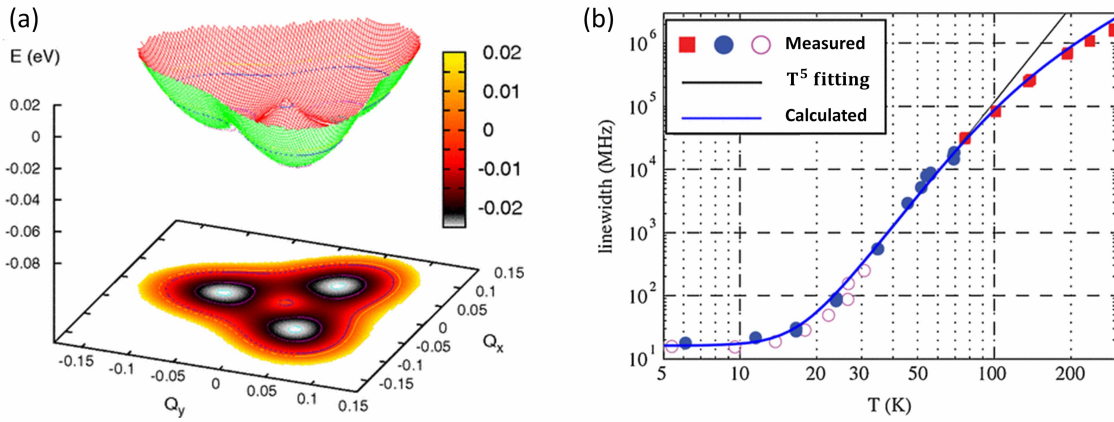


Figure 2.11: **Jahn-Teller effects on the excited (3E) electronic state.** (a) Adiabatic potential energy surface (APES) of the excited state with symmetric displacement coordinates (Q_x and Q_y) for the vibrational mode e . (b) Comparison of the calculated and measured linewidth of the ZPL of the NV^- center as a function of temperature [92]. The solid black line is the T^5 fitting which represents the temperature dependence associated with the optical linewidth [93].

The vibrational mode (e) involved in the $E \otimes e$ Jahn-Teller system, induces transitions between the E_x and E_y levels explained by a two-phonon Raman process [93], which reduces the electronic lifetime of the 3E state. Resulting in the broadening of the optical linewidth due to the dephasing of the optical transition. It was shown by Fu et al. [93], how the width is T^5 temperature dependent. Abtew et al. [92], was able to theoretically reproduce the experimentally measured linewidth via the Jahn-Teller parameters. The width is given as follows,

$$W(T) = \frac{8\pi}{\hbar} \left(\frac{\Omega}{2\pi^2 \hbar^3 v_s^3} \right)^2 C^4 (k_B T)^5 I_4(\hbar\omega_D/k_B T), \quad (2.20)$$

where Ω is the volume of diamond's unit cell, $v_s = 1.2 \times 10^4 \text{ m/s}$ is the speed of sound in diamond, $I_4(x) = \int_0^x dy y^4 e^y (e^y - 1)^2$ is the Debye integral. $C = F\sqrt{1/2m\omega_0^2}$ is the coupling constant where $F = -0.74 \text{ eV \AA}^{-1}$ at $\hbar\omega_0 = 71$ meV with mass (m) of the carbon atom. k_B represents the Boltzmann constant, while $\hbar\omega_D = 50$ meV was needed to reproduce the results measured for the linewidth. The linewidth which is plotted in Fig. 2.11 (b) is then given by,

$$\gamma(T) = \gamma_0 + 2W(T)/(2\pi), \quad (2.21)$$

where $\gamma_0 = 16.2$ MHz. Hizhnyakov et al. [94], also found similar behavior for a T^3 type law of the temperature broadening of the ZPL. They reported that this is due to strong softening of the springs of the center. Their results were for ensemble measurements, only viable for high temperatures. Davies [87], also reported a T^7 law using a model by Maradudin [95], based from linear electron-phonon coupling. Again, their results were based from an ensemble measurement. At this stage, a T^7 contribution is yet to be found experimentally.

Stark shifts related to the change in the static electric field that an emitter is exposed to, due to ionization of nearby impurities, also induces an inhomogeneous broadening of the ZPL due to spectral diffusion [96, 97], rather than the phonon scattering effects discussed previously. Stark effects lead to a shift of the frequency of the ZPL, with observed contributions coming from either linear or quadratic or both vibronic components [96]. It has been reported that the main source for the spectral diffusion is the substitutional nitrogen with an optical threshold ionization energy of 2.2 eV [37, 98]. Not to be confused with the thermal activation ionization energy of a substitutional nitrogen which is 1.7 eV, as discussed earlier on. The difference is due to the Jahn-Teller effect. Stark shift of a few GHz can be observed from an NV center, even from a single charge placed a distance of ~ 10 nm away from the center [99]. Solid state emitters often exhibit spectral diffusion, which in the case of diamond, relies on the quality of the diamond. Spectral diffusion ranging from a few hundred GHz for nanodiamonds (NDs) to a few hundred MHz for pure diamonds [99, 100]. NV centers implanted near the surface, also enhances spectral diffusion due to the surface defects acting as charge traps. However, spectral diffusion can also be stifled via re-pump lasers, which normally leads to the ionization of NV centers [101]. It has recently been shown that changing the wavelength of the excitation laser (532 nm) to 575 nm, wavelength of the ZPL associated with neutral NV center (NV^0), spectral diffusion is suppressed [100]. Since the substitutional nitrogen is no longer ionized at 575 nm, this provides further evidence that the substitutional nitrogen is the main source for spectral diffusion.

2.3 C_{3v} point group symmetry

2.3.1 Uniaxial stress measurements

Clark and Norris [102], studied the photoluminescence polarization of the NV^- center and concluded that it has a trigonal or monoclinic I symmetry depending on the next to neighbor positions of the single substitutional nitrogen atoms. The intensity measurements they used involved the following equation,

$$I(\theta_{ex}) = A(\theta_{ex}) + q(\theta_{ex}) \cos 2(\theta_{em} - \epsilon(\theta_{ex})), \quad (2.22)$$

where A is the amplitude of the field intensity $I(\theta_{ex})$ and q is the oscillating component of the field. θ_{ex} and θ_{em} are the angles of the exciting field and emitted field, respectively. Clark and Norris [102], presented measured values of the polarization ($p(\theta_{ex})$) and phase ($\epsilon(\theta_{ex})$) of the luminescence as the function of the angle of the exciting field, where p is given by,

$$p = \frac{q}{A}. \quad (2.23)$$

The polarization and phase results obtained supported the optical transitions associated with a trigonal or monoclinic symmetry, consistent with suggestions made by Du Preez [70]. Davies and Hamer [56] studied the optical transition of the center in much detail. Following the uniaxial stress splitting studies of cubic crystals, by Hughes and Runciman [103], and other authors, the splitting patterns of degenerate states reported by Davies and Hamer [56], specifically for an NV center were in agreement with a $A_1 \longleftrightarrow E$ electric dipole transition at a trigonal symmetry (C_3 , C_{3i} (S_6), D_3 , C_{3v} , D_{3d}), with A_1 representing the ground state. Under cryogenic temperatures, they were able to apply up to 2 GPa of uniaxial stresses along the (111), (110) and (001) axes of the diamond crystal. Taking into consideration the standard orientation of a trigonal center with axes at [111], [112] and $[\bar{1}10]$, defined as Z , X and Y respectively. The stress perturbation experienced by the electronic states is written in the form,

$$\begin{aligned} V = & A_1(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) + A'_1(\sigma_{yz} + \sigma_{zx} + \sigma_{xy}) \\ & + E_X(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) + E_Y\sqrt{3}(\sigma_{xx} - \sigma_{yy}) \\ & + E'_X(\sigma_{yz} + \sigma_{zx} - \sigma_{xy}) + E'_Y\sqrt{3}(\sigma_{yz} - \sigma_{zx}), \end{aligned} \quad (2.24)$$

where A_1 , A'_1 , E_X , E_Y , E'_X and E'_Y are the electronic operations with σ_{ij} representing the components of the stress tensor with respect to the crystal axes x , y and z . The stress processes induces ZPL splittings depending on the respective interactions within the center resulting in shifts. The shift levels at various directions, defining the stress coupling coefficients are given by the following four splitting parameters [56],

$$\begin{cases} A_1 = [E||A_1||E] - [A||A_1||A] \\ A_2 = \frac{1}{2}[E||A'_1||E] - [A||A'_1||A] \\ B = \frac{1}{\sqrt{2}}[E||E||E] \\ C = \frac{1}{2}[E||E'||E] \end{cases} \quad (2.25)$$

The secular-time evolution matrix then takes the form,

$$\begin{bmatrix} \alpha' - \beta' & \gamma' \\ \gamma' & \alpha' + \beta' \end{bmatrix}, \quad (2.26)$$

where the matrix variables are the eigenvalues and are given by,

$$\begin{cases} \alpha' = A_1(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) + 2A_2(\sigma_{yz} + \sigma_{zx} + \sigma_{xy}) \\ \beta' = B(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) + C(\sigma_{yz} + \sigma_{zx} - \sigma_{xy}) \\ \gamma' = B\sqrt{3}(\sigma_{xx} - \sigma_{yy}) + C\sqrt{3}(\sigma_{yz} - \sigma_{zx}) \end{cases} \quad (2.27)$$

The tensor property of σ_{ij} , states that when the uniaxial stress Γ is applied to a crystal along an arbitrary direction, the elements of the stress tensor will be given by,

$$\sigma_{ij} = \Gamma \cos(\Gamma, i) \cos(\Gamma, j), \quad (2.28)$$

where (Γ, r) is the angle between the direction of Γ with the axis labeled by r . Now, taking into consideration Eq. 2.27 and Eq. 2.28, the stress results along each symmetry axes are treated as follows: the stress directions for the (001) axis are equivalent for the trigonal center. Then one needs only to consider the effects of the [001] stress, giving the following expression,

$$\Delta = A_1 \pm 2B, \quad (2.29)$$

As for the (111) crystal axis, there are two inequivalent stress directions, which can take the form $[111]$ and $[11\bar{1}]$, given respectively by,

$$\Delta = A_1 + 2A_2, \quad (2.30)$$

and

$$\Delta = A_1 - \frac{2}{3}A_2 \pm \frac{4}{3}, \quad (2.31)$$

The (110) crystal axis also has two inequivalent stress directions, taking the form $[110]$ and $[1\bar{1}0]$, respectively giving,

$$\Delta = A_1 + A_2 \pm (C - B), \quad (2.32)$$

and

$$\Delta = A_1 - A_2 \pm (-C - B), \quad (2.33)$$

Davies and Hamer [56], provides with a summary and results of the effects of stress on the ZPL absorption line of the center. The comparison between the experimental results and modeled theoretical values ascertained a trigonal symmetry for the center.

2.3.2 Group theory

It is common knowledge that the Hamiltonian $\hat{H}$ symmetry dictates the structure of the eigenstates associated with it. Practically, from the atomic orbital perspective, the associated quantum numbers originate due to the rotational invariance of the Hamiltonian which regulates them. Taking this approach, consider an invariant $\hat{H}$ of a system under unitary transformations $\{\hat{U}_i\}$, such that,

$$\hat{U}_i \hat{H} \hat{U}_i^\dagger = \hat{H}, \quad (2.34)$$

for every $\hat{U}_i$. From the Schrödinger equation,

$$\hat{H} |\psi_n\rangle = E_n |\psi_n\rangle, \quad (2.35)$$

the solution must satisfy,

$$\hat{U}_i \hat{H} \hat{U}_i^\dagger |\psi_n\rangle = E_n |\psi_n\rangle, \quad (2.36)$$

and applying symmetry operations by multiplying with $\hat{U}_i^\dagger$ from the left,

$$\hat{H} \hat{U}_i^\dagger |\psi_n\rangle = E_n \hat{U}_i^\dagger |\psi_n\rangle. \quad (2.37)$$

Evidently, this raises the possibility of degeneracy, as the new state $\hat{U}_i^\dagger |\psi_n\rangle$ must have the same energy after symmetry transformation of the original state $|\psi_n\rangle$ [104]. It is worth noting, a system can have more than one symmetry operation. If the set of operators $\{\hat{U}_i\}$ satisfy $\hat{U}_i \hat{H} \hat{U}_i^\dagger = \hat{H}$, it is referred to as the symmetry group of the Hamiltonian. Now, the resulting set of the state $\hat{U}_i^\dagger |\psi_n\rangle$ may have duplicates. However, distinct degenerate states are related by a set of matrices $M_{i,l}$, i.e., $|\psi_n^{(i)}\rangle = \sum_l M_{i,l} |\psi_n^{(l)}\rangle$, representing the irreducible representations (*IRs*) of the symmetry group, classifying each state by its *IRs*.

Electronic configuration

Considering the electronic configuration, in order to find the irreducible representations (*IRs*) for the NV structure. The presence of a vacant lattice site for an NV center implies that there is a missing carbon atom which collapses the covalent bonds between the four carbon atoms, prior to a vacancy generation, which then creates the dangling bonds to the vacancy [105]. This results in the hybridization of the orbitals associated with each atom, i.e., 3 bonds - C atoms around the vacant site and a single bond for N atom. The bonds are represented by vectors ν_i ($i = 1 \cdots 4$). The vectors ν_i can be projected on each of the group *IRs*, using the projection operator [106],

$$\phi_r = P^r \nu_i = \frac{l_r}{h} \sum_e \chi_e^r R_e \Sigma_i \quad (2.38)$$

where P^r is the projection operator to the *IRs*, l_r is the order of the *IRs* r , h is the number of group elements, χ_e^r is the character of the operation R_e in *IR* r , summing over all the elements of a cartesian *IR*. Through the projection operator, we get two totally symmetric *a*-orbitals (a'_1 and a_1) for single electrons which transforms A_1 *IR* and two $e_{x,y}$ - degenerate orbitals (e_x and e_y) which transform as E [107], such that,

$$\begin{cases} a_N = \nu_1 \\ a_c = \frac{\nu_2 + \nu_3 + \nu_4}{3} \\ e_x = 2\nu_2 - \nu_3 + \nu_4 \\ e_y = \frac{\nu_3 + \nu_4}{\sqrt{2}} \end{cases} \quad (2.39)$$

Since the *a*-orbitals lie beneath the *e*-orbitals, they can be energetically ordered. Figure 2.12 (a), shows that the a'_1 -orbital is completely filled by the two lowest energy electrons inside the valence band, and hence it is not involved in the optical excitation decay cycles [108]. The other orbitals are inside the energy gap and will be taken into consideration. In the ground state, the a_1 -orbital is also completely filled by two electrons, while the $e_{x,y}$ -orbitals are half filled with one electron each from the remaining electrons. We can use a two-hole description to describe the system with all the 6 electrons. The projection operator for the total spatial wave function then becomes,

$$\psi_r = P^r \phi_1 \phi_2 = \frac{l_r}{h} \sum_e \chi_e^r R_e \phi_1 \phi_2 \quad (2.40)$$

where $\phi_{1,2}$ are the single-electron orbitals. Since each electron has a half spin, a two-hole system generates singlet and triplet states. The spatial states presents with details of all the possible wave functions which transform as IRs , depicted in Tab. 2.3. The total wave function can be separated into a spatial and spin wave

Table 2.3: Wave functions and the state symmetry for the electronic configurations e^2 and ae of the center [107].

Electron configuration	State symmetry	Wave function	m_s
e^2	3A_2	$ e_x e_y - e_y e_x\rangle \otimes \uparrow\downarrow + \downarrow\uparrow\rangle$	0
		$ e_x e_y - e_y e_x\rangle \otimes \downarrow\downarrow\rangle$	-1
		$ e_x e_y - e_y e_x\rangle \otimes \uparrow\uparrow\rangle$	+1
e^2	1E	$ e_x e_x - e_y e_y\rangle \otimes \uparrow\downarrow - \downarrow\uparrow\rangle$	0
		$ e_x e_y + e_y e_x\rangle \otimes \uparrow\downarrow - \downarrow\uparrow\rangle$	0
	1A_1	$ e_x e_x + e_y e_y\rangle \otimes \uparrow\downarrow - \downarrow\uparrow\rangle$	0
ae	3E	$ a_1 e_x + e_x a_1\rangle \otimes \uparrow\downarrow + \downarrow\uparrow\rangle$	0
		$ a_1 e_x\rangle \otimes \downarrow\downarrow\rangle$	-1
		$ a_1 e_x\rangle \otimes \uparrow\uparrow\rangle$	+1
		$ a_1 e_y + e_y a_1\rangle \otimes \uparrow\downarrow + \downarrow\uparrow\rangle$	0
		$ a_1 e_y\rangle \otimes \downarrow\downarrow\rangle$	-1
		$ a_1 e_y\rangle \otimes \uparrow\uparrow\rangle$	+1
ae	1E	$ a_1 e_x + e_x a_1\rangle \otimes \uparrow\downarrow - \downarrow\uparrow\rangle$	0
		$ a_1 e_y + e_y a_1\rangle \otimes \uparrow\downarrow - \downarrow\uparrow\rangle$	0

function, $\Psi = \psi_r \Phi_S$, where Ψ is the spatial part and has a cartesian symmetry, ψ_r is the projection operator discussed earlier and Φ_S is the spin part for either a spin singlet ($S = 0$) or a spin triplet ($S = 1$). According to the first Hund's rule [107], the two spins of the minimum energy configuration are co-aligned, which implies a spin triplet ground state. And also, the Pauli's principle requires that the total wave function, ψ_r , to be anti-symmetric regarding the exchange of particles. Hence, the ground state must be made of a spatial anti-symmetric part and a symmetric spin triplet. Since A_1 denotes a symmetrical orbital and the degenerate E is unstable, the ground state must have A_2 symmetry with a spin triplet denoted by a superscript we get 3A_2 , as depicted in Tab. 2.3.

C_{3v} symmetry and electronic transitions

The NV center has a specific symmetry, regarding its orientation axis within the diamond lattice. Under investigation, it is possible to observe that the center is invariant under certain rotations by $2\pi n/3$ (e.g., 0° , 120° and -120°) around the NV axis, represented by C_3^+ and C_3^- . The center is also invariant under reflections R_1 , R_2 and R_3 in the symmetry plane containing the NV axis and any of the three nearest neighbor carbons. Together with the identity operation e , these are the symmetry operations $\{e, C_3^+, C_3^-, R_1, R_2, R_3\}$ of a point group symmetry, denoted as C_{3v} . The C_{3v} point group is a trigonal point group of the order of six [107].

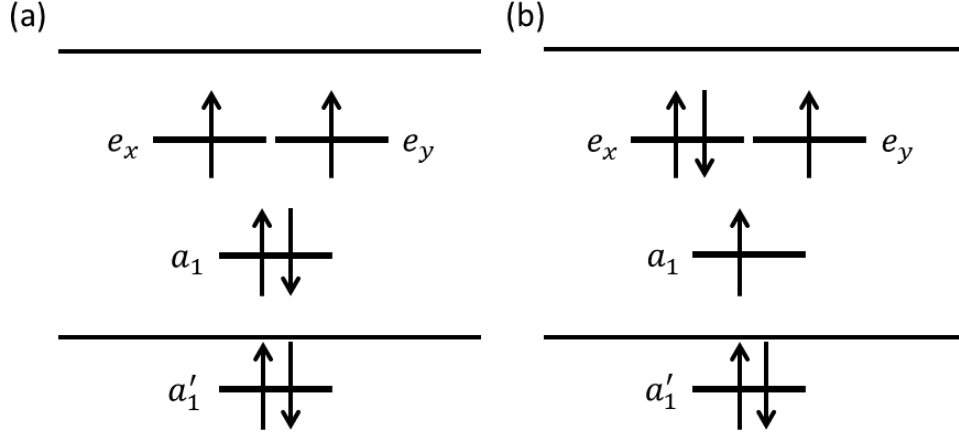


Figure 2.12: **A schematic of the ground state level configuration.** (a) The a -orbital is completely filled. The wave function is denoted as $|e_x e_y\rangle$ with a total spin of $|m_s\rangle = |-1\rangle$ for 3A_2 state symmetry. (b) Only one of the a -orbitals is completely filled. The wave function is denoted as $|a_1 e_y\rangle$ with a total spin of $|m_s\rangle = |-1\rangle$ for 3E state symmetry.

The symmetry operations are represented by a set of matrices called a group representation. The building blocks for all the possible representations are three irreducible representations (*IRs*) labelled A_1 , A_2 and E according to the Mulliken notation with dimensions one, one and two, respectively. The matrix representations of the IRs for the C_{3v} group is given in Tab. 2.4. A_1 represents all the group operations by 1, while A_2 represents the rotations $\{e, C_3^+, C_3^-\}$ by 1 and the reflections $\{R, R_2, R_3\}$ by -1 . The energy levels associated with these representations are nondegenerate, where an eigenstate can transform into itself under any of the symmetry operations, only picking a negative sign under reflection if it ever transforms as A_2 . E is two-dimensional, and hence its corresponding energy level is degenerate with two eigenstates that transform into each other with matrix representations that includes both cartesian and spherical components ($\xi = \mp \frac{1}{\sqrt{2}}(x \pm y)$), also given in Tab. 2.4.

Table 2.4: Irreducible representations of the group C_{3v} . [107].

C_{3v}	e	C_3^+	C_3^-	R_1	R_2	R_3
A_1	1	1	1	1	1	1
A_2	1	1	1	-1	-1	-1
E	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$

The symmetry of the system provides with information regarding the symmetries of the wave functions and the prediction of the selection rules governing the center's transitions. Predicting the selection rules without knowing the exact wave functions, requires the use of group theory, which states that, the wave functions of a system can be characterized by the way they transform under symmetry operations [104]. For instance, the understanding of the allowed electric dipole transitions between

energy eigenstates of a system can be gained from symmetry considerations. The spatial doublet associated with the spin triplet excited state transforms as the E IR, while the spatial part of the spin triplet ground state transforms as A_2 . The orbital doublet of E averages out at room temperature to form a spatial singlet and spin triplet [109]. Because of the dipole interactions, one can access the excited state from the ground state via a green laser (e.g., ~ 532 nm). The optical electric dipole transition between the initial (Ψ_i) and final (Ψ_f) state is allowed such that the dipole matrix element satisfies,

$$\langle \Psi_f | \mathbf{d} \cdot \mathbf{E} | \Psi_i \rangle \neq 0 \quad (2.41)$$

where $\mathbf{d}$ is the electric dipole operator and $\mathbf{E}$ is the electric field. However, the transition can also be forbidden if there is no $\mathbf{d}$ component belonging to the same representation as Ψ_f . Consequently, we can use the symmetry operators that transforms according to the IRs to find the forbidden transitions by writing the dipole operator $\mathbf{d}$ in terms of the symmetry operators. Due to C_{3v} symmetry, the position operator z along the NV axis transforms as A_1 and the cartesian components $\{x, y\}$ transform as E IRs, respectively. Since we also know that the ground state transforms as A_2 and the excited state as E , using Eq. 2.41 we are able to find the allowed transitions whenever $\mathbf{d} \cdot \mathbf{E}$ transforms as E IR. This implies that for the electric field polarized along $\{x, y\}$, the probability for the dipole transition is non-zero, while for the z polarized electric field the probability is zero. It is worth noting that the dipole transition process is spin conservative as the process only operates on the spatial part of the wave function, leaving the spin component the same.

2.4 Electronic properties and spin manipulation

Studies based on the electronic structure of NV centers have been paramount to understanding its optical capabilities, and ever since its insertion it has attracted many contentious debates, with several aspects yet to be consensually agreed upon. A thorough consideration of the structure of the center has to be taken into account in order to extensively understand its electronic properties. It is well established that the trigonal symmetry of NV centers with an even number of electrons is consistent with an adjacent nitrogen-vacancy pair having C_{3v} symmetry [110]. Loubser and van Wyk [111], confirmed the structure of the NV center with an integer spin ($S=1$), via electron paramagnetic resonance (EPR) experiments, observing and interpreting the EPR spectra to be associated with a metastable triplet state in between optically active singlet states (1A and 1E) for a negatively charged center. This was based on their observation of the EPR signal, initially thought to be only detectable under optical illumination with increase in ZPLs and phonon peaks when excited.

The charge state was later effectively affirmed by Mita [78], as elaborated in the previous sections. It was also later established unambiguously by optical hole-burning studies by Reddy et al. [112], that the triplet configuration is actually a ground triplet state (3A) with an optical transition depicted as $^3A \rightarrow ^3E$, which was also substantiated by optically detected magnetic resonance (ODMR) experiments performed by Van Oort et al. [113]. The EPR signal under illumination contention was also resolved by Holliday et al. [114], when they were able to detect a signal in

the absence of any optical pumping. The dependence of the EPR signal strength on optical excitation is well understood to be due to optical spin-polarization [112]. Thus far, the accepted model for the triplet state is described as having six unpaired electrons: 2 electrons from the nitrogen atom and 3 electrons from the surrounding carbon atoms and an additional electron captured by the defect. Lenef and Rand [107], gave the orbital basis states via LCAO for the center having $n = 2, 4$ and 6 active electrons, but wrongly suggested the 2 electron model case to be correct for the negatively charged nitrogen vacancy complex, which was inconsistent with experiments and other theoretical work [115].

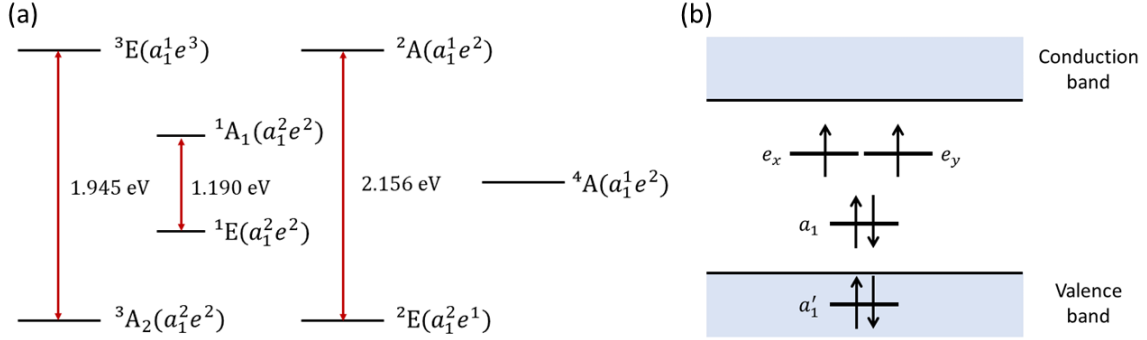


Figure 2.13: **Electronic scheme of the NV center in C_{3v} symmetry with a molecular model.** (a) The electronic levels and the electron occupation of the molecular orbitals of the center together with their respective ZPL energy transitions. (b) Molecular orbitals (MOs) associated with the 6-electron model of the center.

Following the pioneering work by Lenef and Rand [107], Manson et al. [63], gave a more correct and detailed six electron model for the energy levels having optical transitions associated with the electronic structure of the center as shown in Fig. 2.13 (a). The schematic represents the widely accepted electronic structure of an NV center, with electron occupation of the molecular orbitals. The 6 electrons occupy sp^3 formed dangling bonds of the vacancy complex which is made up of two A_1 (a_1 , a'_1) and one degenerate E (e_x , e_y) molecular orbitals (MOs), with one of the A_1 orbitals in between the energy band gap while the other is within the valence band, the E orbital is also located in between the band gap, as illustrated in Fig. 2.13 (b). This arrangement of the defect orbital structure approximates a tetrahedral T_d symmetry, as expressed by Coulson and Kearsley [76], i.e., each carbon atom is surrounded by four nearest neighbor atoms forming a regular tetrahedron. Now, the dangling bonds of the carbon and nitrogen atoms can be combined to form individual MOs a_1 and t_2 with A_1 and T_2 symmetry, respectively. When a nitrogen atom replaces a carbon atom, the tetrahedron symmetry reduces to a trigonal symmetry, causing t_2 to split into a_1 and e orbitals, occupied by the 6 electrons, representing a C_{3v} symmetry. The orbital treatment of the ground state is given: while ignoring the a'_1 -orbital, the electron configuration of the ground state is given by $a_1^2 e^2$ (e^2) where the superscript stands for the number of electrons. If ever one electron is excited, as denoted in Fig. 2.12 (b), the configuration changes to $a_1^1 e^3$ (ea_1). The e orbital is lowest in energy. Now, the lowest energy configuration of the system is then given by e^2 , followed by the combination ea_1 , and the highest by a_1^2 . Since the optical transition is related to triplet states, the lowest energy configuration leads to a triplet ground state $^3A(e^2)$ and two singlet states $^1A_1(e^2)$ and $^1E(e^2)$. The ea_1 energy configuration leads to the

triplet excited state ${}^3E(ea_1)$ and the singlet excited state ${}^1E(ea_1)$, while the highest energy configuration a_1^2 leads to the singlet ground state ${}^1A_1(a_1^2)$.

2.4.1 Optically detected magnetic resonance

ODMR is commonly used to detect and characterize the orientation of the NV centers within the diamond matrix. This takes into consideration the electron spin states of the center. The ground state of the NV^- center is known to be a spin triplet state (3A) with degenerate sub-levels $|m_s\rangle = |0\rangle$ and $|m_s\rangle = \pm 1$ at zero magnetic field. By neglecting the weak hyperfine interactions, the spin-Hamiltonian for the spin triplet ground state (3A) is represented by the Zeeman ($g_e\beta_e\vec{B} \cdot \vec{S}$) and zero-field ($\vec{S} \cdot D_{gs} \cdot \vec{S}$) splittings as follows,

$$H = D_{gs}(S_z^2 + \frac{1}{3}S^2) + g_e\beta_e\vec{B} \cdot (S_x\sin\theta_{NV-B} + S_z\cos\theta_{NV-B}), \quad (2.42)$$

where $D_{gs} = 2.88$ GHz is the zero-field splitting as seen in Fig. 2.14 (a) [116], between the sub-levels of the spin triplet ground state $m_s = 0$ and $m_s = \pm 1$ due to the spin-spin interaction in the defect, $S = 1$ is the total spin angular momentum of the ground state, $g_e\beta_e = 27.98$ GHz T $^{-1}$ is the electron gyromagnetic ratio and θ_{NV-B} is the angle between the magnetic field $\mathbf{B}$ and the NV^- axis, depicted in Fig. 2.7 (b).

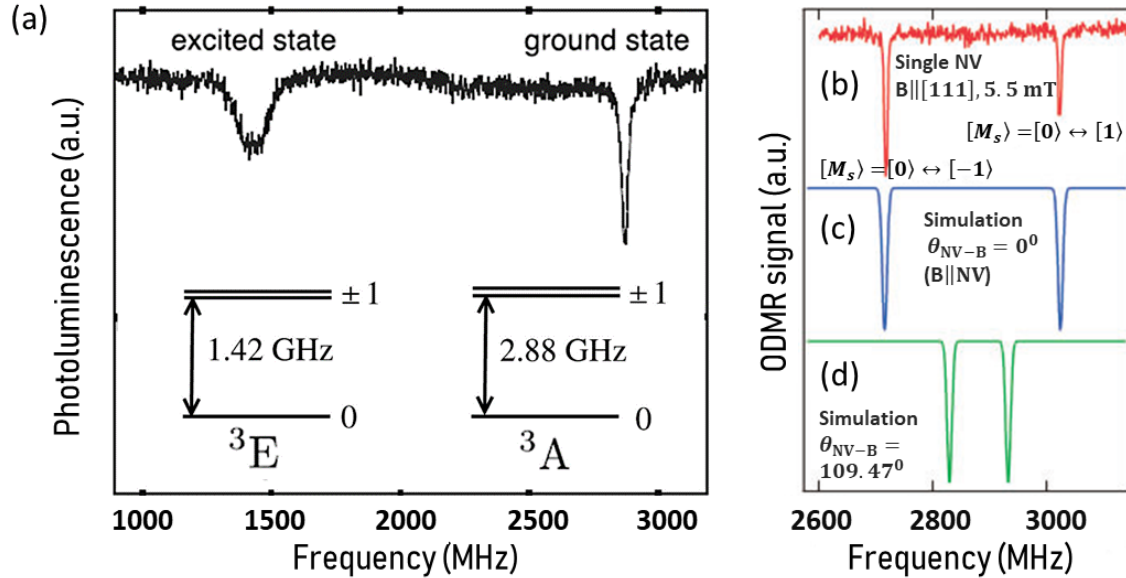


Figure 2.14: **Optically detected magnetic resonance measurements.** (a) ODMR spectra of a single NV^- center with zero field splittings of spin sub-levels $|m_s\rangle = |0\rangle$ and $|m_s\rangle = \pm 1$ in between the energy states 3A_2 , 3E [116]. (b) The effect of the orientation axis of NV^- to the ODMR signal [31].

In order to remove the degeneracy for individual transitions, a magnetic field ($\mathbf{B}$) is applied along the center's possible orientation axis. This allows the separate optical readout of the magnetic resonance for transitions, $m_s = |0\rangle \longleftrightarrow |1\rangle$ and $m_s = |0\rangle \longleftrightarrow |-1\rangle$ [117]. One can also use circularly polarized light at zero magnetic field to manipulate individual transitions owing to microwave polarization selection rules. Now, the spin dependency of the optical readout influences the intensity of the fluorescence from the NV centers [113]. Fukui et al. [31], reported

experimental and simulated results of the spin transitions at low and high frequencies for $m_s = |0\rangle \longleftrightarrow |-1\rangle$ and $m_s = |0\rangle \longleftrightarrow |+1\rangle$, respectively, as seen in Fig. 2.14 (b-d) [31]. The magnetic field at Fig. 2.14 (c), is parallel to the NV axis $[111]$ measured for that orientation while at (d) the magnetic field is parallel to NV axis $[111]$ but measured for the remaining possible orientations, $[1\bar{1}\bar{1}]$, $[\bar{1}1\bar{1}]$ and $[\bar{1}\bar{1}1]$. The results discussed, shows the NV⁻ ODMR frequencies obtained experimentally for $\mathbf{B} = 5.5$ T applied along the $[111]$ orientation axis ($\mathbf{B} \parallel [111]$) as seen in Fig. 2.14 (b). The simulated spectra in Fig. 2.14 (c), produced similar results only when $\theta_{\text{NV-B}} = 0^\circ$ for $\mathbf{B} \parallel \text{NV}$ where $\text{NV} \parallel [1\bar{1}\bar{1}]$, $[\bar{1}1\bar{1}]$, $[\bar{1}\bar{1}1]$. The results in Fig. 2.14 (c), differed from results at (b) due to the variation of $\theta_{\text{NV-B}}$ with respect to the orientation axis. This was to determine the effect of $\mathbf{B}$ on the spin polarization within the NV⁻, and hence the clear identification of the NV axis.

Neumann et al. [116], studied the electron spin resonance (ESR) of the energy states of NV centers, providing with varied frequency positions due to the NV symmetry orientations. They were able to observe photoluminescence intensity fluctuations while applying microwaves through a micro-wire (copper) in close proximity to the NV center. The spin-Hamiltonian for the triplet excited-state, while neglecting the hyperfine interactions, includes the strain-induced fine structure ($E_{es}(S_x^2 - S_y^2)$) splitting and is given by,

$$H = D_{es}(S_z^2 + \frac{2}{3}) + E_{es}(S_z^2 + S_y^2) + g_{es}\mu\vec{B} \cdot \vec{S}, \quad (2.43)$$

where $D_{es} = 1.42$ GHz is the zero-field splitting between the sub-levels of the excited state, E_{es} is the splitting coefficient due to strain while g_{es} and μ are the electron Zeeman g-factor and the Bohr magneton associated with the excited state respectively. If the strain-induced fine structure is negligible such that $|E_{es}(S_x^2 - S_y^2)| \ll |g_{es}\mu\vec{B} \cdot \vec{S}|$, the resonant ESR frequencies associated with the sub-level $m_s = \pm 1$ are given by,

$$\omega_{\pm} = D_{es} \pm g_{es}\mu\mathbf{B}, \quad (2.44)$$

The results obtained were able to affirm both values of D_{es} and g_{es} for the 3E state structure, of which is very useful in quantum diamond-based QIP via full optical control of single spins [117]. A metastable state (Fig. 2.6 (b)), also exists between the ground and excited triplet states with non-radiative inter-system crossing (${}^3E \rightarrow {}^1A_1$), and appear to be responsible for spin polarization measurements and hence critical in the study of the center's spin dynamics [116].

2.4.2 The fine structure of the ground state of NV⁻

The energy level schematic of an NV⁻ center is given in Fig. 2.15. EPR and *ab initio* studies of the electronic structure of the center measured the fine structure splitting of its ground state to be ~ 2.88 GHz [111], between sub-levels $|m_s\rangle = |0\rangle$ and $|m_s\rangle = \pm 1$. However, the ordering of the energy associated with the splitting was introduced much later by level anticrossing studies of the NV center via Raman-heterodyne paramagnetic resonance [118, 119]. The reason for the splitting became a bone of contention for several years, over whether the electronic spin-spin interactions or the spin-orbit interactions or both are responsible for such effects. Lenef and Rand [107], showed by considering the symmetry of the center, that the fine splitting of the ground state into 2 sub-levels, $A_1(0)$ and $E(\pm 1)$, illustrated in

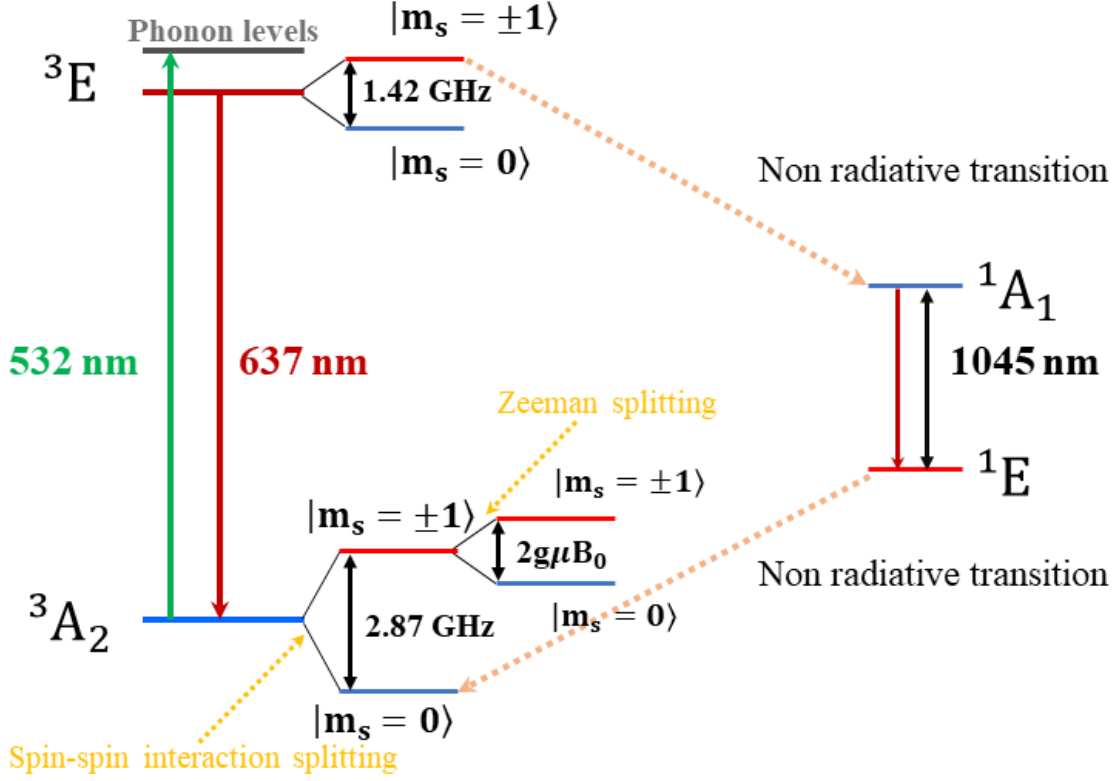


Figure 2.15: **Energy level schematic for NV⁻ center.** The allowed optical and magnetic transitions represented respectively by the radiative (solid arrows) and non-radiative (dashed arrows) transition lines.

Fig. 2.16 (a), is due to the spin-spin interactions, whereas the spin-orbit interactions, though negligible for the ground state [63], are responsible for the second-order (hyperfine) energy splitting. The spin-Hamiltonian describing the fine and hyperfine structures of the ground state 3A is illustrated by the following equation,

$$H_{gs} = D_{gs}[S_z^2 + S(S+1)/3] + A_{gs}^{\parallel} S_z I_z + A_{gs}^{\perp} [S_x I_x + S_y I_y] + P_{gs}[I_z^2 - I(I+1)/3], \quad (2.45)$$

where $D_{gs} \sim 2.88$ GHz is the zero field splitting, with the fine parameter given by the nuclear electric quadrupole (P_{gs}) while the hyperfine parameters are given by axial ($A_{gs}^{\parallel}$) and non-axial ($A_{gs}^{\perp}$) components.

On the other hand, the excited state also exhibit the splitting effects similar to that of the ground state at low temperature. In this case, the spin-orbit interactions are responsible for a 3 sub-level splitting, with two E symmetry ($E(0)$ and $E(\pm 1)$) and one degenerate A_1, A_2 symmetry. The spin-spin interactions further splits the A_1, A_2 symmetry, leading to 4 sub-levels, with degenerate E symmetries. Transverse strain effects on the excited state were also measured by Batalov et al. [120] with interesting results shown in Fig. 2.16 (c), where the degeneracy of E symmetry is lifted due to the strain energy $d_{es}^{\perp} \delta_{\perp} = \sqrt{\delta_x^2 + \delta_y^2}$, resulting in further splitting of the excited state sub-levels $E(0)$ and $E(\pm 1)$ into two triplets, respectively represented by E_x and E_y symmetries.

A magnetic field induced zero-field splitting ($D_{es}^{\parallel}$) for the excited-state sub-levels

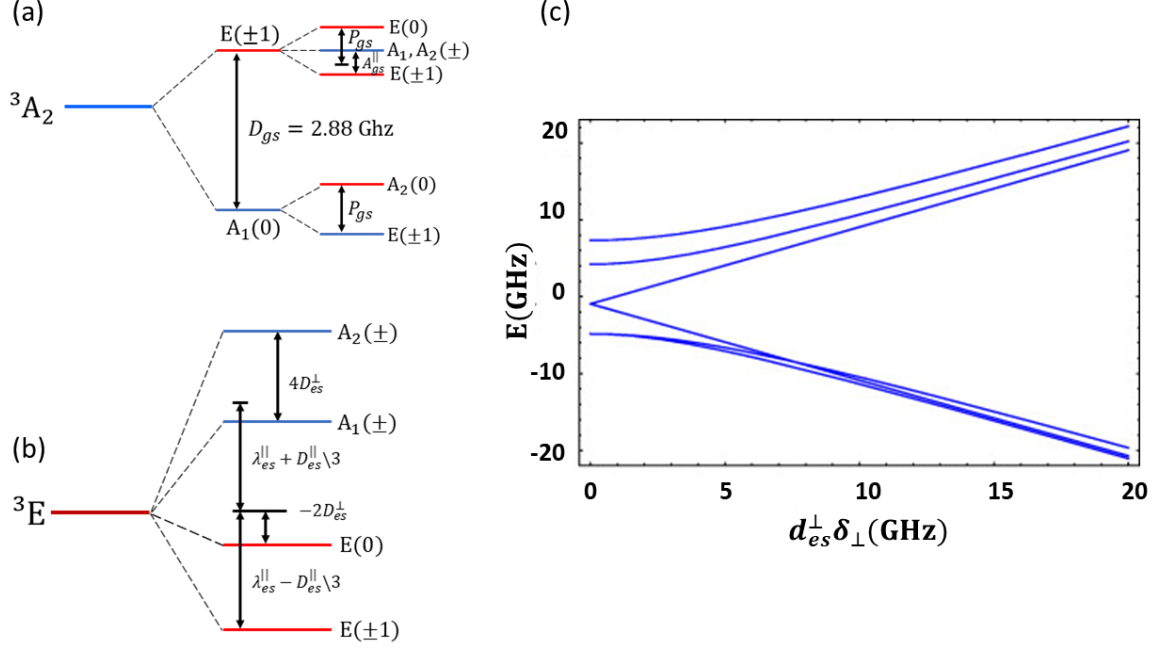


Figure 2.16: **The fine structure splittings of both energy levels.** (a) and (b) Represents the effect of spin-spin, spin-orbit interactions on the ground (3A_2) and excited (3E) states in the presence and absence of strain [82]. (c) The effect of the transverse strain energy on the fine structure of the NV^- [115].

was also determined to be ~ 1.42 GHz, via electron spin resonance (ESR). The following effective Hamiltonian describes the low temperature fine structure of the excited state (3E),

$$\begin{aligned}
 H_{es} = & D_{es}^\parallel [S_z^2 - S(S+1)/3] - \lambda_{es}^\parallel \tau_y \otimes S_z \\
 & + D_{es}^\perp [\tau_z \otimes (S_x^2 + S_y^2) - \tau_x \otimes (S_y S_x + S_x S_y)] \\
 & + \lambda_{es}^\perp [\tau_z \otimes (S_x S_z + S_z S_x) - \tau_x \otimes (S_y S_z + S_z S_y)],
 \end{aligned} \tag{2.46}$$

where the fine structure operators are depicted by the Pauli matrices τ_x , τ_y and τ_z , while the $S = 1$ spin operators are represented by S_x , S_y and S_z . The structure parameters for the spin-spin interactions are given by $D_{es}^\parallel$ and $D_{es}^\perp$ while the spin-orbit interactions are given by the axial component $\lambda^\parallel$ with the non-axial component ($\lambda_{es}^\perp$) having contributions from the spin-spin interactions [64].

The room temperature observation of the fine structure of the excited state (3E) at ~ 142 GHz was reported most recently by Epstein et al. [121], through ODMR experiments. Rogers et al. [109], demonstrated that the observed electronic spin resonance (ESR) measurement is accredited to the temperature dependent time-averaging within the excited state 3E due to phonon interactions over both branches of the fine structure. As a result of the averaging, the zero field spin-level splitting between the sub-levels of 3E is independent of strain within the crystal. This is crucial for the NV^- centers potential advancement in room temperature applications where the spin polarization is stronger. Doherty et al. [64], provides a very detailed interpretation of the fine structure of the NV^- center. The spin-Hamiltonian is also found to be similar to that of the ground state (3A).

Chapter 3

Ion implantation in diamond

3.1 Introduction

We now know from Chap. 2 that each respective fabrication technique for NV color centers has a variant effect in the optimization of crucial parameters for various applications involving NV centers. This includes the modification of magnetic field sensitivity for magnetometry studies, ZPL broadening for improved field-emission and collection efficiencies, PL intensity enhancements for increased flux of single photons and bio-sensing applications. The engineering of NV centers over preselected regions in a diamond substrate necessitates any ion doping technique that affords the user good precision and control over the distribution of the ions. The success of synthesizing diamond in the 1950s, brought about immense discussions in Semiconductor Physics on how to incorporate dopants in the solvents used as ingrowth products for synthetically grown diamonds. It turns out dopants can be integrated in this fashion, however it is extremely difficult to control the ion distribution within the diamond substrate. Alternatively, the careful introduction of ions and high energy particles into the diamond matrix via radiation damage processes presents a better way of introducing dopants with desired densities at any spatial location within the diamond matrix. All of these methods are well established with numerous detailed studies published for each process. In this chapter we study the implantation of ions as the experimental technique of our choice in fabricating isolated NV centers in a relatively pure type IIa diamond sample.

3.2 Ion doping in diamond

The Physics of introducing extrinsic ions in semiconducting materials has long been studied by many capable scientists. This was mainly for the realization of p-type and n-type semiconducting devices that were widely being implemented in the electronics industry at the time with microelectronic devices (i.e., transistors, diodes, lasers, etc.), based on commonly employed semiconducting materials such as Silicon (Si), Gallium Arsenide (GaAs) and Germanium (Ge) [122, 123]. However, diamond was also viewed as an excellent alternative for building superior electronic and optoelectronic devices due to the atomic arrangement of diamond resembling that of two thriving semiconducting materials in Si and Ge [124]. This alerted scientists of the potential possessed by diamond as a super material for similar applications and more [125], propelled even further after the discovery of natural semiconducting diamonds in

1952 by Custers [47]. At the time, the excellent properties of diamond were very appealing in Semiconductor Physics, where at the same time, it became apparent that the same properties that attracted so much attention also hindered any progress in building diamond-based semiconducting devices. There were reported challenges in modifying the electrical and optical properties of diamond by ion doping as compared to other successful semiconducting materials [124].

Now, the science of ion doping in diamond was propelled when Bundy et al. [49], reported the first successful man-made diamonds under HPHT conditions, 3 years after natural semiconducting diamonds were discovered [47]. Soon after the work by Bundy et al. [49], many scientists in the field attempted to synthesize doped diamonds, with some reported success [126–128]. However, there were serious restrictions over the lack of control over important parameters related to doping substrates in preselected areas with any desired impurities [129, 130]. The major implication of such a process was that the whole diamond would be doped non-selectively. Regrettably, most semiconductor applications require ion doping only for certain locations at predetermined densities for any semiconducting material, including diamond [124]. Alternatively, scientist began to explore the forceful injection of ions in the diamond matrix via ion implantation proposed a few years before semiconducting diamonds were discovered. Ion implantation gave some hope that one can ensure the doping of ions at desired areas with predetermined ion densities.

While investigating this process in 1965, Wentorf Jr and Darrow [131], reported that a diamond surface became conducting as the result of ion bombardment in a glow discharge producing low energy ions (eV). Soon after, Vavilov et al. [132] followed this up by measuring the semiconducting activation energies of boron and lithium ions doped in diamond at keV energy levels. The reported conductivity due only to the implanted dopants proved to be a complex process, leading to many contradicting claims made by scientists in the field [124]. The doping of ions in diamond via ion implantation solely for the fabrication of viable electronic and optoelectronic devices has since been very much a challenging task despite some recent encouraging reports. A successful semiconducting diamond requires controlled doping of both acceptors and donors (i.e., p-type and n-type doping) [123, 125]. The p-type doping in diamond has been shown with boron electron acceptors perfectly integrated into the crystallographic structure of a diamond substrate [132, 133]. However, similar results for suitable n-type doping have been far more elusive [134].

The low concentration doping of boron by ion implantation with annealing showed to have produced p-type acceptor states in the diamond situated at 0.37 eV above the valence band [132], as depicted in Fig. 3.1. One of the commonly found n-type deep donor centers in diamond is substitutional nitrogen N_s [84, 135], with an ionization energy of 1.7 eV below the conduction band, according to electrical measurements. The ionization level lies too deep to transfer adequate amount of electrons within the conduction band at room temperature [136]. Suitable electronic devices require the dopant states to be much shallower than 1.7 eV. Another viable choice for donor centers is the much heavier phosphorus P dopant which is found to be 0.6 eV deep below the conduction band [137], which is shallower than N_s donors. However, the conductivity caused by P donors at room temperature is relatively poor [138]. This is due to the excessive radiation damage imposed by the heavier P dopants, which effectively requires annealing to reconfigure the diamond structure. Following disappointments with conventional ion implantation and annealing, cold implantation

rapid annealing (CIRA) was imposed for the fabrication of P n-type dopant diamonds at varied temperatures [124]. At high temperatures, the annealing process was found to be damaging to the P-doped layers [139], and may even deactivate the activated P-dopants. At lower temperatures, the residual vacancy density is high, and hence low quality P-doped layers are formed with high resistance for Hall-effect measurements to be performed successfully [140]. Hence, what is currently required is a smaller radii n-type dopant with shallow donor levels that will leave far less residual damage on the substrate [138].

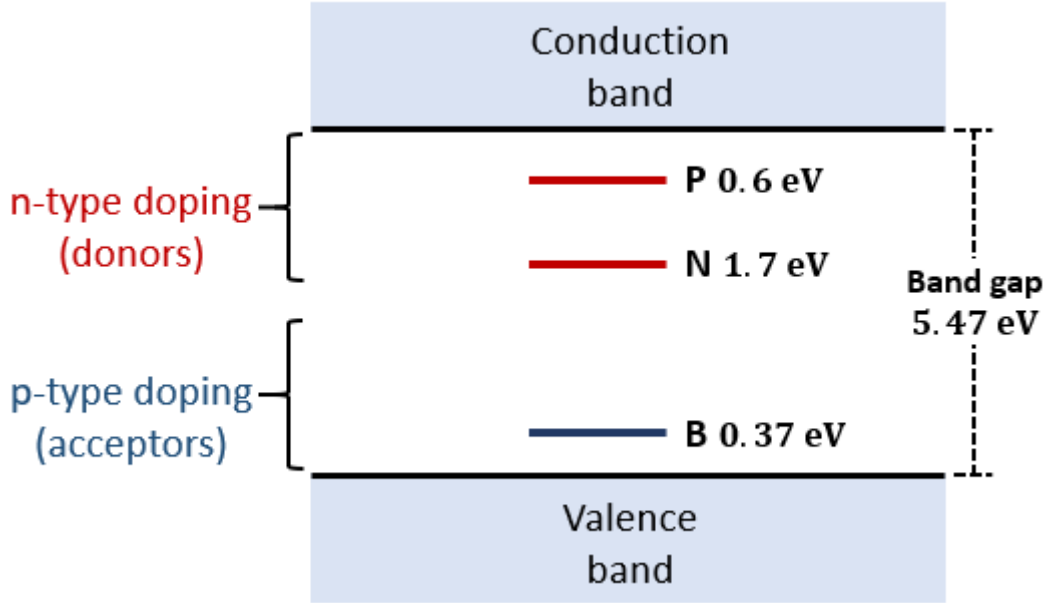


Figure 3.1: **Band gap states in diamond.** The energy states for n-type donors represented by Phosphorus (P 0.6 eV) and Nitrogen (N 1.7 eV) dopants below the conduction band, and a p-type donor represented by Boron (B 0.37 eV) dopant above the valence band.

Due to slow progress, research based on semiconducting diamonds for electronic use has been declining during the last decade or so. However, the application of ion implantation in diamond has since gained some renewed momentum, mainly due to the fabrication of isolated luminescent defect centers (i.e., NV centers) in diamond that can serve as qubits for QIP [141]. In the next sections we investigate ion implantation for the purpose of fabricating isolated NV centers for QIP.

3.3 Ion-solid interactions

The process in which an energetic particle is accelerated into a solid material is known as an ion-solid interaction process, and has been studied extensively in the field of material science since the early 1900s. Ernest Rutherford is credited as being one of the first scientists to experimentally observe such an effect [142]. The experiment in question involved the bombardment of alpha (α) particles from an α -particle emitting Radon source onto a metal foil. This demonstrated that energetic particles can be stopped and scattered by matter, subsequently introducing into science the Physics of ion-solid interaction [143]. Consequently, ion beam technology was developed.

Zeigler et al. [143], gives a detailed study on the development and advancement of the aforementioned technology with various processes and applications presented over the years, including among others ion beam analysis (IBA), substrate sputtering, ion beam mixing and artificially induced ion implantation [144].

3.3.1 Ion implantation

Ion implantation is known as a harsh, non-equilibrium and low temperature process in which ions (ranging from a few keV to MeV) are forcefully injected into the near surface region of any solid material [144]. The ions interact with the target atoms by breaking their chemical bonds and displacing them from their lattice sites, thereby altering the atomic structure of the target material and in other cases altering also the elemental composition of the target material if the target atoms differ from the implanted ions [144, 145]. The modification of the lattice atomic structure through the transfer of energy from a projectile ion to a target atom is known as radiation damage [144]. Furthermore, the interaction between the energetic ions and the target atoms usually results in the creation of point defects, which can migrate and cluster with each other, resulting in extended defects or dislocation loops. Figure 3.2, depicts the possible defects formed by ion implantation, ranging from vacancies, interstitials and simple complex defects such as a pairing between a vacancy and an interstitial (i.e., Frenkel pairs). For a broader inspection on the subject the reader can refer to text by Dresselhaus and Kalish [144]. Ion radiation damage dictates that the incident energy (E_i) of the incident ion must be greater than the displacement energy (E_d) of the target atom. Under proper transient conditions, a single incident ion with enough incident energy can dislodge multiple-target atoms which in turn can displace other target atoms, causing a collision cascade [143].

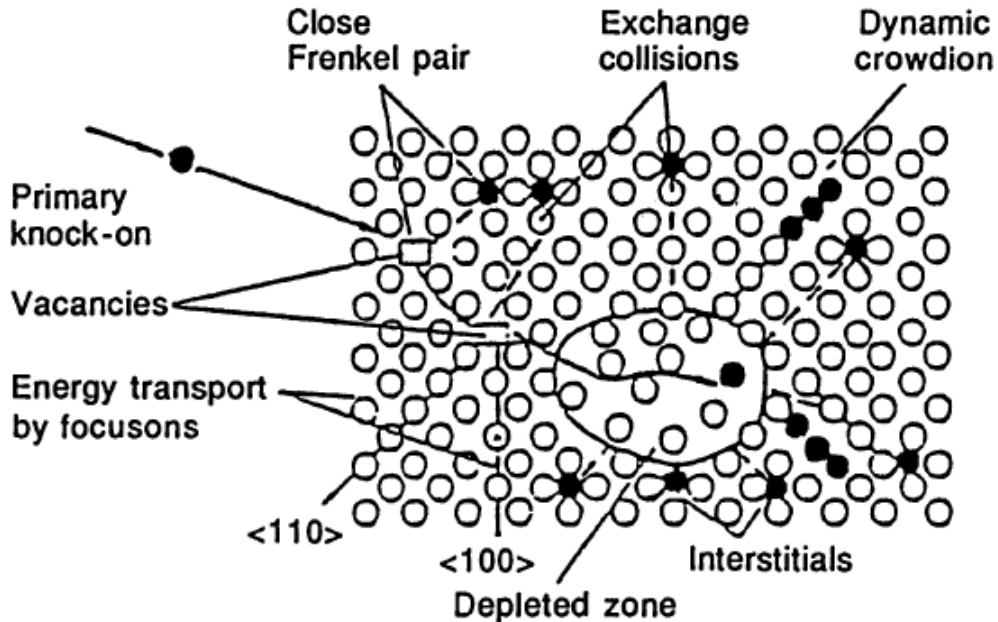


Figure 3.2: **Ion implantation interaction processes.** Illustration of possible defects induced by ion implantation [144].

Currently, ion implantation is the preferred radiation damage process of

introducing foreign atoms in a controlled way to avoid adverse effects on the properties of any given material, including the lattice structure of a crystal substrate, provided proper annealing procedures are employed. The annealing procedure follows the ion implantation process to remove any undesirable implantation-related damage and any graphitisation in the case of diamond substrates [68]. In the present case, we investigate the introduction of nitrogen (N) ions into a relatively pure diamond crystal for the fabrication of isolated NV centers [68]. The method is preferred due to the advantages it presents to the user, such as the easy regulation of the concentration of the NV centers fabricated due to the control over the N ion dosage and energies directed over any desired region on the sample, while the tailored doping profiles and reproducibility of results also makes it the more appealing process. Through this process, the N ions are accelerated through the diamond crystal surface and into the diamond lattice, interacting with the carbon (C) lattice atoms of diamond [143, 144]. A single N ion will undergo energy loss process (electronic and nuclear stopping) until it eventually stops within the diamond matrix or manages to shoot through depending on the thickness of the material and the energy of the injected ion.

3.3.2 Energy-loss process

Injected ions travel as far as the incident energy E_i allows them. A single ion travels through the thickness of the material, experiencing energy losses because of elastic and inelastic collisions it experiences against the target-atom nuclei and target electrons, governed by the ion mass and the target density. If the energy of the incident ion is greater than the displacement energy E_d of a single C target atom, then the C atom will be dislodged from its lattice point, causing a cascading processes through the diamond matrix resulting in primary knock-on events involving recoiling C target atoms, in which each dislodged C atom gains enough energy from the ion, which then causes secondary knock-on events in which other host atoms are also displaced from their lattice sites. Depending on the thickness of the target material and the incident ion energy, the process continues until the energy involved is no longer sufficient enough to dislodge any other atoms, eventually bringing into a halt any transient particle within the diamond matrix, otherwise the injected ion will pass through the target material [144, 146].

The crystal penetrating ion loses its energy via scattering effects involving the Coulomb interactions with the target atoms and electrons. The energy loss determines the penetration depth as well as the level of damage created within the lattice structure. The ion-solid interactions that are involved are represented by the well-documented elastic and inelastic collision processes as mentioned above [143]: electronic scattering, nuclear scattering and nuclear reaction effects. Nuclear scattering is the collisional elastic scattering process involving the incident ion and the target lattice atoms. The process results in the transfer of elastic energy from the moving ion to the stationary target atoms without altering the nuclear states of both colliding particles. Electronic scattering and nuclear reaction processes are both inelastic interactions between the incident ion and the cloud of electrons surrounding target-atom nuclei, in which both the nuclear and electronic states can be altered. These collisions within the diamond matrix are responsible for slowing down the implanted ion until it eventually comes to rest. The slowing down of an ion in matter is determined by the energy loss dE per unit length dx , generally known as the

stopping power represented as follows [144, 146],

$$\frac{dE}{dx} = NS(E), \quad (3.1)$$

where N is number of atoms per unit volume. In a collision event, the energy T lost by an ion with N target atoms per unit volume is given by,

$$-NS(E) \equiv -N \int T d\sigma, \quad (3.2)$$

where the negative sign indicates the loss of energy [143], $d\sigma$ is the differential collision cross-section. The aforementioned scattering events play a significant role in the loss of energy experienced by the incident ion. At low energy implants, the nuclear scattering dominates in stopping the incident ion represented by the **nuclear stopping power** $S_n(E) = (dE/dx)_n$, whereas at high energy implants the electronic scattering dominates the stopping of the ion and is represented by the **electronic stopping power** $S_e(E) = (dE/dx)_e$ [144], as depicted in Fig. 3.3, where E_2 and E_4 represent the energy regimes dominated by each stopping power, whereas E_3 is the energy below in which both the nuclear and electronic stopping power are comparable. The effect of the nuclear reactions to the motion of the incident ion is considerably small as compared to both the electronic and nuclear scattering processes and hence negligible in modeled calculations for the energy losses experienced by the ion. The approximated Hamiltonian describing each colliding event is hence divided into two components. The total stopping power due to nuclear and electronic processes is thus given by [144, 146],

$$\begin{aligned} S(E) &= S_n(E) + S_e(E) \\ &= N(\varepsilon_n + \varepsilon_e), \end{aligned} \quad (3.3)$$

where N is the atomic density of the scattering target atoms, ε_n is the nuclear stopping cross section and ε_e is the electronic stopping cross section.

The nuclear stopping process

The elastic scattering processes that takes place during the interaction of a moving incident ion with the nuclei of the target atoms is described by a repulsive Coulombic nuclear potential, $V(r)$ multiplied by the screening function $\Phi(r/a)$ [147], between the ion and a target atom, written as follows,

$$V(r) = \frac{Z_1 Z_2 e^2}{4\pi\epsilon_0 r} \Phi\left(\frac{r}{a}\right), \quad (3.4)$$

where Z_1 and Z_2 are the atomic numbers of the ion and target atom, respectively, e the electronic charge, ϵ_0 the permittivity of free space, r the interatomic distance and Φ is the screening function due to the electron clouds screening the nuclei where a represents the screening length. This scattering of the projectile ions by the screened potential of the target atoms is known as Rutherford Scattering.

The nuclear stopping power $S_n(E)$ dominates at low energy regimes as described in Fig. 3.3, where maximum damage usually occurs and increases as the mass of implanted ions increases. In practice, the nuclear stopping process implies that

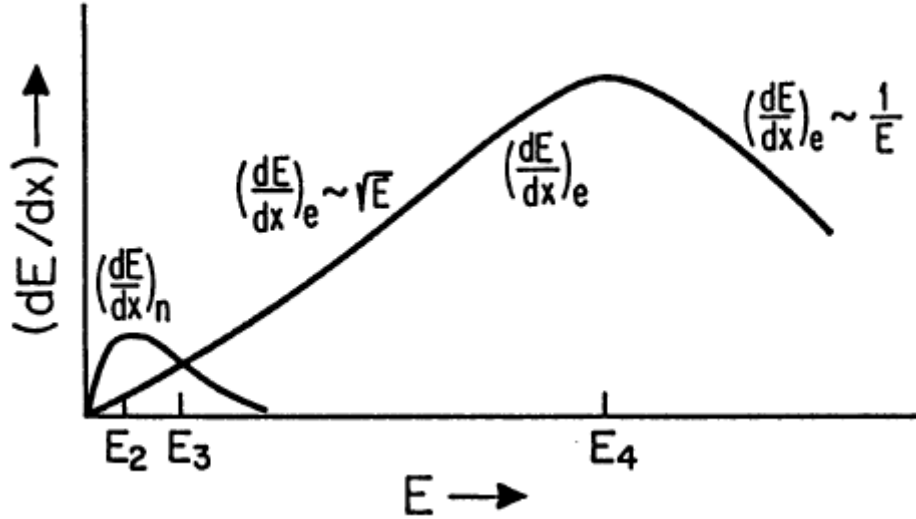


Figure 3.3: **Dependence of the nuclear and electronic stopping power on the energy of the projected ion.** At low energy implants (E_2) nuclear stopping power dominates in stopping the incident ion, while at higher energy implants (E_4) electronic stopping power dominates the stopping of the ion. At E_3 , the nuclear and electronic stopping power are comparable [144].

whenever an injected energetic ion penetrates a target material it loses energy as it collides with the nuclei of the target atoms, displacing many atoms from their lattice sites. This forces the moving ion to slow down, reaching low energies where the electronic stopping power begins to decrease and the nuclear stopping power begins to dominate. The nuclear energy loss is given by the following equation [146, 147],

$$S_n(E) = N \frac{\pi^2}{2} E^{-2} a \left[\frac{Z_1 Z_2 M_1}{M_1 + M_2} \right], \quad (3.5)$$

where N is the atomic concentration in the target material, a the lattice constant of the target lattice structure, E is the energy of the incident ion, M_1 and M_2 are the atomic masses of the ion and target atom, respectively. From Eq. 3.5, nuclear stopping is inversely proportional to the square of the energy of the incident ion (i.e., $S_n(E) \propto E^{-2}$). The nuclear stopping power together with the nuclear displacement energy becomes very significant in ion radiation damage processes implanted at very low energies.

The electronic stopping process

The electronic stopping process involves the interaction of the moving incident ion with the target electrons. This is an inelastic fast-collision process that leads to the excitation and ionization of the target atoms. Electronic stopping is a far more complex process as compared to nuclear stopping, and is usually modeled into multiple parts by comparing the velocity (v_1) of the ion to the Bohr velocity ($v_0 = e^2/\hbar$) [148], where e and $\hbar$ represents the electronic charge and Planck's constant, respectively.

According to Fig. 3.3, the electronic stopping power $S_e(E)$ dominates at high energies and ultimately depends on the velocity of the ion. This is where the energetic incident ion interacts with clouds of electrons of the target atoms, causing a direct

kinetic energy transfer to the electrons inducing a stopping force, slowing down the ion until the nuclear stopping process begins to dominate. Due to the high energy of the injected ions, the transient ion interacts less with the target atom-nuclei, which results in minimal target atom displacements for electronic stopping. Lindhard and Scharff [145], derived a relationship between the electronic stopping power and the energy of the incident ion as follows,

$$S_e(E) = \frac{8\pi e^2 a_0}{\epsilon_0} \frac{Z_1 Z_2}{(Z_1^{\frac{2}{3}} + Z_2^{\frac{2}{3}})^{\frac{3}{2}}} \left[\frac{E}{E_0} \right]^{\frac{1}{2}}, \quad (3.6)$$

where a_0 is the Bohr radius, E the energy of the incident ion and E_0 the Bohr energy. All other parameters are similar to Eq. 3.4 and Eq. 3.5. With this model, the electrons in the target material are viewed as a free electron gas interacting with a positive charge of the projectile. Also, the electronic stopping is proportional to the ion velocity (i.e., $S_e(E) \propto \sqrt{E}$) and does not allow any deviation in the projectile trajectory [146, 147]. The energy regions for the electronic stopping regime ranges from around 100 keV to 10 MeV. In this work we report on low keV energy regions, where the nuclear stopping power is more likely to dominate.

3.3.3 Projected ion range

Since the injected ion collides possibly with multiple target atoms, directing it into multiple directions, the ion does not travel to its resting position in a straight path. And hence, the distance traveled is integrated into a range R . The net penetration distance of the ion into the target material, measured along the trajectory of the incident ion is known as the projected range R_p . The projected ion range is integral in estimating the damage within the crystal lattice, and is obtained by integrating over Eq. 3.3 [144, 146],

$$R_p = \int_{E_i}^0 \frac{dE}{\left(\frac{dE}{dx} \right)_n + \left(\frac{dE}{dx} \right)_e}, \quad (3.7)$$

where the integration limits are from the initial ion energy to zero. Determining the projected ion range from the ion fluence (Ω_f) $> 10^{10}$ ions/cm² is through a statistical process, where the ion concentration is given by [144],

$$N(x) = N_p \exp \left[\frac{-(x - R_p)^2}{2\Delta R_p^2} \right], \quad (3.8)$$

where R_p is the projected range and accounts for the mean distribution depth of the ion and ΔR_p is the standard deviation for the distribution, which is essentially the longitudinal ion range straggling. The range straggling is the average fluctuation in the projected range, due to the uncertainty of the process, where the ions scatter and come to rest at distances less or greater than the projected range.

The peak concentration N_p at the center of a Gaussian shape distribution, depicted in Fig. 3.4, relates the ion fluence with ion depth distribution measured along the direction of the beam x . The peak concentration is given by [144],

$$N_p = \frac{\Omega_f}{\sqrt{2\pi}\Delta R_p}, \quad (3.9)$$

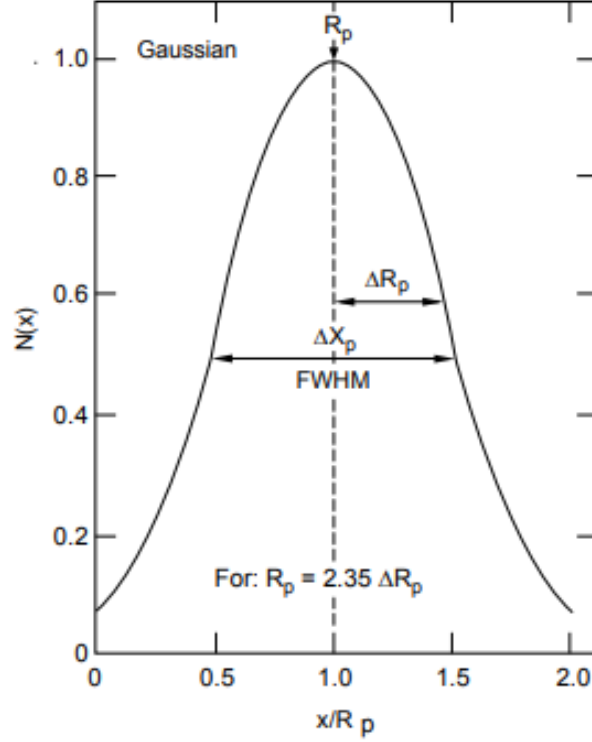


Figure 3.4: **Gaussian range distribution of implanted ion.** The Gaussian distribution of the implanted ion with $R_p = 2.25\Delta R_p$ and full width half maximum (FWHM) of ΔX_p [146].

where Ω_f is the ion fluence. At low ion concentration in the absence of channeling effects, the probability function is approximated by a Gaussian profile, whereas for high ion concentration in the presence of channeling effects, the probability function deviates from the Gaussian profile.

3.3.4 Crystallographic channeling effects

In principle, the theory based on projected ranges of energetic ions for ion irradiation is thus far limited to amorphous materials with disordered atomic structures, or more generally, isotropic and homogeneous target materials where the transient ions and the target atoms move chaotically with respect to each another. The impact parameter distribution depends mainly on the energy E of the ion, the atomic numbers of both the incident ion and the target atom, Z_1 and Z_2 , respectively. In the case of a single crystal (monocrystalline) with a periodically arrayed and perfectly ordered atomic structure, the orientation of the target material with respect to a probing beam also becomes an important parameter. When an incoming beam is parallel to a close-packed row of atoms in a single crystal target, the trajectory of the beam is channeled through the open spaces between the rows of atoms by the positive atomic potentials from the atoms. Hence, the dependence on the crystal orientation with respect to the injected ion is referred to as channeling or the channeling effect [144, 146].

When the ion channels through the material, it penetrates much deeper into the target material while making small angle collisions with the atomic rows reducing

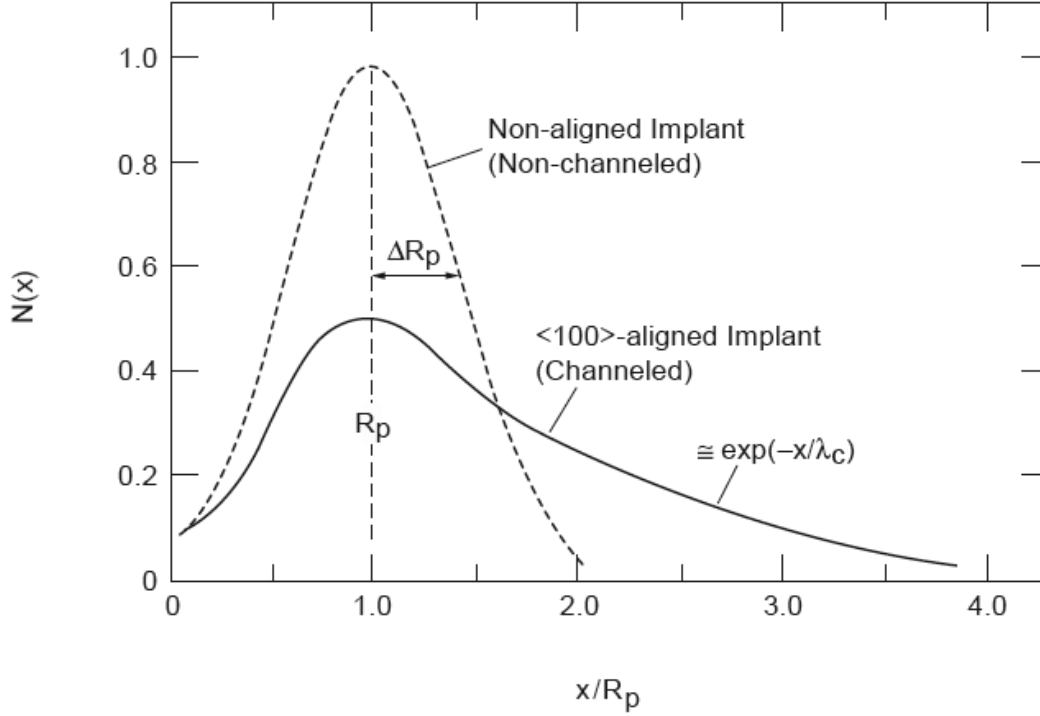


Figure 3.5: **Range distribution for an ion channeled along (100) axis.** The solid line shows the range distribution for a channeled ion in comparison with a Gaussian distribution (dashed line) for an ion undergoing no channeling effects [146].

the scattering yield in the substrate. Figure 3.5, gives the range (solid line) of a channeled incident ion along the (100) axis compared with a Gaussian range distribution (dashed line) of an incident ion experiencing no channeling effects. The depth distribution of the channeled ion is significantly reduced while the projected range R_p along x has significantly increased, due to the reduced scattering yield within the target material. For channeling to take effect, the injection of the incident ion must be aligned within a critical angle ($\psi_c < 5^\circ$) with respect to the crystal axes. This effect is usually avoided by injecting ions at an angle of about 7° with the target crystal axes. There are many published work on the interaction of a forcefully injected ion with a solid material, the reader can look at texts by Dresselhaus and Kalish [144], and Nastasi and Mayer [146], for more explicit details on the subject.

3.4 Ion distribution and calculated damage

The effects that an irradiated ion has on a crystal material such as diamond can be simulated using the Stopping and Range of Ions in Matter (SRIM) program. SRIM, along with its built-in calculation program TRIM, the Transport of Ions in Matter, is a Monte-Carlo simulation program that uses the Binary Collision Approximation (BCA) to predict the structural effects that a penetrating energetic ion has inside a solid material. It was first introduced by Ziegler and Biersack [147], in the early 1980s. In their text, extensive theoretical background of the implantation of ions is revised and used to facilitate the operation of the simulation program. The program is widely referenced in literature and it is well-known for its accuracy in simulating ion radiation damage in crystals. To keep up with new scientific developments, the

program has been updated approximately every five years ever since its inception. In this study SRIM-2008.03 version is used to perform calculations related to the damage and penetration depth incurred in diamond by the forceful injection of extrinsic N ions.

SRIM follows a statistical procedure where an ion is injected into a target material. The ion shoots straight across the material until it collides with a target atom where an impact parameter is randomly selected. TRIM proceeds to calculate the kinematics of the collision, and follows the trajectory of the recoiling target atom which also experiences collisions with other target atoms, consequently creating a branch of recoiling target atoms. Once all the recoiling target atoms attain energies below the the cutoff energy (E_{co}), the program returns and follows the motion of the original implanted ion. The ion proceeds with a new energy and direction of motion until a new statistically selected collision takes place creating another branch of recoils. The process continues until the energy of the ion is below the displacement energy E_d where it can no longer dislodge any more target atoms and eventually comes to rest. The program stores all the collision events involving the primary ion and target atoms, and proceeds to follow a new injected ion [143, 147].

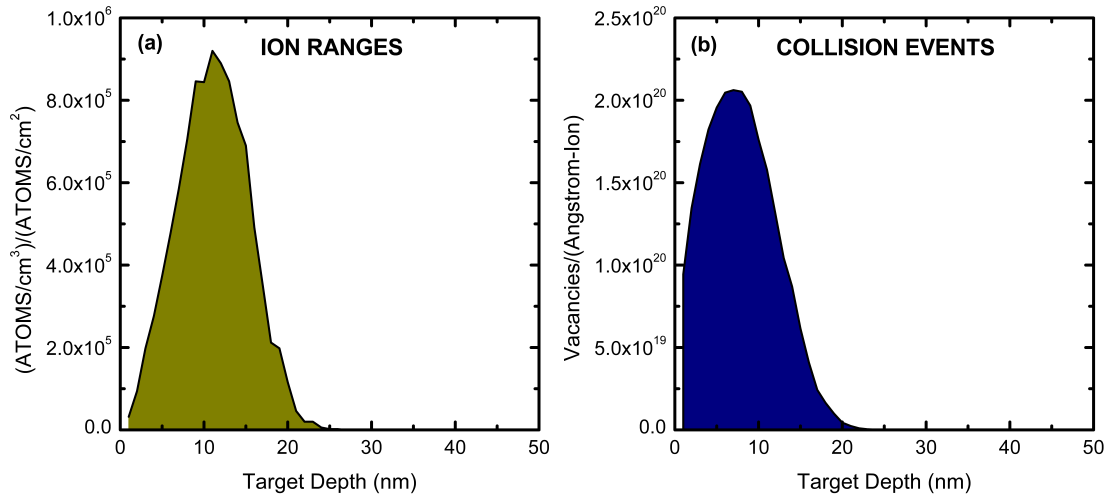


Figure 3.6: **SRIM** calculations for 7 keV nitrogen beam incident on a diamond crystal. Details from calculations with full damage cascades. (a) Depth profile of the N ions. (b) Vacancy distribution due to cascading of C atoms.

In this current study, a simulation involving N ions implanted in diamond at low energies ($\sim$ keV), was carried out in order to give a precise indication of the projected range and ion distribution that the ion implants can cause in the diamond sample before the actual experiment was performed. This follows the collisions that a single incident N ion experiences whilst traveling through the diamond matrix and the impact it has on the stationary target C atoms. The simulated results are based on input parameters such as ion type, ion energy, angle of incidence, target material, target atoms, the displacement energy of the target atoms and their density. A simulation for detailed calculation with full damage cascades was done for 7 keV N ions. This was done on a desired C layer width of about 1000 Å for implanted ions into diamond with a density of ~ 3.52 g/cm³ and a displacement energy E_d set at ~ 50 eV for diamond C ions. The simulation was done for about 5000 ions, which is

sufficient statistics to predict the depth to which most of the ions will stop and the damage distribution which is the vacancies that are created.

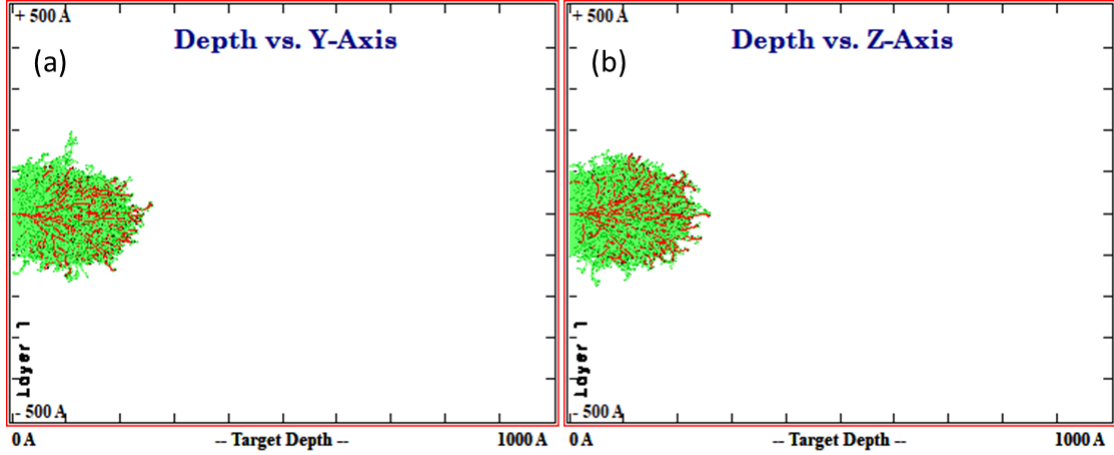


Figure 3.7: **SRIM** calculations for 7 keV nitrogen beam incident on a diamond crystal. (a) Ion distribution in red with collision cascades of the carbon recoils in green in the Y transverse coordinate. (b) Similar to (a), with only a change in the transverse coordinate to Z.

The model calculations give a good approximation of the ion depth and the scattering of the target atoms, however, they do not account for any ion channeling and possible phase changes experienced during ion implantation. Figures 3.6 and 3.7, are illustrations of direct SRIM output. Figure 3.6, depicts separate SRIM simulated plots for the (a) ion range or depth profile of the implanted ions and (b) vacancy distribution of the target atoms for implantation of 7 keV N ions into a diamond sample. With the collision events, given as the number of vacancies per angstrom ion as a function of depth, it is possible to determine the estimated damage (vacancy/ion), in the material when the plot is divided by 10^{-8} and multiplied by the ion fluence (ions/cm²) used in the experiment, to show the vacancy density (vac/cm³). Figure 3.7, describes the incident ion distribution in Y and Z transverse coordinates. The red paths represents the N ion distribution within the diamond matrix, while the green paths represents the carbon recoils and the dark spots denotes the stopping positions of the primary ions injected at an incident angle of $\sim 7^\circ$ with the surface. It follows that the radiation damage and range distribution of the implanted ions are predicted to be in an 20 nm^3 volume from the surface of the diamond. Further details on the results based on SRIM will be given in Chap. 5.

3.4.1 Damage recovery with thermal annealing

As mentioned in the succeeding sections, the ion implantation process involves the exchange of energy between the implanted ions and the target atoms of a solid material [143, 147, 148]. The energy exchange can be varied by controlling both the ion dosage and ion energy during implants. Unlike other semiconducting materials or covalently bonded solids like Si which at high ion doses, normally reverts back to an amorphous state (i.e., non-crystalline form of Si without the large-scale structural repetition of the Si crystalline structure.) [149], the structural damage of the diamond crystalline due to high ion implantation doses leads to an undesirable

graphite-like state, which is detrimental to the electrical properties required for semiconducting diamond. This is due to the breakage of the strong sp^3 bonds of diamond upon ion impact that may rearrange to the more stable sp^2 bonds associated with graphite. This is another level of complexity involving irradiation damage in diamond as compared to other materials [149]. Diamond reverting back to graphite is known as graphitization of diamond caused by a high damage density during implantation [150, 151]. The damage density threshold has been established to be about $\sim 1 \times 10^{22}$ vac/cm³ [149, 151]. It is referred to as the graphitization threshold or amorphization threshold for diamond in literature. From ion-doping studies it has been deduced that the defects that form during ion implantation are primarily vacant lattice sites and interstitials due to the foreign atoms [70, 124, 136]. Hence, it can be suggested that the damage accumulation is due to interactions between the vacancies and interstitials, possibly by recombinations between the two defects. It has also been inferred by other scientists that the recombination is substrate-temperature dependent [124, 136]. At $T \approx 50^\circ\text{C}$, the mobility of the interstitials is inhibited while that of the vacancies is virtually non-existent. At $50^\circ\text{C} < T < 500^\circ\text{C}$, the interstitials become mobile and interact with the vacancies, eventually annihilating them. At $T > 500^\circ\text{C}$, both the vacancies and interstitials are mobile and diffuse within the substrate and can agglomerate to form extended defects.

Thermal annealing of N implanted diamond

It is well known that heat treatment of a semiconducting material implanted below the amorphisation threshold can restore the structural integrity of the material damaged during the implantation process [70], while also inducing the formation of defects [56, 152]. There's a batch of studies based on the effects of annealing following the ion implantation of diamond substrates above and below the graphitization limit [153]. Most of the studies are based on the changes of the electrical conductivity measured during a set of annealing processes, as a function of temperature and time when the substrate undergoes conversion either to graphite or anneals back to diamond [154, 155]. These studies have established that the electrical conductivity in graphite is much more prominent than in diamond. Now, during N ion implantation below the graphitization limit, substitutional nitrogen N_s and vacancies are created along with other defects [56]. Many scientists have suggested and proven that vacancies are mobile at temperatures ranging above $500^\circ\text{C} - 600^\circ\text{C}$ [56, 70, 152]. The N_s is a stable defect with an activation energy of about ~ 5 eV measured at temperatures above $\sim 1700^\circ\text{C}$, which is a high energy barrier and hence the formation of defects related to the coupling of N_s with vacancies depend on the mobility of the vacancies [156, 157]. These mobile vacancies usually get trapped by the substitutional N_s which brings about the formation of both NV center species (i.e., NV^0 and NV^-) [156]. The mobility of the NV center related defect species in diamond is crucial to any understanding of the formation of NV centers, as the concentration of the centers due to ion implantation has been shown to increase during annealing [157]. The formation process involves the five valence electrons of the N_s atom and three unpaired electrons within the vacant lattice site [157]. Three electrons from N_s form covalent bonds with the carbon atoms of the host material while the two non-bonded electrons are called a lone-pair. Two of the three electrons associated with the vacancy form two quasi-covalent bonds while the third remains unpaired. The single unpaired electron of the vacancy is responsible for the paramagnetic nature of NV^0 ,

while for the NV^- , the vacancy site holds an extra electron coming from the lattice (nitrogen donors) which then form a spin-pair with the unpaired electron.

Chapter 4

Experimental considerations: instrumentation and sample preparation

4.1 Introduction

In this chapter we discuss the experimental techniques implemented in order to successfully fabricate isolated NV centers in a pure type IIa diamond sample. Discussions will be centered around the instrumentation used for ion implantation and heat treatment processes undertaken to ensure a controlled amount of ion induced damage desired on the above-mentioned diamond sample employed for this project. The chapter also gives an in depth overview of the PL intensity characterization technique implemented to ascertain the fabrication of the desired defects during the ion implantation process and the subsequent thermal annealing process. Lastly, the chapter also gives adequate information regarding the preparation techniques for the diamond sample used throughout the duration of this study.

4.2 Experimental equipments

4.2.1 The Ion implanter

In this project, ion implantation was the preferred fabrication technique to introduce foreign ions into a diamond sample in a repeatable and controlled way. The instrument that was used was the Varian-Extrion 200–20A2F ion implanter based at iThemba LABS, Gauteng, South Africa. A photograph of the aforementioned ion implanter is depicted in Fig. 4.1. The ion implanter is specially suited for the incorporation of dopants into semiconducting materials via electrostatic beam scanning of target wafers, mainly for manufacturing commercial semiconductor devices. The instrumentation was also modified for research implantation purposes.

As with various other modified ion implanters used in research today, this specific ion implanter is made up of five major components that efficiently operate together to transport ions from a desired source through a processing chamber to the target specimen [158–160]. Figure 4.2, shows a schematic of a typical ion implanter with the five major components listed as follows: the ion source, magnetic particle filter, electrostatic accelerator, beam manipulating system and an end station which is



Figure 4.1: **Photograph of the ion implanter at iThemba LABS.** A Varian-Extrion model 200-20A2F.

modified for research applications and does not include the usual wafer processing assembly on production type semiconductor wafer processing ion implanters. Each component plays a crucial role in the ion implantation process where the entire ion implantation system uses high energy beams to physically inject the desired dopant species into a target material of choice, usually a semiconducting material. The dopant species range from solids to gaseous materials generated from appropriate sources [159, 161].

In operation, the ion source generates plasma having the required ion species to be implanted. The hot ionized beam is extracted from a hot cathode arc discharge ion source by an electrostatic field induced from a 23 keV energy supply. The 2 keV from the electrodes help direct the charged ions towards a 90° magnetic particle filter, where the magnetic current can be tuned in order to filter out only a beam of desired ions with specific atomic weight. The unwanted ions are collected by the magnetic walls of the analyzing magnet chamber while a beam of the desired ions is focused through a variable slit, which in turn also controls the intensity of the traveling beam by opening and closing. The resolved ion beam then enters an accelerating tube which provides the energy required for proper ion implantation.

The acceleration tube can be varied in three modes (i.e., drift mode, post acceleration and post deceleration modes), depending on the required implantation energy. The drift mode refers to the mode where the beam energy remains unchanged from the source energy, while the post acceleration and post deceleration modes refers to the acceleration and deceleration of the ion beam energy with energies ranging between 25 keV – 180 keV and 0 keV – 7 keV, respectively [162]. The acceleration is

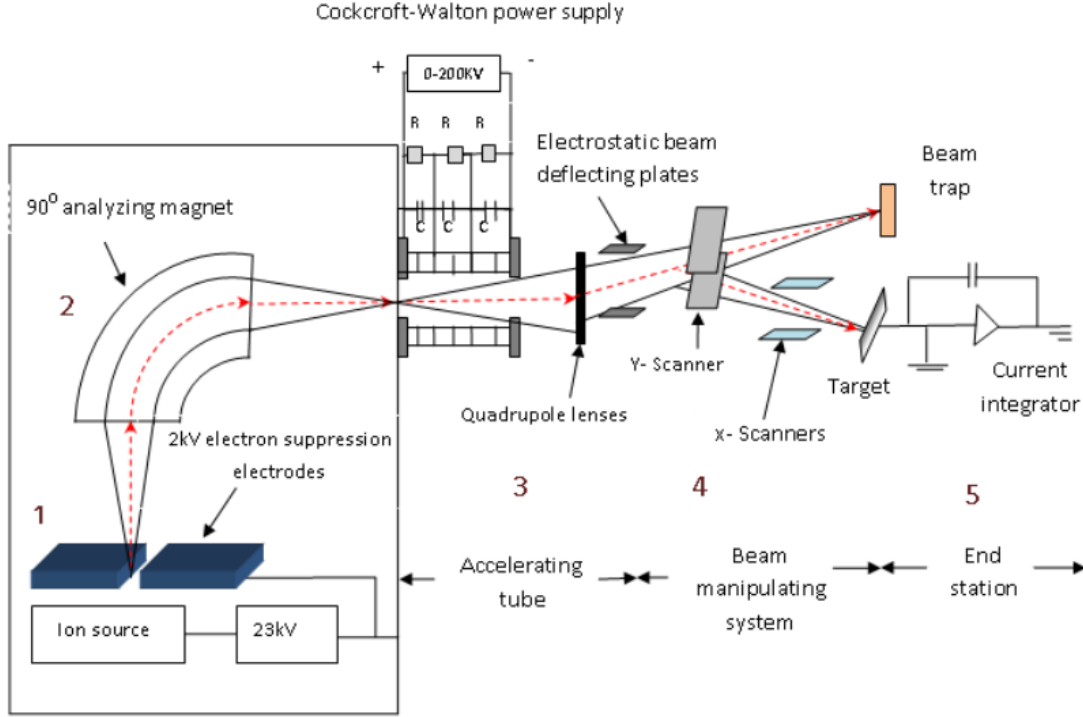


Figure 4.2: **Schematic diagram of an ion implantation system.** A schematic of the ion implanter made up of 5 components: ion source, magnetic particle filter, electrostatic accelerator, beam manipulating system and the end station [162].

provided by a high frequency Cockcroft–Walton power supply integrated into the accelerating tube, as seen in Fig. 4.2. The 25 kV N ion beam from the source was decelerated to 7 kV in the acceleration tube.

The first component met by the ion beam as it enters the manipulating system is a set of electrostatic quadrupole lenses to refocus the beam towards the horizontal (X) and vertical (Y) electrostatic beam deflecting plates. The plates deflect the beam in the vertical and horizontal planes, and are used to scan the beam across the surface wafer in a raster fashion to uniformly cover the scanned area. The target material is usually in a clean target chamber. Finally, the ion beam is sampled by a Faraday cup assembly inside located at the end station of the system to calculate the implanted ion fluence. The ion fluence can be measured from the integrated current measured at four corner Faraday cups located in the end station assembly of the ion implanter. A current integrator measures the ion fluence to be implanted into the sample and deflects the beam away from the target after the desired ion fluence has been reached.

4.2.2 Laboratory tube furnace

Immediately after implantation, heat treatment is required to restore the integrity of the implanted sample while also affecting the concentration of the desired defects. For this project, a commercial Carbolite (Gero model) Wire Wound Tube Furnace CFT 17/300, as depicted in Fig. 4.3, was used to ensure the mobility energy for vacancies created is activated. The instrument is specified as a 1700°C horizontal tube furnace with a 9 cm accessory tube for gas flow and computer control with full

data logging capabilities. It is located at the Wits University premises (School of Physics, University of the Witwatersrand, Johannesburg).



Figure 4.3: **A photograph of a Carbolite high temperature horizontal thermal tube furnace.** A wire wound tube furnace (CTF 17/300) with a 0°C – 1700°C temperature range.

The design is fitted with high temperature recrystallized alumina (RCA) worktubes for thermal uniformity that is specifically designed for high temperature applications, as seen from the schematic in Fig. 4.4.

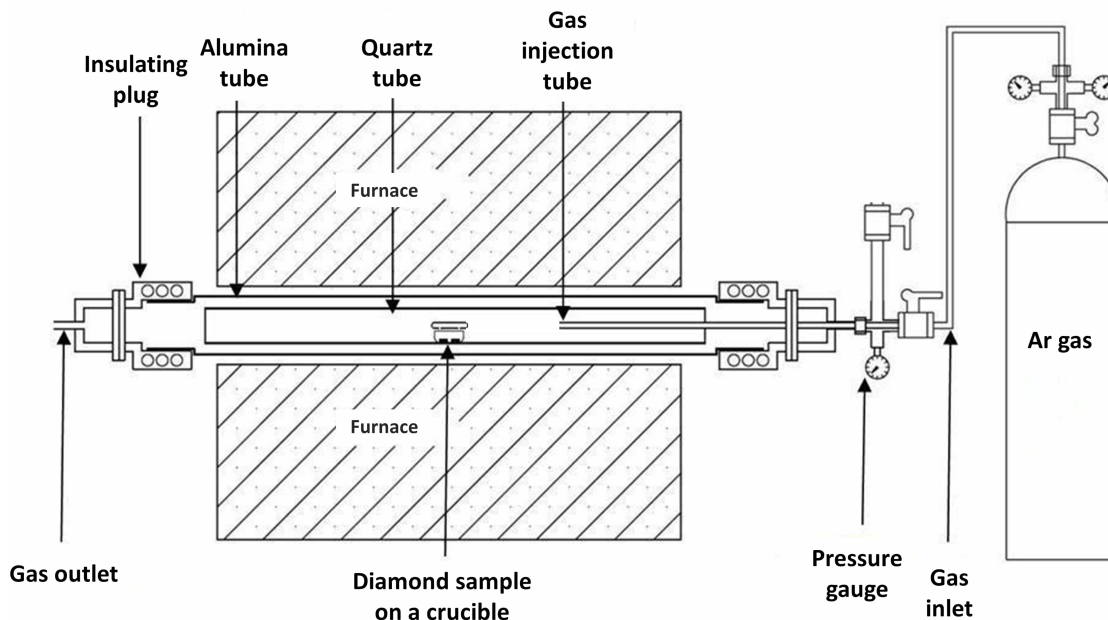


Figure 4.4: **Schematic of a typical horizontal furnace tube.** A diamond sample annealed in a presence of Ar gas enclosed by an RCA high temperature tube [163].

During operation, the sample is placed in a quartz boat crucible, which is then carefully inserted into a quartz worktube having a 9 cm diameter and 75 cm

length in dimensions. The boat is placed at the center of the furnace tube to allow for homogeneous temperature distribution. The tube is then tightly sealed with cylindrical end guards at both ends fitted with seal rings and attached to insulating plugs for optimum temperature uniformity. A continuous high-purity argon (Ar) gas flow is administered into the quartz tube through a gas nozzle available on the end guards, so as to avoid an oxidizing atmosphere to prevent graphitization during the annealing process. The diamond was annealed for 30 minutes at 800 °C. Lastly, in order to remove any traces of contamination and formation of graphite on the sample surface, an annealed substrate is placed inside an oxidizing acid solution and left to boil for a given time [144, 164].

4.2.3 Photoluminescence spectroscopy

Photoluminescence is a luminescence phenomenon which is defined as a spontaneous radiative energy transition process that involves photon absorption and emission from any form of matter [165, 166]. It is categorized into two photon emission processes: fluorescence and phosphorescence. The aforementioned processes are distinguished by their excitation lifetimes (τ). Fluorescence decays faster after excitation with a lifetime lapse of about ~ 10 ns, while phosphorescence decays much slower with a lifetime lapse of about ~ 0.1 s [167]. In this study, an Argon (Ar) laser source with wavelength of 514.5 nm is used to verify the availability of NV center defects in diamond which fluoresce at a much faster emission rate (> 10 ns). We make use of photoluminescence (PL) spectroscopy to investigate the optical properties pertaining NV centers within a diamond material.

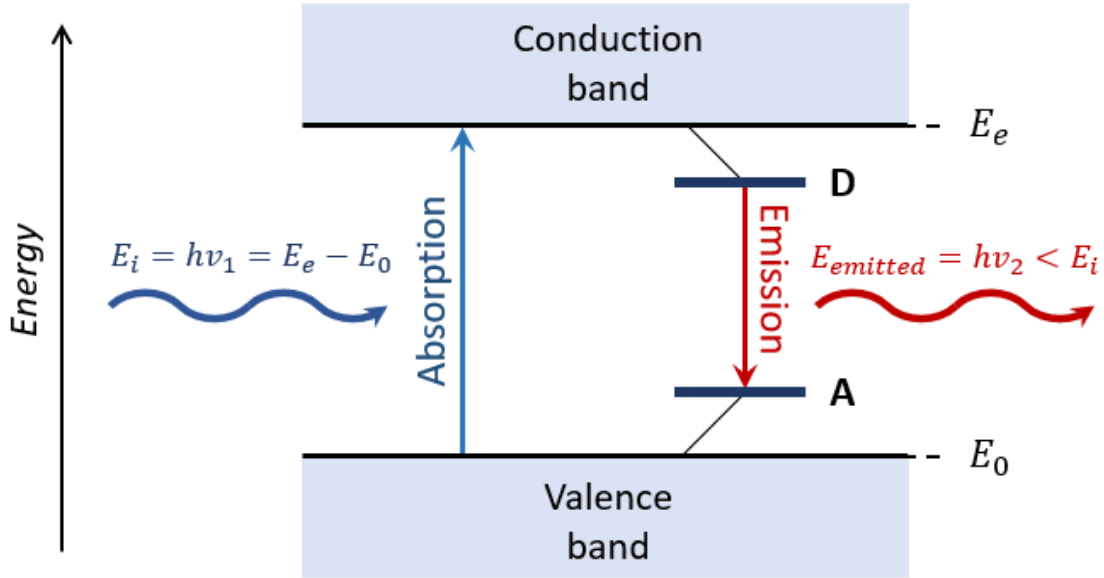


Figure 4.5: **Schematic diagram for band-to-band excitation process.** A photon with incident energy (E_i) excites an electron from its ground state energy (E_0) to an excited state (E_e). For $E_i \geq E_g$, photoluminescence generation takes place, with electron and hole donor-acceptor ($D \rightarrow A$) emission pair, and emits a photon.

The photo-excitation of semiconducting materials in particular, with energy equaling that of the band gap of the material (i.e., $E_i = hv_1 = E_g$), creates an excess

of electron-hole recombination pairs [168, 169]. If the excitation energy is greater than the band gap energy, then it can excite defect levels within the band gap of the material. The aforementioned laser source with energy of 2.41 eV (514.5 nm) is absorbed by the NV centers and excites the ground state defect electrons to excited state levels located inside the energy gap (as expatiated in Sec. 2.3). The process results in the emission of photons with energy of 1.945 eV and 2.156 eV for NV^- and NV^0 centers, respectively. This is a band gap characteristic between the electronic states of the conduction and valence bands. The radiative recombination of the electrons and holes due to the photo-excitation of semiconductors results in photo induced luminescence, i.e., the emission of photons of energy less than the energy of the incident photons ($E_{\text{emitted}} = h\nu_2 < E_i$), between the donor and acceptor energy levels ($\text{D} \rightarrow \text{A}$) [167], depicted in Fig. 4.5.

PL spectroscopy is then the measurement of photon emissions from a material; mainly due to an excited electron falling back to its ground state during photon excitation. The process provides valuable information regarding the electronic structures, emission mechanisms of the material and the defect composition of the material. Modern instruments are currently available to provide spectra of intensity vs wavelength, obtained from the dispersed optical signal in PL measurements. PL studies of diamond have long been utilized to characterize the various defects embedded inside the diamond matrix. In the case of NV centers, the spectra is well-known to have ZPLs at 637 nm and 575 nm for NV^- and NV^0 , respectively, whenever an NV center region is illuminated with a green laser source, i.e., a laser light source with wavelength ranging from 514 nm–570 nm. The ZPLs for both charged states of the center correspond to the emitted photon energies that are mentioned above. Thus, the studied sample for this project was also subjected to PL intensity characterization, to determine the presence of NV center defects before and after the ion implantation process.

Raman spectrometer

When a sample is illuminated with light, photoluminescence due to the ionization of the the atomic electrons in the material is not the only phenomena that takes place. A Raman scattering process can also occur during the illumination process, where a very small fraction of the incident light is scattered. The process involves a photon inelastically interacting with a molecule and losing a certain amount of energy, allowing the molecule to vibrate. The Raman scattering results in a Raman effect, where the scattered photon has less energy. The associated light exhibits a frequency shift. The various frequency shifts associated with different molecular vibrations give rise to a spectrum that is characteristic of a specific compound.

Sir Chandrasekhara V. Raman is credited as the first person to demonstrate such a phenomena in 1928, when he used sunlight filtered through a prism and toluene as the scattering medium. It is worth noting for the reader that Raman analysis is not included in the scope of this thesis, since most of the work is based on photoluminescence effects. However, we make use of a Raman spectroscopy system for material analysis due to the high spectral resolution associated with the system [170]. Therefore, for comprehensive understanding of the subject of Raman spectroscopy, please refer to the following texts: Karr [171], Brüesch [172], Brüesch [173].

PL experimental system

The instrumentation that was used for this particular work on the diamond substrate was the Horiba Jobin-Yvon LabRam HR800 spectrometer, as shown in Fig. 4.6, located at the Raman and Luminescence laboratory, School of Physics and Microscopy and Microanalysis unit, University of the Witwatersrand. The setup consists of four principal components per unit: this includes two lasers (He-Ne laser for 633 nm excitation and an Argon Ion laser for 514.5 nm excitation), an optical microscope system, a spectrometer and an optical detection system. Another essential component for this unit is a motorized micrometer movement (x,y) stage, which is integrated into the system to allow the accurate study of various sized samples at very small position intervals. A preprogrammed (*LabSpec*) software automatically controls the movements of the stage when carrying out the PL intensity mapping measurements, with an adjustable step-size resolution as small as 0.1 μm .

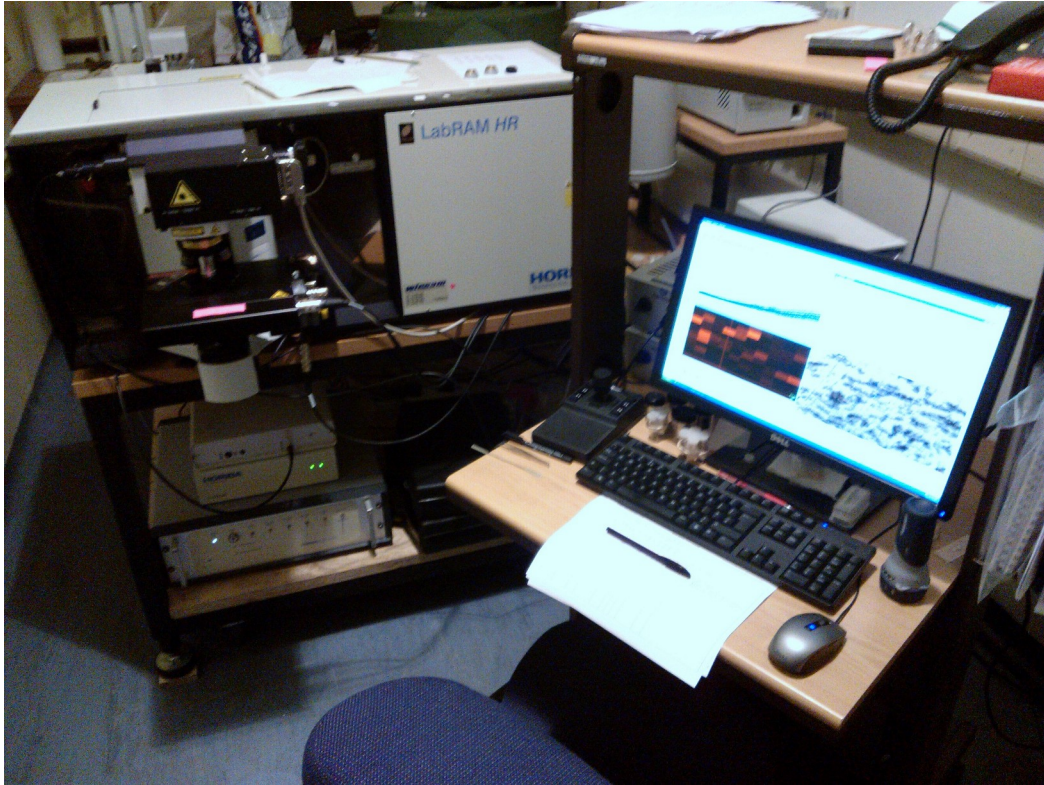


Figure 4.6: **The Horiba Jobin Yvon LabRam HR800 spectrometer.** A photograph of an operational Raman/PL spectrometer hardware taking measurements.

Figure 4.7, represents the schematic of the system during operation with either lasers 1 (He-Ne) or 2 (Argon) entering the spectrometer. Plasma line filters are fitted at each laser entry point to filter out any laser plasma emission lines. The laser beam then goes through an Optical Density (OD) wheel for wavelength intensity modification, and then gets totally reflected by an edge filter and directed towards a sample placed on top of a computer controlled (x,y) stage. The stage is positioned under an Olympus system microscope model BX40, equipped with a range of objectives with different numerical apertures (N.A.). The excitation laser beam is focused through any of the objectives onto the sample where the scattered light is

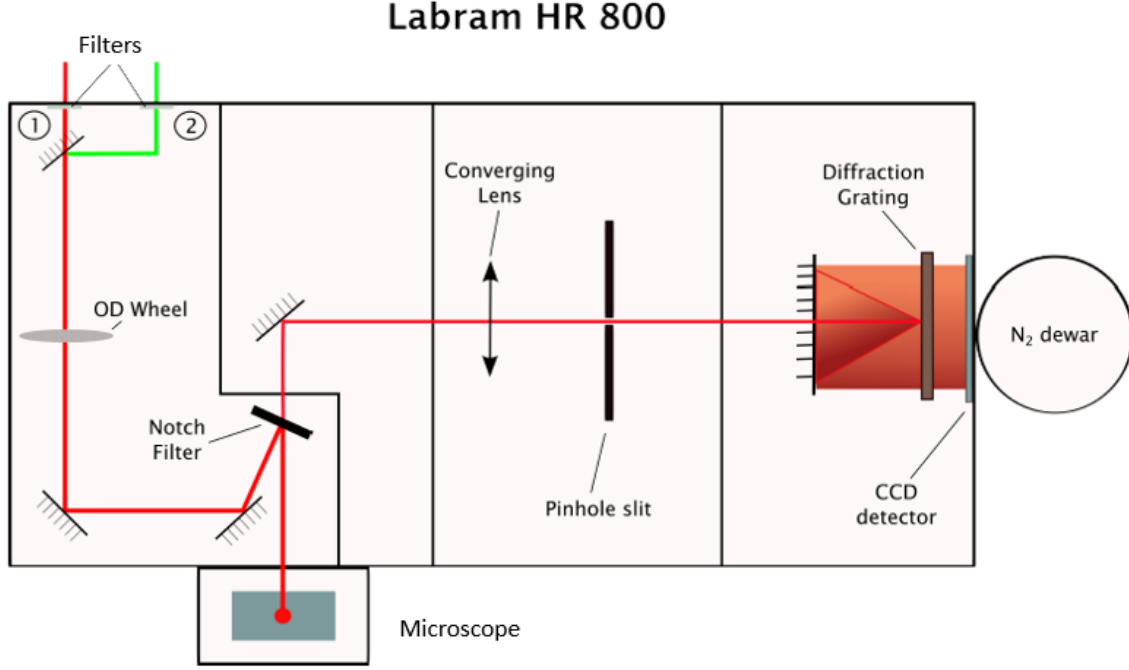


Figure 4.7: **Schematic of a Raman spectrometer.** Laser light is directed into a specimen by optical components. The resulting fluorescence is dispersed and directed to a CCD detection system for imaging.

collected in a backscattering configuration by the same objective. The edge filter reflects any backscattered laser light, while the PL and Raman scattered photons from the sample are allowed to pass through. The PL scattered light is then focused by a converging lens through a pinhole where an image of the sample is formed. The light can then be collimated and directed into a diffraction grating where it is dispersed according to its wavelength, and eventually goes to a *Symphony* charge coupled device (CCD) detection system which is nitrogen cooled for increased signal detection. A TV monitor is attached to the CCD detection camera for viewing of the sample or laser on sample.

4.3 Sample preparation

A CVD grown $2 \times 2 \times 0.3 \text{ mm}^3$ type IIa single-crystal diamond sample, with N concentration given as $<1 \text{ ppm}$, was used in the experimental investigation for NV center fabrication. A low density “electronic grade” $6 \times 6 \times 0.5 \text{ mm}^3$ CVD polycrystalline diamond with a 10^7 cm^{-2} luminescent defect concentration counting over $100 \mu\text{m}^2$ regions for low defect locations, mostly affirmed to be NV centers around the grain boundaries was used as reference for both PL and imaging experiments. Both diamond samples are courtesy of Element Six. Through out this thesis, the former diamond will be referred to as the investigated diamond while the latter diamond sample will simply be referred to as the reference diamond.

4.3.1 Implantation process

PL experiments were performed to study any NV center defect composition on both the aforementioned samples. This was done before the ion implantation process on the investigated diamond sample. The reference diamond showed a notable amount of NV center activity as expected, while the investigated diamond showed no PL signal associated with NV centers. This was followed by a SRIM simulation which was conducted before the ion implantation process for 5000 N ions injected in a diamond material with 7 keV ion implant energy, as indicated in Sec. C. The simulation gave a good indication of the expected depth and ion damage distribution. Table 4.1, shows the implantation parameters that were set for N and C implants at symmetric and well-defined positions.

Table 4.1: Initial dose and energy to be used for irradiation.

Carbon (Ins.)	Nitrogen (Outs.)	Fluence (ions/cm ²)	Implant Energy (keV)
1	A	5×10^9	7
2	B	5×10^{10}	7
3	C	5×10^{11}	7
4	D	5×10^{12}	7

Nitrogen (N₂) and carbon monoxide (CO) gases were used to produce the ions required for N and C implants, respectively. The implantation process was performed at room temperature. The implants were done on eight separate regions on the investigated sample, with N implants (A–B) on the outside and C implants (1–4) on the inside of the diamond sample from the center, as depicted in Fig. 4.8 (c).

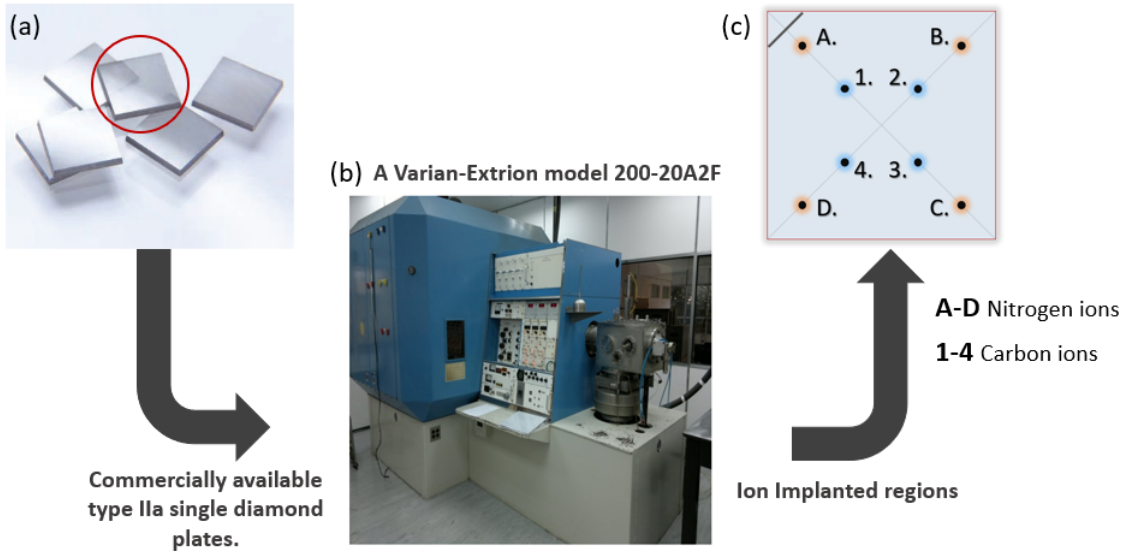


Figure 4.8: **Ion implantation process.** (a) A single commercially available laser marked diamond plate undergoes an ion implantation process. (b) A Varian-Extrion model 200-20A2F ion implanter. (c) Ion implanted diamond plate with regions A–D for N and 1–4 for C implants.

The implanted face had a laser mark as a reference point for easy identification of the implanted regions. The choice of N implants was to fabricate NV center point

defects through a combination of N_s point defects with vacant lattice sites, while the C implants was used to create vacancies and investigate the possibility of the existing intrinsic nitrogen in the sample in forming NV centers after annealing. The low energy low implants for N and C ions were done at iThemba LABS, as mentioned at the beginning of Sec. 4.2, where a special hole-drilled mask was made suitable for this project. The diamond was placed on a sample holder and covered with the hole-drilled mask positioned such that it could rotate at a fixed point over the sample.

Figure 4.9, shows the aforementioned mask where the smallest hole sits above the center of the diamond while the two holes on the right are used for C and N implantation. The small hole is about $\sim 120\text{ }\mu\text{m}$ in diameter, while the holes on the right are each about $\sim 250\text{ }\mu\text{m}$ and are $\sim 400\text{ }\mu\text{m}$ apart. The regions were implanted individually, by covering up all the holes except for one sitting above any region of choice, e.g., closing all the holes but the second hole from the center for N implants over region A. From the given example, if the mask can be subsequently rotated clockwise at an angle of about 90° , it covers all the regions for N and C implants except for one region between A–D at a time. Similarly, for regions 1–4, all the holes are covered except for the first hole from the center, and subsequently rotated at an angle of 90° each time for C implants.

To reduce any channeling effects, the sample holder was tilted at angle between $5^\circ - 7^\circ$ with respect to the normal incidence of the implantation beam. Table 4.1, shows the fluences used for each implant, increasing chronologically by one order of magnitude with beam energy of about 7 keV for each implant region. The measured scanning beam is directed across the covering mask during implants while being sampled by four Faraday cups each with an area of $\sim 0.2\text{ cm}^2$, located at the extremities of the scanning beam, where the current reaching the sample can be measured for uniformity. After implantation, the investigated diamond was subjected to ultrasonic vibrations in a 1:1 Ethanol and Methanol solution for 30 minutes to remove any residual surface contamination, and finally rinsed in deionized water.

4.3.2 PL intensity analysis after ion implantation

After the implantation process, a PL intensity analysis process was used to study the formation of NV center defects and any structural changes due to the implantation process. A 514.5 nm coherent argon ion laser source was used for laser excitation. The light was focused onto the investigated sample by a visible long working distance $50\times$ (N.A. = 0.50, Working distance = 10.6 mm) microscope objective with a spot size of $2\text{ }\mu\text{m}$ on the surface of the sample. The objective coincidentally collected the backscattered light composed of the scattered Rayleigh light, the scattered Raman signal and the PL signal from the sample. An edge filter was used to reflect the backscattering Rayleigh light while transmitting both the Raman and PL signals through to the spectrometer for further processing. The room temperature PL signal from the scattered light was then analyzed by a spectrograph with a 600 lines/mm grating and a CCD detection system cooled in liquid nitrogen for better sensitivity. The mappings were carried out over a $2100\text{ }\mu\text{m} \times 2100\text{ }\mu\text{m}$ square area spanning over 51×51 grid points across the whole sample with grid intervals of about $50\text{ }\mu\text{m}$. The system configuration used for PL measurements taken at cryogenic conditions was the same to the one used for room temperature measurements. A 150 lines/mm

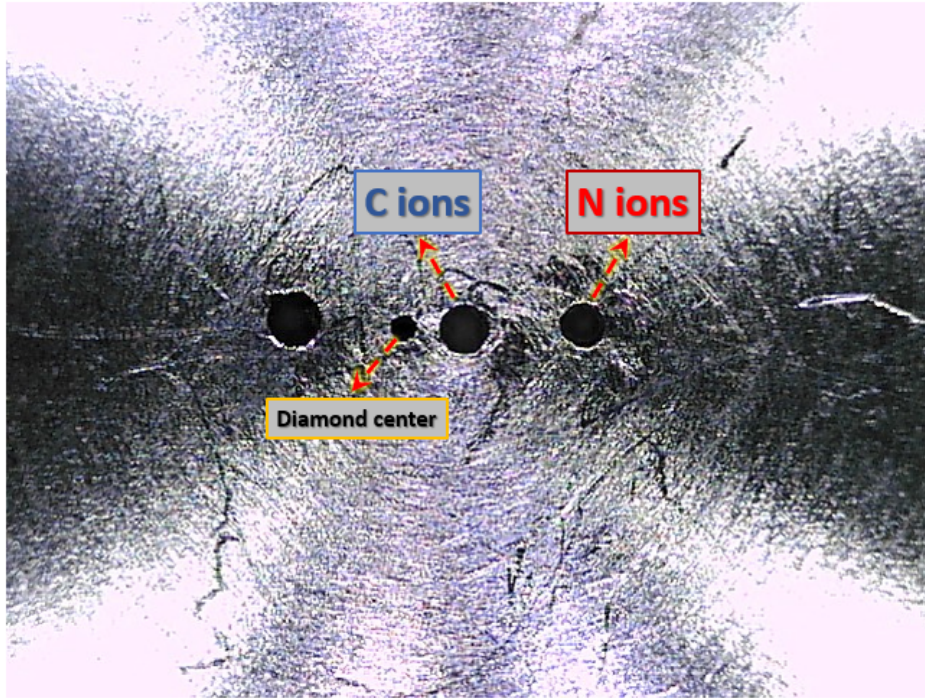


Figure 4.9: **Photograph of mask used for ion implantation.** The mask was made such that the small hole is directly above the center of the diamond, with the holes on the right used for C and N implantation.

grating was used, which offered a much better spectral range as compared to the 600 lines/mm. This was used mainly to reduce the data acquisition time due to the much larger $\sim 220\text{ }\mu\text{m}$ spectral resolution associated with the 150 lines/mm grating. At this stage, the spectral features related to NV centers were slightly visible from the investigated diamond sample, even before annealing (please refer to Chap. 5).

4.3.3 Annealing

The implanted sample was slid in a horizontal quartz tube for heat treatment where an tube furnace was preheated in an argon environment to a temperature of 800°C at a ramping rate of $10^{\circ}\text{C}/\text{minute}$. After reaching the set temperature, the sample was annealed for about 30 minutes. The sample was allowed to cool down to avoid Graphitization of the diamond surface. After annealing, the sample was boiled in an oxidizing acid solution of 1:3:4 nitric, sulfuric and perchloric acids for 30 minutes, to remove any traces of contamination that could have been introduced during the annealing process. This was followed by ultrasonic cleaning in an alcohol solution and subsequently rinsed in deionized water to remove any visible inorganic/organic contamination on the diamond surface.

4.3.4 PL intensity analysis after implantation and annealing

The PL measurement process was again used after the investigated diamond was annealed at 800°C for 30 minutes, under the same system configuration that was used before annealing.

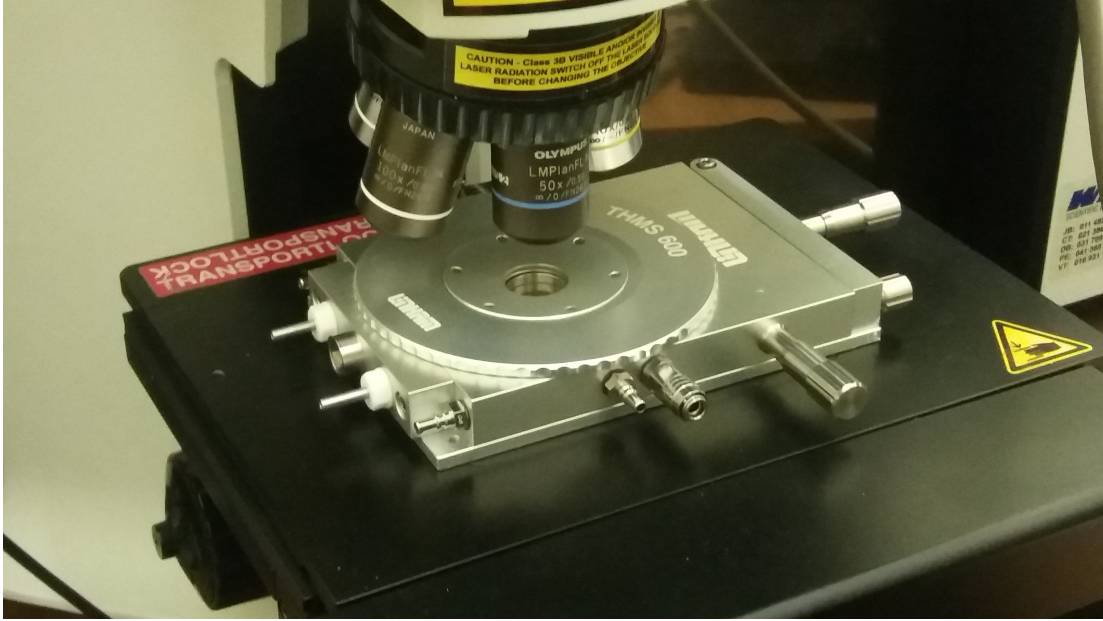


Figure 4.10: **A photograph of a Linkam THMS600 cryostat.** The cryostat is placed on a lowered micrometer movement (x,y) stage for low temperature PL measurements.

To sharpen the ZPL peaks, low temperature dependent PL measurements were also taken by using a Linkam THMS600 model cryostat system. This particular cryostat system is a heating and cooling stage that enables the microscopic acquisition of Raman and PL spectra at various temperatures ranging from 77 K – 873 K. The apparatus was placed on top of a lowered (x,y) motorized stage as seen in Fig. 4.10. The stage was used at a low temperature range, where it was cooled by liquid nitrogen to a low temperature of ~ 77 K. The investigated sample was then set on top of a highly polished silver element enclosed inside a small chamber (fitting sample size of about 22 mm) covered with glass during operation, through which the liquid nitrogen was circulating. The liquid nitrogen was pumped from a storage dewar into the cryostat where a small part of it was diverted into the system chamber as nitrogen gas, which modified the atmosphere of the chamber before going down to low temperature range. This is essential for preventing condensation and crystallization of ice onto the sample due to air in the atmosphere. Since the sample was enclosed inside a chamber, a long working distance objective was suitable to take the PL measurements.

Chapter 5

Results and discussions

This chapter consolidates all the results pertaining to the preparation of the investigated diamond sample, obtained from the preceding chapter. The first section presents in much great detail the simulated results for ion implantation as a precursor to the introduction of the foreign N ion species inside the diamond matrix for NV center fabrication. The second section presents the analysis of the PL intensity results of both the investigated and reference diamond. The PL measurements, mainly focuses on the presence of both charge states of the NV center defect at N implanted regions within the diamond surfaces. Moreover, a comparison of the NV centers fabricated in all the investigated regions with different ion concentrations is made. Finally, in the last section, we discuss the results presented.

5.1 SRIM simulation for N ion implantation

Low ion implantation energy depicted in Tab. 4.1, was intentionally used during each regional ion implantation process to ensure very low concentration of vacancies created in proximity to the diamond surface. Low fluences were used to minimize any chance of irrecoverable diamond surface damage. A low density of the created vacancies due to N ion implantation within the diamond sample offers a high probability of obtaining isolated NV centers [174, 175], a requirement for any successful development of NV center quantum systems [25, 57, 176, 177]. Figure 5.1, shows the simulated damage and N ion profiles in a diamond material due to irradiation damage of 7 keV $^{14}\text{N}^+$ ions. The energetic ions penetrate the sample resulting in an estimated depth profile of ~ 24 nm from the surface with an ion distribution peak of ~ 11 nm. The SRIM simulated damage profile has peak width of ~ 21 nm with damage peak of ~ 7 nm from the surface of the material. The SRIM simulation calculates the ion and target vacancy production, resulting in a mean number of vacancies created by each ion per angstrom length. The mean number is then multiplied by the fluence to be used during implantation, resulting the damage density (i.e., vacancy concentration), ρ_v in units of (vacancies/cm³), represented by the following equation [148],

$$\rho_v = \text{Mean number of vacancies} \times \text{Ion fluence}, \quad (5.1)$$

where the units of ρ_v can be worked out as follows,

$$\begin{aligned} \rho_v(\text{units}) &= (\text{vacancies/ion}/10^{-8}\text{cm}) \times (\text{ions}/\text{cm}^2) \\ &= (\text{vacancies}/\text{cm}^3). \end{aligned} \quad (5.2)$$

The damage profile in Fig. 5.1 represents the damage density due to the highest implanted fluence (i.e., region D). As discussed in Sec. 3.4.1, studies over the years have shown that the damage density induced by ion irradiation in diamond exceeding values of $\sim 1 \times 10^{22}$ vac/cm³ result in the graphitization of the damaged region upon annealing. The implanted fluence for region D resulted in a damage density of about $\sim 9.4 \times 10^{19}$ vac/cm³ at the surface of the diamond and reaching a maximum of $\sim 2.1 \times 10^{20}$ vac/cm³. The damage incurred in region D was far below the reported

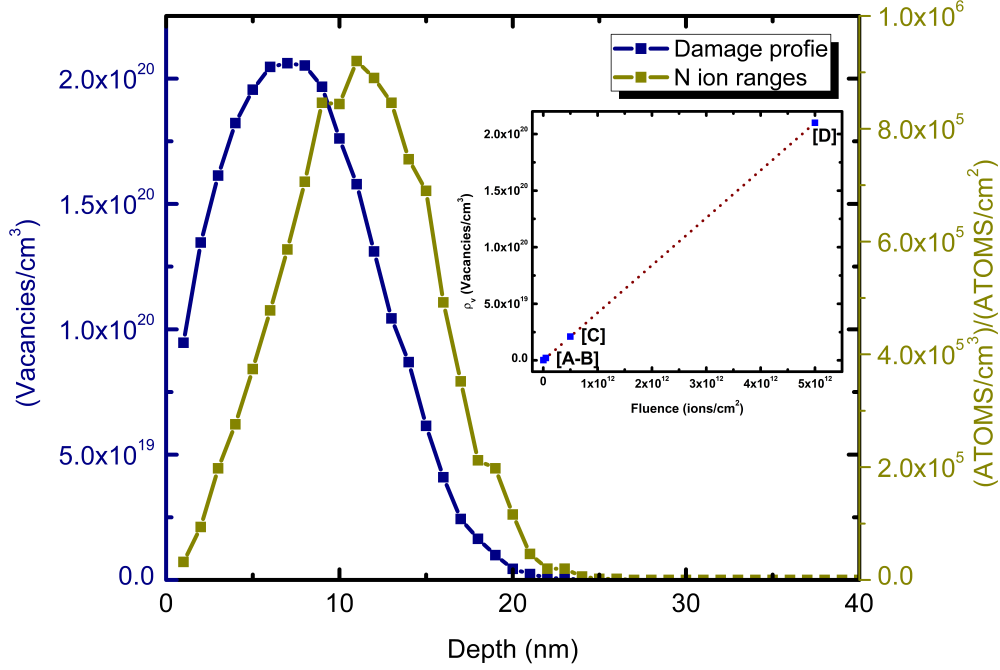


Figure 5.1: **SRIM simulation for the damage and ion depth profiles.** The predicted damage on a diamond material caused by N ions with incident implant energy of 7 keV. The depth profile of the damage stretches ~ 21 nm into the material with a damage peak at ~ 7 nm from the surface while the ion depth profile is about ~ 24 nm in the width from the surface with an ion distribution peak at ~ 11 nm. The insert represents the linear relationship between the ion fluence and the vacancy concentration in the simulated damage at the peak of the damage density.

graphitization limit by at least two order of magnitude which indicated that the structural integrity of diamond could easily be recovered following thermal annealing of the sample. Moreover, the vacancy concentration decreases linearly with ion fluence by one order of magnitude from regions D $\rightarrow$ A, while the depth profiles remain the same. The insert in Fig. 5.1, represent the linear relationship between the vacancy concentration and the fluence used for ion implantation. The SRIM output for 7 keV ion energy shows that 36 vacancies are created for every ion penetrating the sample with low ion range straggling of ~ 4 nm (the reader can refer to Appx. C). The fabrication of NV centers depends on the overlap of created vacancies and the implanted N ions and the capturing of the vacancies by the stable N_s atoms during annealing. Other authors have also reported a relationship between the ion energy and yield of NV centers while monitoring the critical limit of graphitization

due to the fluence [178–180].

5.2 Analysis of the PL spectra of diamond samples

The PL intensity results are presented in this section for the investigated diamond before and after N ion implantation. A laser excitation scan on a $2000\text{ }\mu\text{m} \times 2000\text{ }\mu\text{m}$ diamond surface area was carried out. The laser spot size of about $2\text{ }\mu\text{m}$ was focused on the diamond surface, scanning over 51×51 grid points with $50\text{ }\mu\text{m}$ grid intervals, as mentioned in Sec. 4.3. This implies that the scanned grid spots made up only 10% of the diamond surface, with at least 6×6 scans around the implanted regions with an area of about $\sim 250\text{ }\mu\text{m}^2$, estimated from the hole sizes of the mask used for implantation. A similar system configuration was used for PL measurements of the reference diamond and the Raman analysis of the investigated diamond.

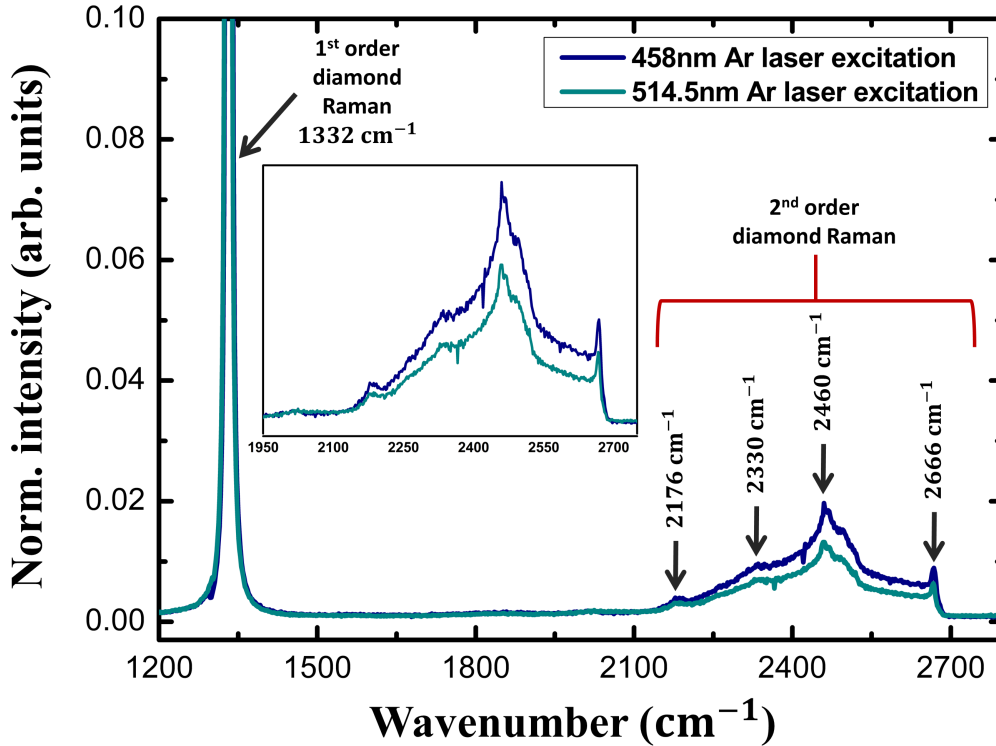


Figure 5.2: **Raman spectra of the investigated diamond.** A Raman spectra of an unimplanted region within the diamond sample with a Raman peak of 1332 cm^{-1} from a laser excitation wavelength of 458 nm and 514.5 nm at room temperature. The inset shows the 2nd order Raman ranging from 1950 cm^{-1} – 2750 cm^{-1} .

Figure 5.2, shows the Raman spectra for a randomly selected spot on the unimplanted “investigated” diamond at room temperature. An Argon (Ar) gas laser with wavelengths of 458 nm and 514.5 nm was employed for excitation. The resulting spectra had similar features overlapping each other for both the excitation wavelengths. The features are related to the 1st and 2nd order Raman for diamond. The Raman sharp peak for diamond due to the Raman effect was first studied by Ramaswamy [181], when he reported sharp and intense Raman lines corresponding

to frequency shifts of 1332 cm^{-1} . Thereafter, the results were supported by many other scientists with research output based on a number of optically varying diamond types which showed only slight variations of the Raman frequency shift (in cm^{-1}) [35, 182]. The Raman shift in wave numbers is calculated from the excitation laser photons (λ_{ex}) and the diamond scattered photons (λ_{sca}), described mathematically by a simple equation,

$$\nu[\text{cm}^{-1}] = \frac{10^7}{\lambda_{ex}[\text{nm}]} - \frac{10^7}{\lambda_{sca}[\text{nm}]} \quad (5.3)$$

Hence, with knowledge of the Raman sharp peak for diamond the absolute wavelength for the diamond scattered photons can be attained from the same equation.

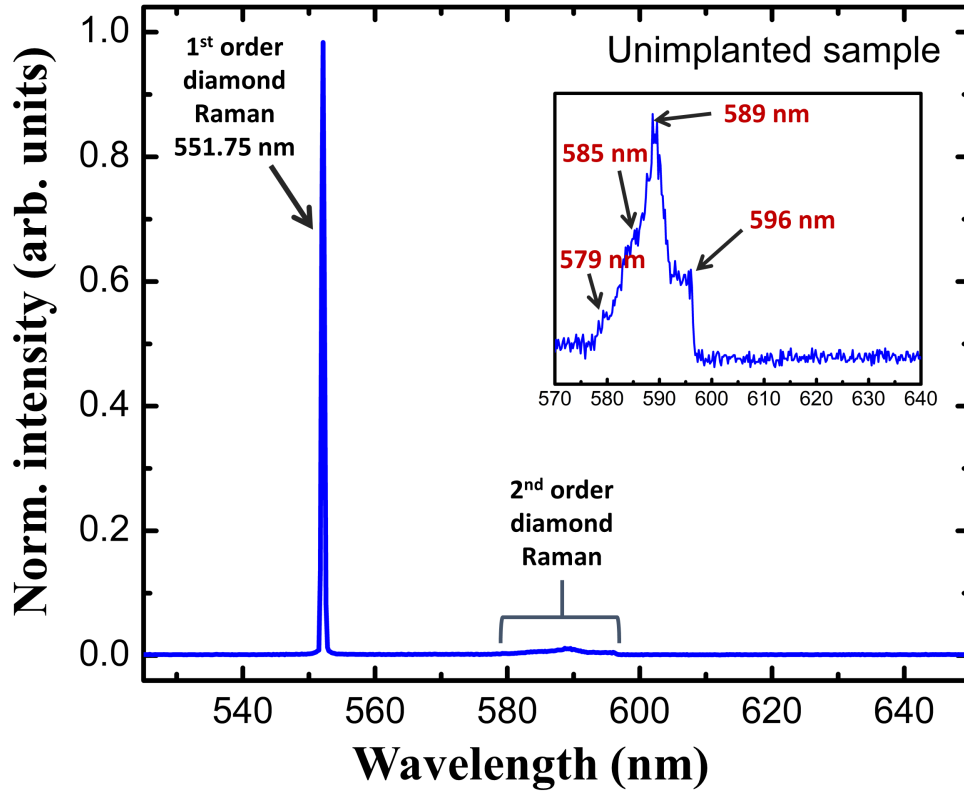


Figure 5.3: **PL intensity spectra of an unimplanted diamond sample.** A typical PL spectra of the unimplanted sample with a Raman peak of 551.75 nm from a laser excitation wavelength of 514.5 nm at room temperature. The inset shows a zoomed in PL spectra of the sample in the range of 570 nm–640 nm.

Figure 5.3, shows a PL spectra of the investigated diamond. A reference 1st order Raman peak of $\sim 551.75\text{ nm}$ from a laser excitation wavelength of 514.5 nm is clearly visible. Apart from the 1st order Raman peak, two emission peaks are clearly visible at 589 nm and 596 nm, while two other peaks are faintly visible at 579 nm and 585 nm. The insert reveals that the four peaks form part of the second order Raman for diamond, as seen in Fig. 5.2. The second order Raman spectrum for diamond was first presented by Krishnan [183], while investigating a colorless UV transparent diamond type using a Hilger medium quartz spectrograph during the early days of Raman spectroscopy. He found that it is made up of several distinct Raman lines. The sample used is likely to have

been a rare type IIa diamond, according to Tab. 2.2. The Raman lines reported corresponded to frequency shifts ranging from lattice octaves 2176 cm^{-1} – 2666 cm^{-1} , i.e., 2176 cm^{-1} (579.4 nm), 2190 cm^{-1} (579.8 nm), 2225 cm^{-1} (581 nm), 2253 cm^{-1} (581.96 nm), 2299 cm^{-1} (583.5 nm), 2330 cm^{-1} (584.6 nm), 2430 cm^{-1} (588 nm), 2460 cm^{-1} (589.1 nm), 2502 cm^{-1} (590.5 nm), 2666 cm^{-1} (596.3 nm). The other peaks associated with the 2nd order Raman are very faint, probably due to the spectral resolution used for the PL measurements. Furthermore, the spectra for the unimplanted diamond shows no ZPLs associated with both NV^0 and NV^- .

PL intensity of reference diamond

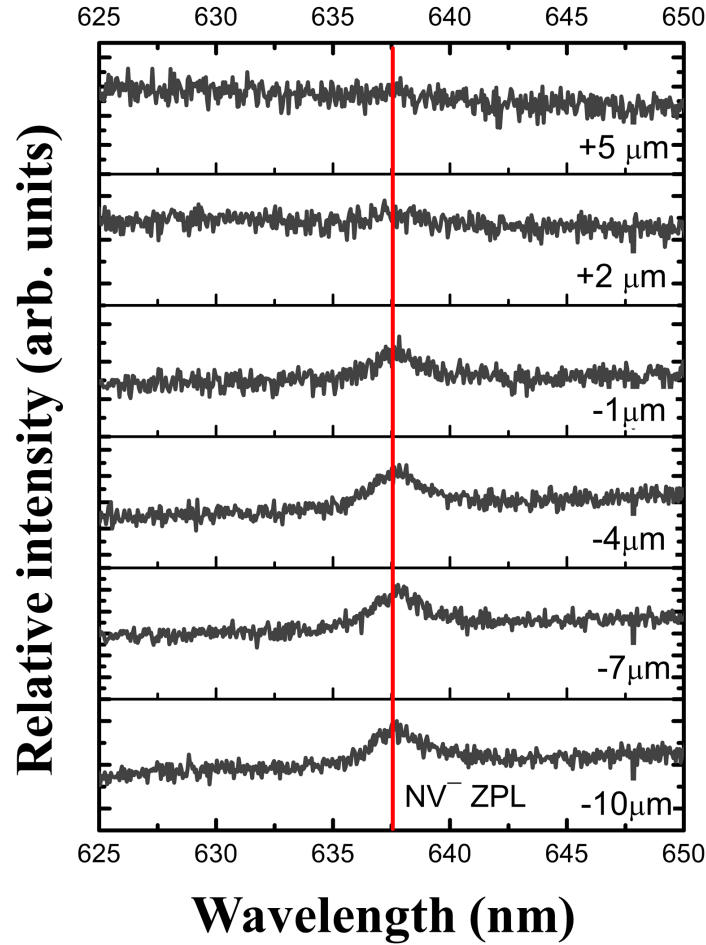


Figure 5.4: **PL spectra for the reference diamond.** The z-stack PL spectra for NV^- at six different depths from one spot. The excitation beam is focused from $10\text{ }\mu\text{m}$ below the diamond surface to $5\text{ }\mu\text{m}$ above the surface in six steps.

As indicated in Sec. 4.3, a polycrystalline diamond with NV centers around its grain boundaries was used as reference for the unimplanted diamond sample. Figure 5.4, shows a z-stack PL analysis of the reference diamond zoomed in around 637 nm for NV^- at room temperature. The z-stack is comprised of six different depths each with steps of $3\text{ }\mu\text{m}$ on one single spot where the excitation beam is focused from $10\text{ }\mu\text{m}$ below the diamond sample to $5\text{ }\mu\text{m}$ above the surface. The sample reveals a strong peak intensity at 637 nm below the diamond surface relative to the PL

intensity above the surface (μm -length). Studies with much greater details and analysis have been conducted on a similar diamond sample for QIP purposes [184].

5.2.1 Room temperature PL analysis

PL measurements are presented at room temperature for all the implanted regions of the investigated diamond sample before and after annealing. Due to factors such as low NV center yield and low spectral resolution, the PL spectra for each region is zoomed in to the respective ZPLs for NV^0 and NV^- defect centers.

PL intensity zoomed in at 575 nm

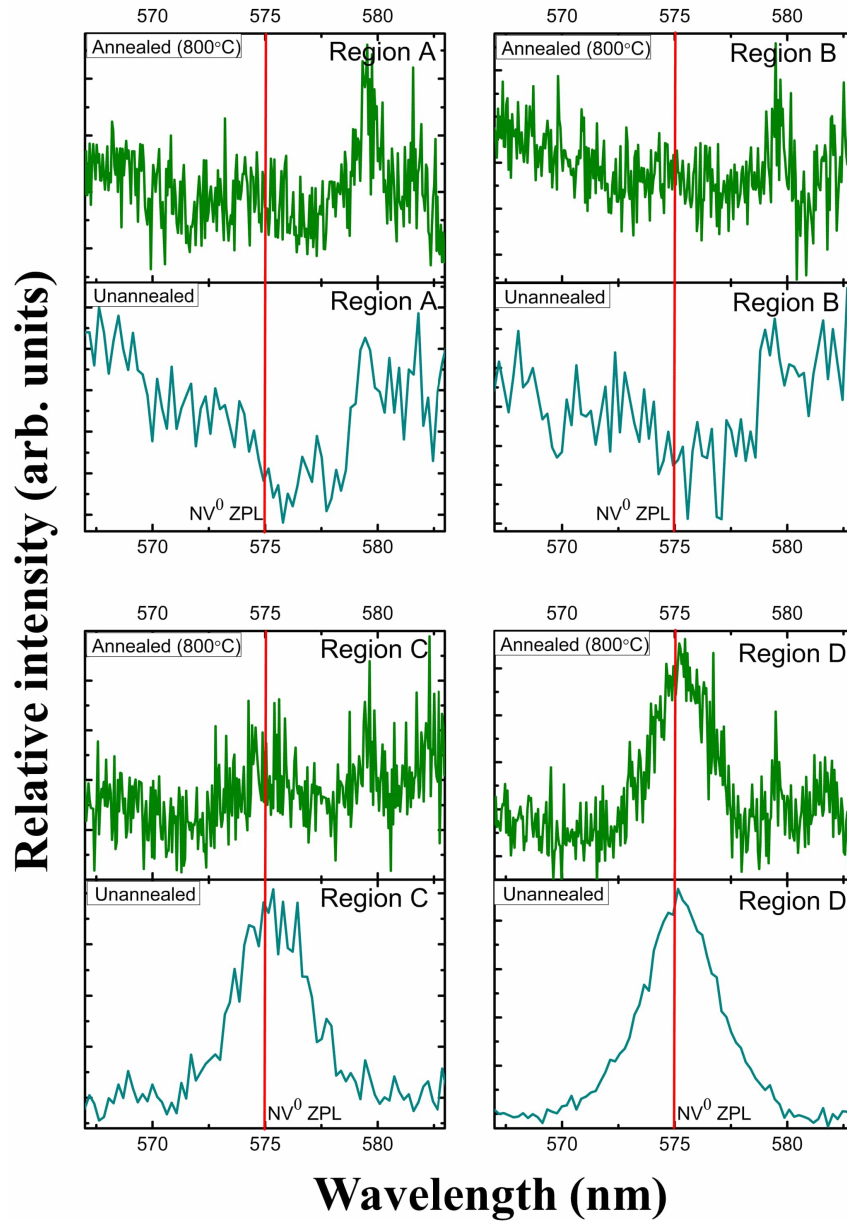


Figure 5.5: **PL spectra zoomed around NV^0 .** The PL spectra at room temperature, where the top half shows the PL spectra for the implanted and annealed sample, while the bottom half shows the spectra for implanted sample.

The PL spectra in Fig. 5.5, shows spectral details zoomed in a range of 567–583 nm. The analysis of the PL spectra is mainly focused on NV^0 (575 nm) center. The bottom half spectra shows the PL measurements after ion implantation while the top half is for the implanted sample after thermal annealing. Regions C and D reveal a sharp peak spectra at 575 nm as expected due to the higher fluence used for each respective region, while regions A and B reveal no signal for NV center activity.

PL intensity zoomed in at 637 nm

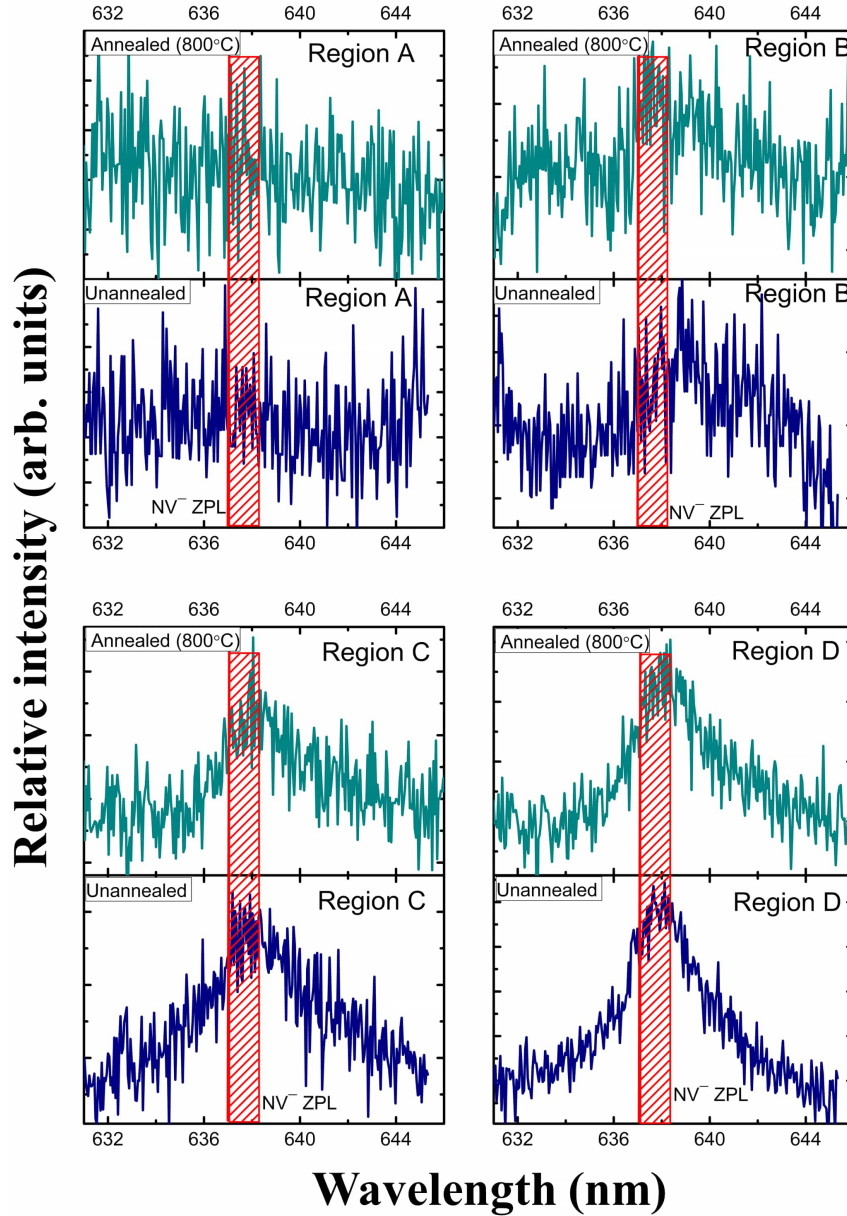


Figure 5.6: **PL spectra zoomed around NV^- .** The PL spectra at room temperature, where the top half shows the PL spectra for the implanted and annealed sample, while the bottom half shows the spectra for the implanted sample.

The PL spectra in Fig. 5.6, shows spectral details zoomed in a range of 631–646 nm. The PL analysis is focused on the NV^- (637 nm) center. The top and bottom halves

are situated similar to Fig. 5.5. Regions C and D reveal sharp peaks at 637 nm, while region B reveals a faint peak around NV⁻ ZPL. Region A on the other hand reveals a noisy spectrum with no signal for NV center activity.

5.2.2 Low temperature (77 K) PL analysis

Low temperature PL measurements were conducted on the investigated diamond sample after ion implantation. The results presented are centered around the regions implanted with N ions increasing in ion fluence by one order of magnitude from A–D. The intensity for each spectra is normalized to the diamond first-order Raman peak, while the insets show spectral details in the range of 570 nm–640 nm.

After ion implantation

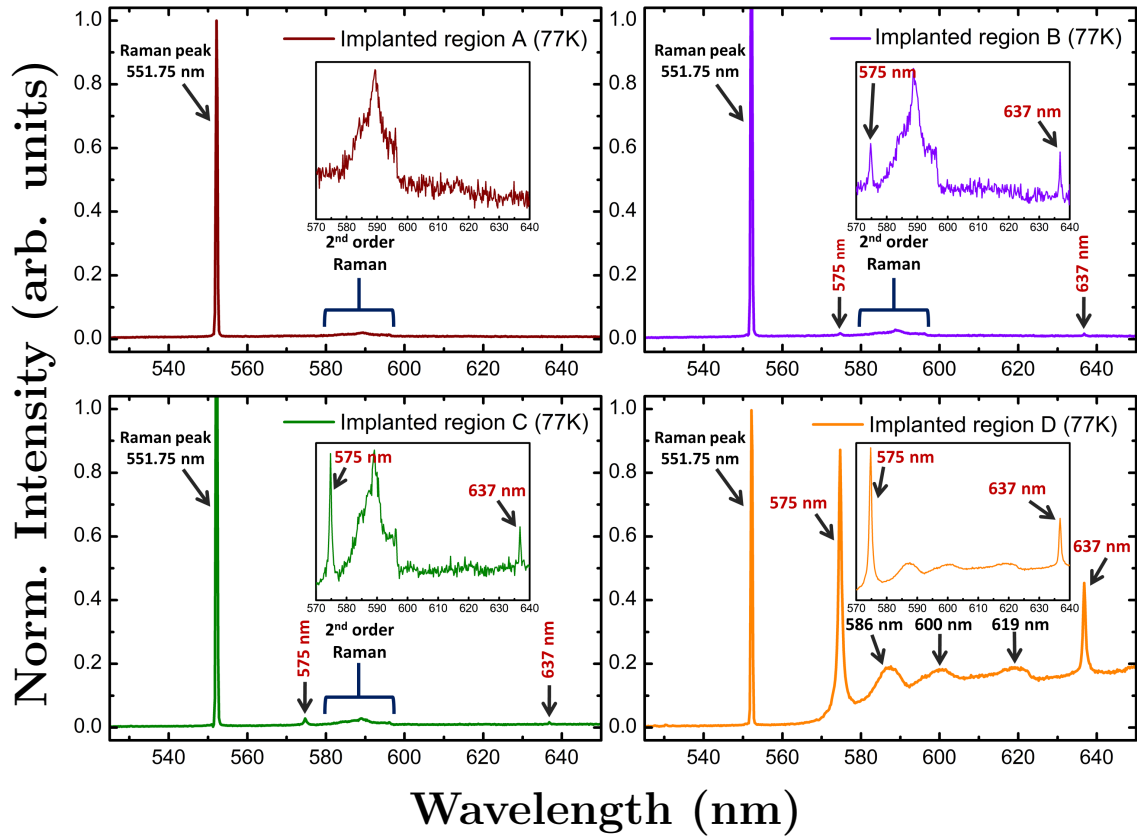


Figure 5.7: **Low temp. PL spectra of implanted diamond.** The PL spectra is normalized to the first-order Raman peak for N implanted regions A–D with increasing fluence. The inset shows a zoomed PL spectra of the sample in the range of 570–640 nm.

In Fig. 5.7, the implanted region A with the lowest fluence looks identical to both the Raman and PL spectra in Figs. 5.2 & 5.3, presented above with similar 2nd order Raman features. Region B with ion fluence greater than the one used in region A reveal two additional sharp peaks at 575 nm and 637 nm, corresponding to NV⁰ and NV⁻, respectively. The PL spectra for region C reveal much of the same but sharper peaks as compared to the peaks observed in region A and B.

The faint PL spectral peaks associated with the 2nd order Raman have also been individually reported by other authors in literature, particularly after ion implantation [185–188]. Region D implanted with the highest fluence reveal much broader and well-defined peaks as compared to the other preceding regions. The 2nd order Raman that was clearly visible in all the other regions, seem to diffuse into separate peaks. Broad peaks at 586 nm, 600 nm and 619 nm are clearly visible. The last two broad peaks at 600 nm and 619 nm are not associated with the 2nd order Raman peak. The ZPL for the newly formed NV^0 (575 nm) center also seem to be much stronger than that of the NV^- (637 nm) center for the ion irradiated only diamond sample. This is in line with previous studies that suggest that the NV^0 center is more likely to form during ion implantation than the NV^- , since the latter requires an extra electron from the neighboring sites to be added in any adjacent pairing of a N_s and a vacant lattice site.

After ion implantation and thermal annealing

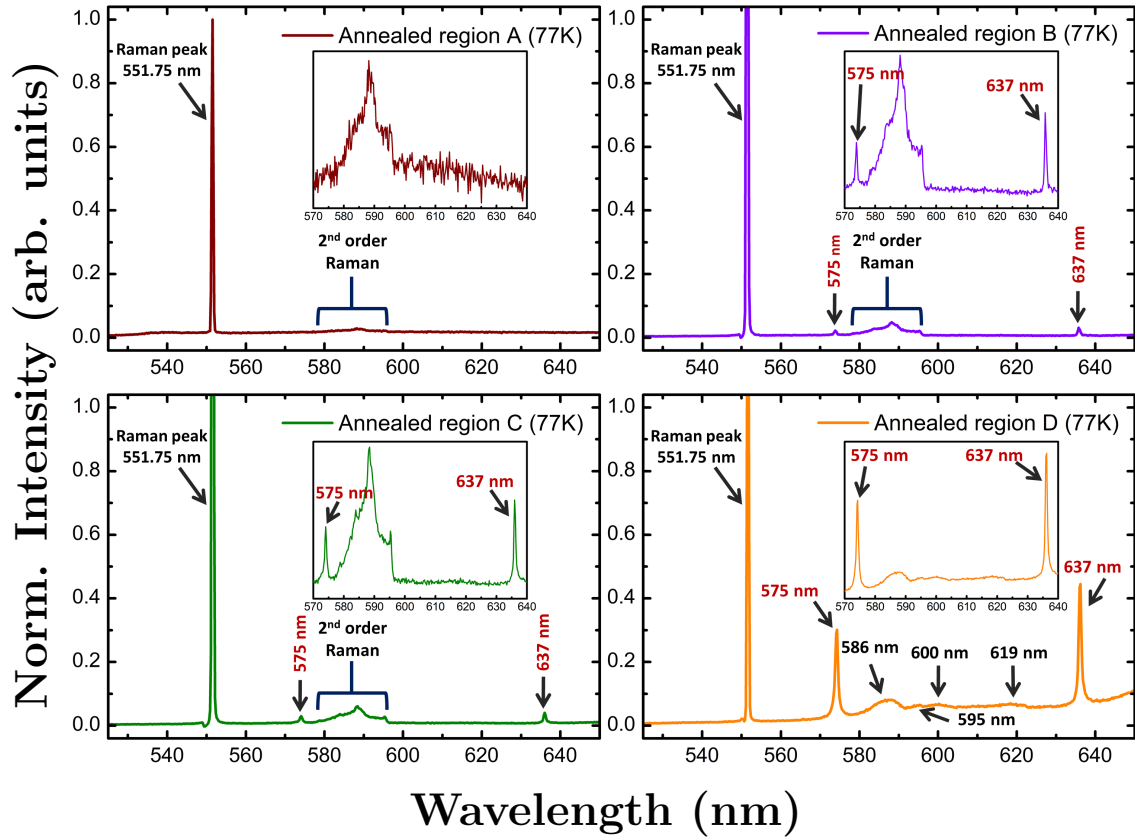


Figure 5.8: **Low temp. PL spectra of annealed diamond.** The PL spectra is normalized to the first-order Raman peak for N implanted regions A–D with increasing fluence. The inset shows a zoomed PL spectra of the sample in the range of 570 nm–640 nm.

Low temperature PL measurements on the the investigated diamond were carried out once again after thermal treatment of the sample with PL analysis similar to Fig. 5.7, i.e., only focusing on the four N implanted regions. Figure 5.8, shows a familiar but much relaxed broadband emission spectrum (particularly region D with

a much greater damage) as compared to the previously studied PL spectra for the ion implanted but unannealed sample. Furthermore, the regions reveal more of the same peaks as before, i.e., both distinct Raman peaks, as well as emission lines for both the charged states of the NV center defect. The 637 nm PL spectral peak for the NV^- center is more prominent than the 575 nm for the NV^0 center after annealing the diamond sample. The spectral features in region C are similar to that of region B in Fig. 5.8.

After annealing, PL analysis of the C implanted regions (1 $\rightarrow$ 4) was also carried out, as shown in Fig. 5.9. The emission spectra from all the regions are similar to that of Figs. 5.2 & 5.3, with both Raman peaks clearly visible (refer to inserts for 2nd order Raman). Both charged states of NV center defects are clearly absent, even for region 4 which was implanted with the highest fluence that is similar to the one used for N implants in region D. Significant changes of the emission spectra as the ion implantation fluence is increased from regions 1 $\rightarrow$ 4 are undetectable in Fig. 5.9 as compared to Figs. 5.7 & 5.8, with a minor exception for region 4 which has two faint peaks at 573 nm and 610 nm.

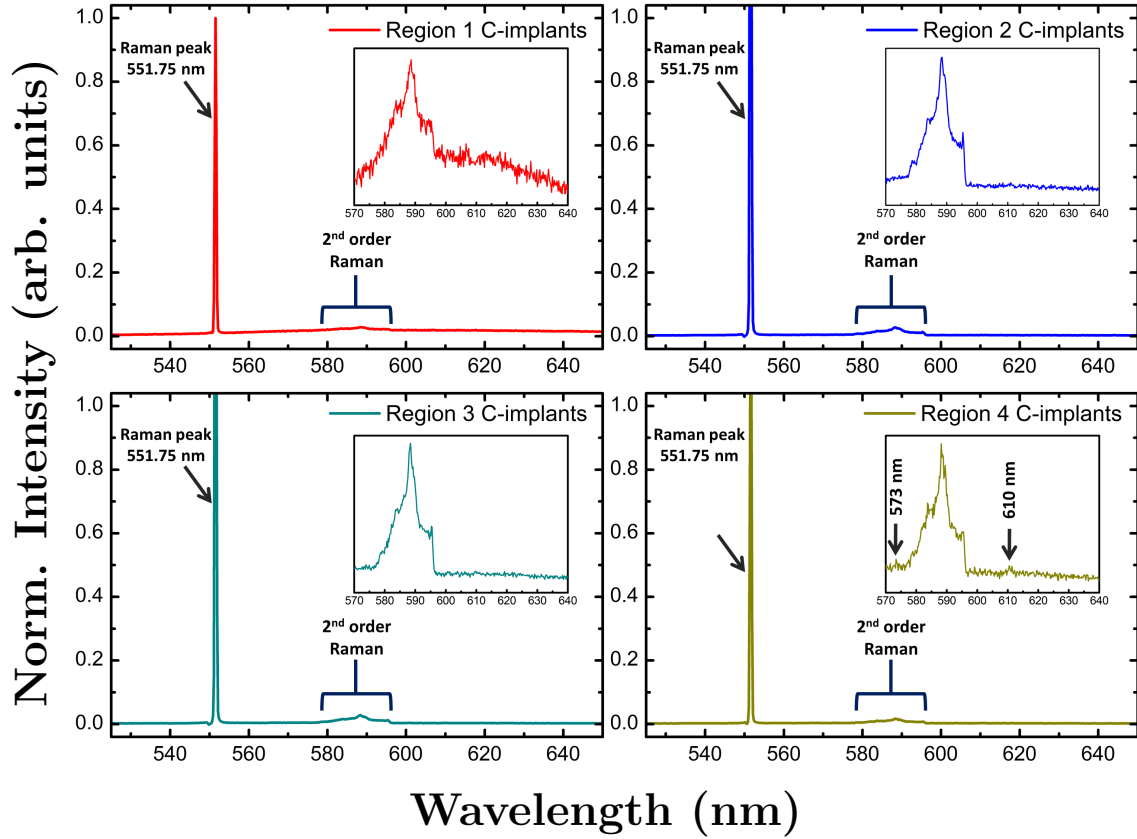


Figure 5.9: **Low temp. PL spectra of annealed diamond.** The PL spectra is normalized to the first-order Raman peak for C implanted regions 1–4 with increasing fluence. The inset shows a zoomed PL spectra of the sample in the range of 570 nm–640 nm.

Thermal annealing of the region with high fluence injection of N ions inside the diamond matrix intelligibly suppressed the 2nd order Raman (see region D in Fig. 5.8), while the C implants did not affect the 2nd order Raman of the annealed sample even at high ion fluence that was comparable to N implants. The PL analysis

for C implants confirm the low N concentration within the diamond matrix of the investigated sample. This is because the C implants had no evident impact in the formation of the NV centers in the investigated diamond used for this project, which is a CVD type IIa with very limited impurities (including N_s) as indicated in Tab. 2.2. Recalling from the previous chapters, the formation of NV centers in diamond via ion implantation depends on the availability of vacant lattice sites in proximity to substitutional nitrogen (N_s).

PL intensity from unimplanted regions

The intensity map of the annealed investigated diamond sample at low temperature (77 K) in Fig. 5.13 revealed three more regions with NV^- center activity where two (2 & 3) of these regions are in proximity to the N implanted regions C & D, while one is in proximity to C implanted region 4. The PL intensity measurements of these regions is also presented. All of these unimplanted regions look very similar to each other with sharp peaks at 575 nm and 637 nm, with the latter more prominent than the former (similar to Fig. 5.8). Similarly to other cases apart from region D in Figs. 5.2 & 5.3, both the 1st and 2nd order Raman diamond peaks are distinctly visible. Conclusively, the mobility of the vacancies during annealing had a favorable effect in the formation of possible low concentration of NV center defects in the unimplanted regions very close to the high fluence implanted regions, which was not the case before annealing.

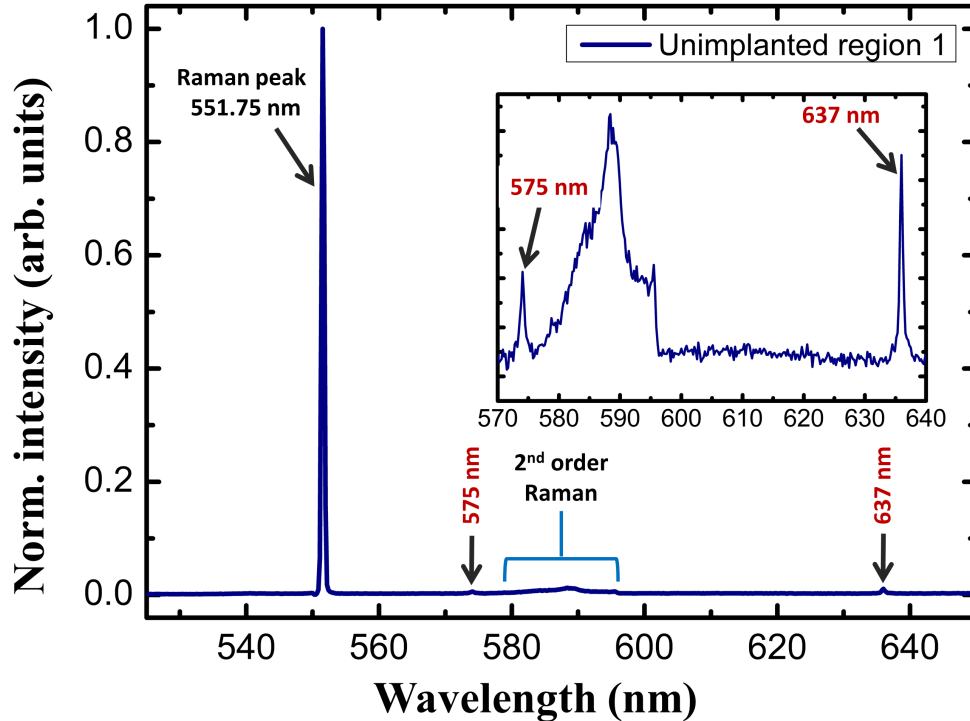


Figure 5.10: **PL spectra of the unimplanted region 1.** The PL spectra is normalized to the first-order Raman peak. The inset shows a zoomed PL spectra of the sample in the range of 570 nm–640 nm.

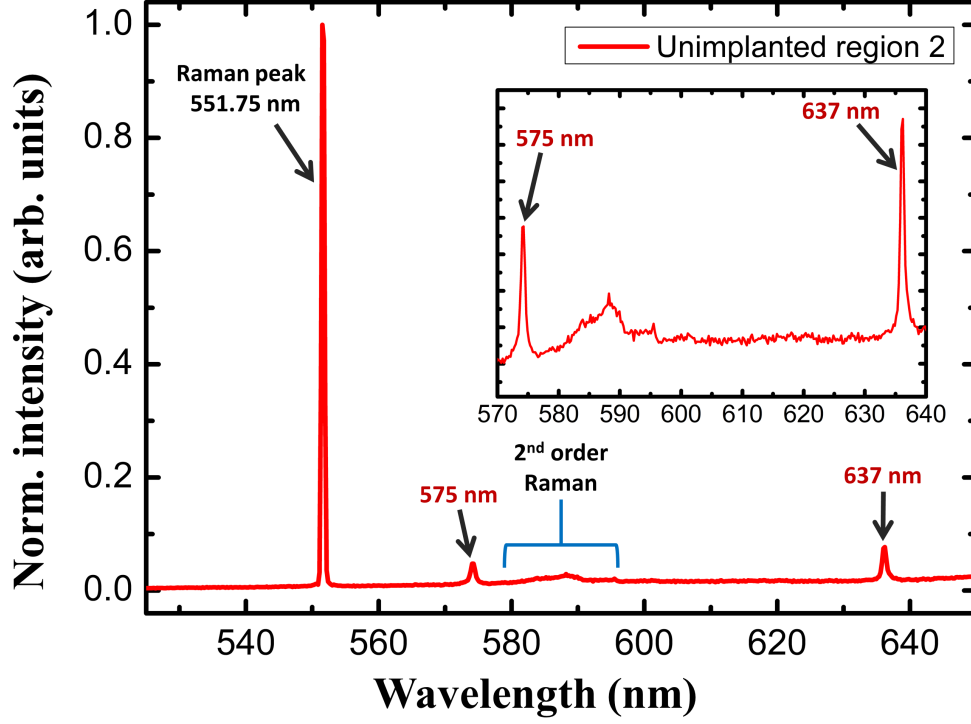


Figure 5.11: **PL spectra of the unimplanted region 2.** The PL spectra is normalized to the first-order Raman peak. The inset shows a zoomed PL spectra of the sample in the range of 570 nm–640 nm.

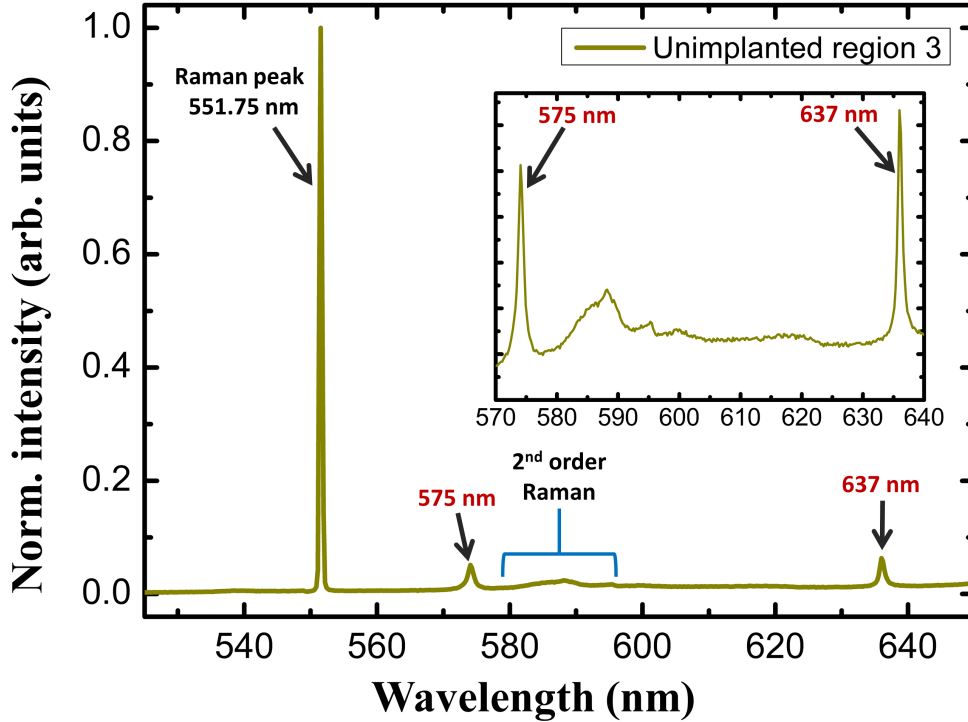


Figure 5.12: **PL spectra of the unimplanted region 3.** The PL spectra is normalized to the first-order Raman peak. The inset shows a zoomed PL spectra of the sample in the range of 570 nm–640 nm.

2D intensity map of NV centers

The intensity map of NV^- centers after annealing at low temperature is shown in Fig. 5.13. This gives a good idea of the positions of the N implanted regions in the investigated diamond sample. Unfortunately, the implantation positions are slightly asymmetric as compared to the description in Fig. 4.8 (c). There is also a slight gradation to the intensity of the peaks which is due to a slight change in focus across the diamond, likely from the combination of stage and microscope cryostat not being perfectly flat. Nonetheless, certain regions with NV^- center activity are visually detectable. Evidently, the implanted region D is clearly visible while the implanted regions C & D are faintly visible. Region A on the other hand, is not visible for any created NV^- centers, as was also confirmed by the PL analysis presented above. The intensity map also shows NV^- activity at unimplanted regions 1–3, mainly due to the mobility of the vacancies created during the ion implantation process, in proximity to the implanted regions. The PL measurements demonstrated above for each respective region was taken precisely at the regional positions corresponding to the map positions in Fig. 5.13.

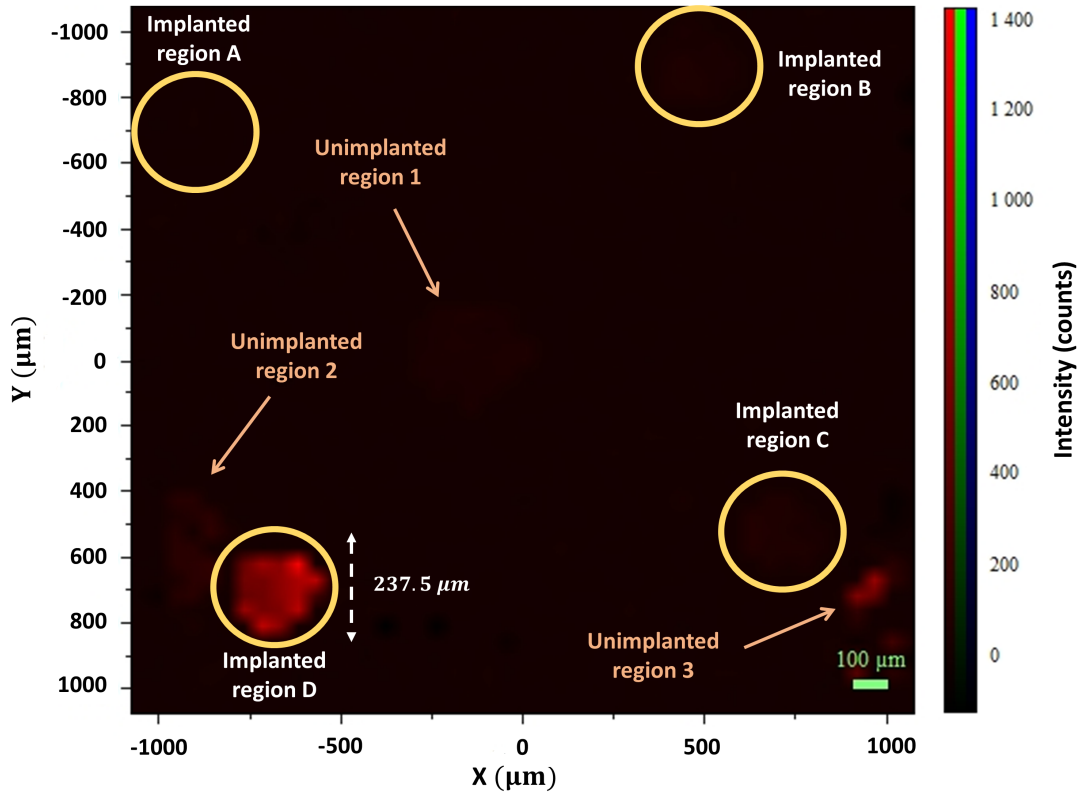


Figure 5.13: **Intensity map (77 K) for NV^- centers after annealing.** The intensity map of the $2000\text{ }\mu\text{m} \times 2000\text{ }\mu\text{m}$ sized diamond sample scanning over 51×51 grid points with $\sim 50\text{ }\mu\text{m}$ grid intervals. Relatively strong intensity signals for regions D, while regions C and B exhibit similar weak signals. No NV^- activity for region A. NV^- center activity ranging from weak to strong are also visible from unimplanted regions 1–3.

5.3 Discussions

It has been shown that the yield for NV center formation increases with ion fluence even at a constant ion energy. The predicted depth of vacancies within the diamond sample due to low energy extrinsic ions ($N \sim 7$ keV) and the recoiling C atoms is in proximity to the diamond surface. The low energy implantation employed in this work ensured a spatial resolution in the nm range but compromised on the yield of NV centers due to the narrow projected range. This is because the number of fabricated NV defects per implanted nitrogen ion are well below unity for low energy implantations (< 30 keV) where range straggling is small enough to enable high placement accuracy atoms. The probability of obtaining NV centers in diamond within the predicted region is also limited by the level of damage (vacancy concentration) incurred in the diamond lattice along with the availability of substitutional nitrogen ions (N_s) created in the vicinity of the N stopping position. This is evident with increase in the photoluminescence intensity when the N implantation fluence was increased.

Thermal annealing effects on the sample were also observed by increase in NV^- yield after heat treatment, i.e., thermal annealing induced diffusion of the vacancies, which were then trapped by the implanted N_s , increasing the NV^- yield. Both charge states of the NV center were produced after ion implantation, however the NV center activity was dominated by the stable NV^0 center for high fluence implantation. Upon annealing, the PL results showcased the photochromic effect that exists between the charge states where the NV^- center dominated the NV center activity. For future work on NV^- center production, it would be beneficial to establish the overall influence of thermal treatment on the photo-conversion properties of the charge states by annealing an implanted diamond sample via temperature cycles ranging from $600^\circ\text{C} - 2000^\circ\text{C}$.

The main objective of fabricating a seemingly low yield of NV centers in low N concentrated diamonds was achieved. However, other characterization techniques are also required to conclusively support this claim. Imaging techniques are required to view the spatial distribution of single and isolated NV centers, while an interferometer experiment is needful to characterize the photon distribution from NV centers for a single photon source.

Chapter 6

Optical beam manipulation studies

The optical pumping process plays a crucial role in the excitation of light absorbing crystal defects such as NV centers in diamond, particularly when the characteristic properties of a propagating laser beam can be varied (i.e., beam direction, beam shape, polarization, etc.), to adapt to specific fundamental applications in PL intensity measurements, optical imaging techniques and characterization experiments for photon distribution. In this chapter, the manipulation of laser light using optical elements is plainly elucidated and demonstrated with the use of a home built experimental setup. Experimental discussions will be based on the holographic methods imposed by a diffractive computer-controlled device known as a Spatial Light Modulator (SLM) for mode modulation. This involves the direct modification of a light beam by computer encoded holograms which are capable of altering the propagation direction and shape of incident light fields.

6.1 Introduction

Pioneering work in laser beam shaping can be traced back to the 1980s but its full development was only attained in the following decades [189]. Over this period, different techniques were elucidated to reshape amplitude and phase, either internal or external to resonator cavities. In these techniques the use of amplitude and phase as well as refractive, adaptive or diffractive optical elements was very common. Along this line, holographic methods emerged as one of the most powerful techniques, prompted by the development of modern computer-controlled devices, such as Spatial Light Modulators (SLMs) and Digital Micromirror Devices (DMDs) [190–193]. SLMs are pixelated screens formed by several hundreds of thousands of cells filled with molecules of transparent (LCD) or reflective liquid crystal on silicon (LCoS). The molecular alignment within the pixels dictates the type of modulation the SLM imparts to the light beam: phase-only, amplitude-only or both. The device is controlled via a calibrated voltage that rotates the liquid crystal molecules by a predefined angle, resulting in a form of birefringent material for a particular orientation of incoming polarized light. The voltage is regulated on each pixel using digital holograms, gray scale images with 255 tones of gray. A local phase shift is induced by the rotation of the molecules at each pixel, resulting in the reshaping of an input field.

Along with a very high accuracy in the generated light fields [194, 195], digital holographic devices are very flexible, a feature that has afforded, the development of

friendly-user multitouch screens for optical tweezers [196–198]. This flexibility allows also for the rapid reconfiguration of the digital hologram [199, 200], to change the shape and/or position of the output field, a feature that has shown advantages in optical tweezers [201], particle tracking [202, 203], characterization of complex light fields [204–210] and confocal microscope scanning [211] among many others.

Here we provide a self-contained tutorial aimed at the generation of sequential spatial modes encoded on corresponding holograms. To this end, we first introduce the Laguerre-Gaussian (LG) and Hermite-Gaussian (HG) infinite basis sets (Sec. 6.2), which can be used as encoding modes for beam scanning. Afterwards, detailed explanation of two commonly used techniques for beam shaping: phase-only and complex amplitude modulation, followed by an explanation on the generation of the digital holograms (Sec. 6.3).

6.2 Laguerre-Gaussian and Hermite Gaussian modes.

Any electromagnetic field traveling in free-space obeys the wave equation. Well-known solutions to the wave equation in the paraxial regime can be given in cylindrical and Cartesian coordinates. The former is given in terms of the generalized Laguerre polynomials $L_p^\ell(x)$ modulated by a Gaussian envelope, which forms an infinite orthogonal set of solutions, known as the Laguerre-Gaussian, LG_p^ℓ , modes [212]:

$$LG_p^\ell(\rho, \varphi, z) = \sqrt{\frac{2p!}{\pi(\ell+p)!}} \left[\frac{\sqrt{2}\rho}{\omega(z)} \right]^\ell L_p^\ell \left[\frac{2\rho^2}{\omega^2(z)} \right] \frac{\exp[i(2p+\ell+1)\zeta(z)]}{\omega(z)} \\ \times \exp \left[-\frac{\rho^2}{\omega^2(z)} \right] \exp \left[\frac{-ik\rho^2}{2R(z)} \right] \exp[-i\ell\varphi], \quad (6.1)$$

where, (ρ, φ, z) is the position vector of the cylindrical coordinates, ℓ is an integer number that accounts for the number of times the phase wraps around the optical axis, p is a positive integer that accounts for the number of maxima ($p+1$) along the transverse direction. Each solution represents a paraboloidal wave with radius of curvature $R(z) = z[1 + (z_R/z)^2]$, beam waist ω_0 and Rayleigh range z_R ; $\omega(z) = \omega_0\sqrt{1 + (z/z_R)^2}$ is the beam width as function of z and $\zeta(z) = \arctan(z/z_R)$ is the Gouy phase. Figure 6.1(a) shows the intensity distributions of the first few $LG_p^\ell(x)$ modes with combinations of $p = [0, 1, 3]$ and $\ell = [0, 1, 2, 4]$.

In Cartesian coordinates, the paraxial wave equation allows as solutions the Hermite-Gaussian modes, HG_{nm} , a product of Hermite polynomials $H(x)$ and a Gaussian envelope, with n and m positive integers:

$$HG_{nm}(x, y, z) = \frac{1}{\omega(z)} \sqrt{\frac{2^{-(n+m-1)}}{\pi n! m!}} \exp[i(n+m+1)\zeta(z)] H_n \left[\frac{\sqrt{2}x}{\omega(z)} \right] \\ \times H_m \left[\frac{\sqrt{2}y}{\omega(z)} \right] \exp \left[-\frac{x^2 + y^2}{\omega^2(z)} \right] \exp \left[\frac{-ik(x^2 + y^2)}{2R(z)} \right] \exp[-ikz]. \quad (6.2)$$

The parameters ω , $R(z)$, ω_0 , z_R and $\zeta(z)$ are the same as for the LG_p^ℓ modes. The positive integer subindexes n and m are related to the number of bright lobes of

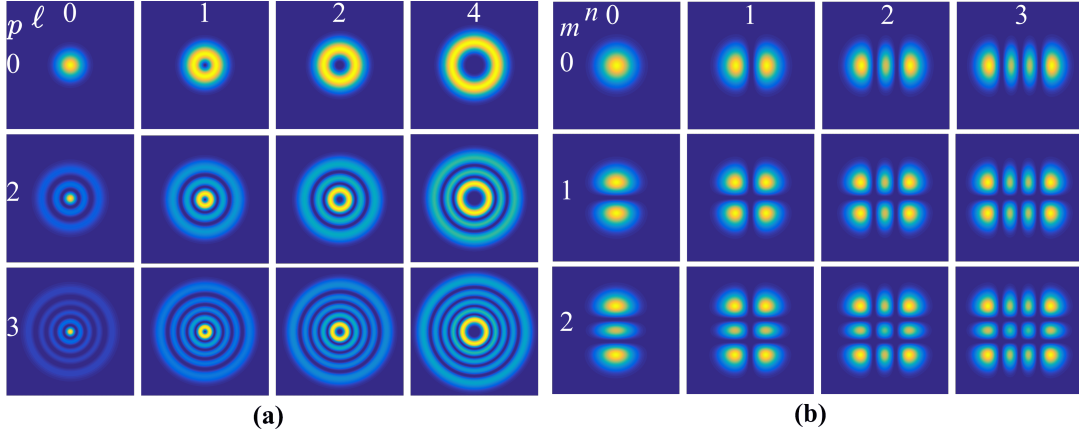


Figure 6.1: **Theoretical 2D intensity profiles of LG_p^ℓ and HG_{nm} modes.** Intensity distribution of (a) LG modes with $l = [0, 1, 2, 3, 4]$, $p = [0, 2, 3]$ and (b) HG modes with $n = [0, 1, 2, 3]$ $m = [0, 1, 2]$.

the transverse intensity profile along x and y respectively. Figure 6.1 (b) shows the intensity profile of the modes described by combinations of $n = [0, 1, 2, 3]$ and $m = [0, 1, 2]$.

6.3 Experimental modulation of modes

Shaping of light fields in both amplitude and phase, requires in general a transfer function capable of modulating both, amplitude and phase. Since most SLMs allow only the direct control of the phase, several techniques have been proposed to indirectly modulate the amplitude [194, 195, 213–218]. In this section we will briefly explain two of these techniques, phase-only and complex amplitude modulation.

6.3.1 Mode modulation using phase holograms

In order to generate a phase-only hologram capable to reproduce the amplitude changes in LG_p^ℓ modes, it is sufficient, in a first approximation, to encode the changes of sign given by the Laguerre polynomial L_p^ℓ in the radial direction. This, in combination with an azimuthal phase variation, generates the transfer function [194],

$$t(\rho, \varphi) = \exp \{i [\ell \varphi + \pi \Theta(\rho)]\}, \quad (6.3)$$

where, $\Theta(\rho)$ is the Heaviside function that takes into account the sign variations of the Laguerre-Gauss function and is given by,

$$\Theta(\rho) = \Theta \left[L_p^{|\ell|} \left(\frac{2\rho^2}{\omega_0^2} \right) \right]. \quad (6.4)$$

The above transfer function can be encoded on the SLM along with a linear phase grating, to separate the different diffraction orders. The transfer function of a linear phase grating is given by,

$$t_g(x, y) = \exp [i2\pi(ux + vy)], \quad (6.5)$$

where u and v are the spatial frequencies of the grating along the horizontal and vertical direction respectively. A lens of focal length f is placed at a distance f from the SLM to separate the diffraction orders in the focal plane of the lens. The final coordinates U and V of the first diffraction order are related to the grating frequencies, the focal length f and the wavelength of the incident field, by the relations $U = u\lambda f$ and $V = v\lambda f$, respectively. Hence, the transfer function in terms of U and V takes the form,

$$t_g(x, y) = \exp \left[i2\pi \left(x \frac{U}{\lambda f} + y \frac{V}{\lambda f} \right) \right]. \quad (6.6)$$

Hence, the hologram to generate the LG_p^ℓ mode combined with the diffraction grating takes the final form,

$$\Phi = \text{mod} \left\{ \ell\varphi + \pi\Theta \left[L_p^{|\ell|} \left(\frac{2\rho^2}{\omega_0^2} \right) \right] + 2\pi \left(x \frac{U}{\lambda f} + y \frac{V}{\lambda f} \right), 2\pi \right\}. \quad (6.7)$$

In the above equation, $\text{mod}[x]$ represents the modulus function that wraps the phase around 2π . A similar approach can be followed to generate HG_{nm} beams [218]. Figure 6.2 shows the amplitude, phase and holograms for LG_p^ℓ 6.2(a) and HG_{nm} 6.2(b) modes.

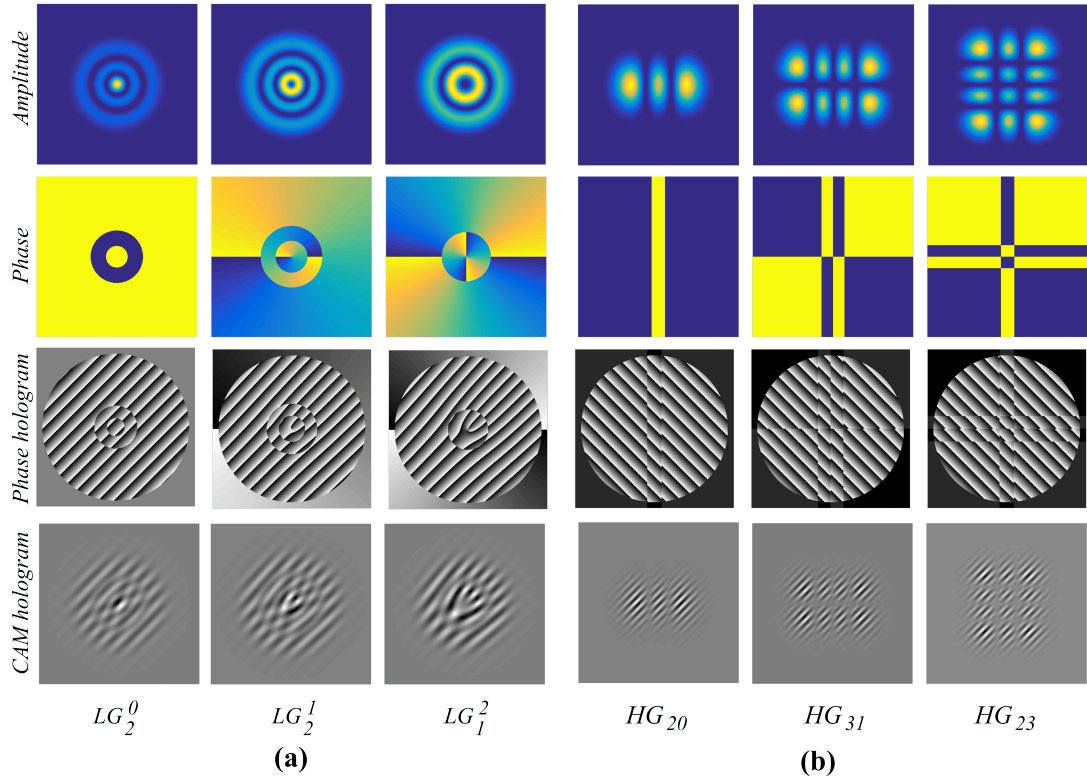
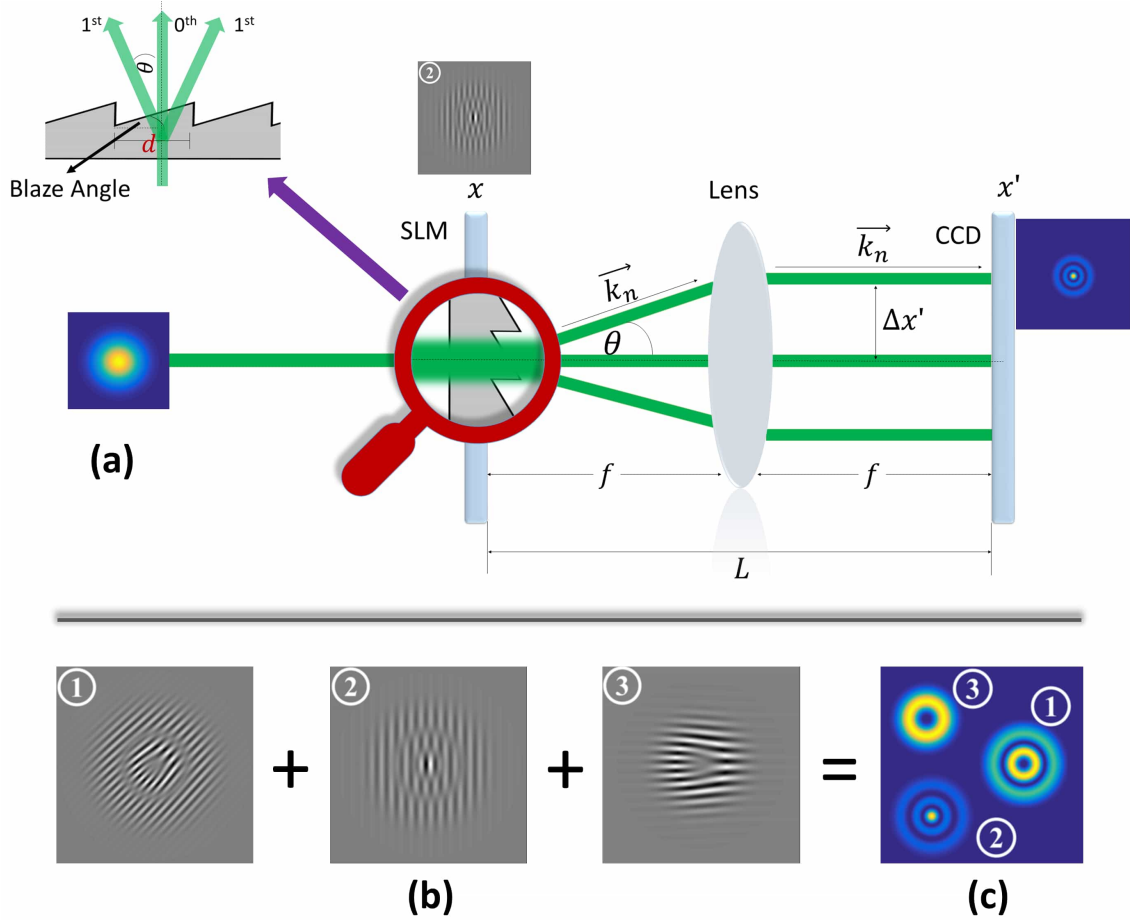


Figure 6.2: **Digital holograms, phase and amplitude for LG_p^ℓ and HG_{nm} modes.** The first row shows the amplitude while the corresponding phase profiles are given in the second row. Phase only and complex-amplitude modulation (CAM) holograms shown in the third and fourth row, respectively were encoded on the SLM to generate (a) LG_p^ℓ and (b) HG_{nm} modes.



6.3.2 Mode modulation using complex amplitude modulation

Complex amplitude modulation can be achieved in many ways, in this tutorial we will only focus on the method proposed by Arrizon *et al.* [214] that produces the highest quality mode compared to other methods [213, 217]. To start with, let's consider a field of amplitude $A(\mathbf{r})$ and phase $\phi(\mathbf{r})$ of the form,

$$U(\mathbf{r}) = A(\mathbf{r}) \exp[i\phi(\mathbf{r})] \quad (6.8)$$

with $A(\mathbf{r})$ and $\phi(\mathbf{r})$ in the intervals $[0,1]$ and $[-\pi, \pi]$, respectively. One way to indirectly modulate the amplitude from phase modulation can be done by writing Eq. 6.8 as

$$h(\mathbf{r}) = \exp\{i\Phi[A(\mathbf{r}), \phi(\mathbf{r})]\} \quad (6.9)$$

Everything reduces to finding the function $\Phi[A(\mathbf{r}), \phi(\mathbf{r})]$. This can be done by expanding Eq. 6.9 as a Fourier series of the form

$$h(\mathbf{r}) = \sum_{q=-\infty}^{\infty} c_q^A \exp[iq\phi(\mathbf{r})], \quad (6.10)$$

where,

$$c_q^A = \frac{1}{2\pi} \int_{-\pi}^{\pi} \exp\{i\Phi[A(\mathbf{r}), \phi(\mathbf{r})]\} \exp[-iq\phi(\mathbf{r})] d\phi. \quad (6.11)$$

The field $U(\mathbf{r})$, can be recovered from the first term of the above equation provided,

$$c_1^A = \frac{1}{2\pi} \int_{-\pi}^{\pi} \exp\{i\Phi[A(\mathbf{r}), \phi(\mathbf{r})]\} \exp[-i\phi(\mathbf{r})] d\phi = A(\mathbf{r})a, \quad (6.12)$$

with a a positive constant. Equation 6.12 can be fulfilled if,

$$\int_{-\pi}^{\pi} \sin\{i\Phi[A(\mathbf{r}), \phi(\mathbf{r})]\} d\phi = 0, \quad (6.13)$$

$$\int_{-\pi}^{\pi} \cos\{i\Phi[A(\mathbf{r}), \phi(\mathbf{r})]\} d\phi = 2\pi a, \quad (6.14)$$

which provides an appropriate basis to determine $\Phi[A(\mathbf{r}), \phi(\mathbf{r})]$. In Eq. 6.14 the value of the constant a is in the interval $[0,1]$, which limits the efficiency of the generated hologram. While different solutions to Eqs. 6.13 and 6.14 can be found, here we will only focus on a solution with odd symmetry, namely,

$$\Phi[A(\mathbf{r}), \phi(\mathbf{r})] = f[A(\mathbf{r})] \sin[\phi(\mathbf{r})], \quad (6.15)$$

which corresponds to type 3 hologram in reference [214], according to which $h(\mathbf{r}) = \exp\{if[A(\mathbf{r})] \sin[\phi(\mathbf{r})]\}$ can be expanded, using the Jacobi-Anger identity as,

$$\exp\{if[A(\mathbf{r})] \sin[\phi(\mathbf{r})]\} = \sum_{s=-\infty}^{\infty} J_s\{f[A(\mathbf{r})]\} \exp[is\phi(\mathbf{r})], \quad (6.16)$$

where, J_s are the Bessel function of order s . Direct comparison of Eqs. 6.16 and 6.10 yields,

$$c_q^A(\mathbf{r}) = J_q\{f[A(\mathbf{r})]\}. \quad (6.17)$$

Equation 6.12 yields the final expression

$$c_1^A(\mathbf{r}) = J_1\{f[A(\mathbf{r})]\} = A(\mathbf{r})a, \quad (6.18)$$

where $J_1(x)$ is the first order Bessel function. Finally, $f[A(\mathbf{r})]$ can be obtained by numerical inversion of Eq. 6.18 as,

$$f[A(\mathbf{r})] = J_1^{-1}[A(\mathbf{r})a] \quad (6.19)$$

The inversion of $J_1(x)$ is guaranteed in the interval $[0, x_m]$, being $x_m = 1.84$ the value where $J_1(x)$ reaches its first maximum $J_1(x_m) = 0.5819$. This restriction limits the values of $\phi[A(\mathbf{r}), \phi(\mathbf{r})]$ to the reduced domain $[-0.586\pi, 0.586\pi]$, which implies that the maximum phase shift that can be obtained with this method is $\Delta\phi = 1.17\pi$.

To generate the required holograms to transform an input light field into LG_p^ℓ or HG_{nm} , we can consider the SLM to be located at $z = 0$ and simplify Eqs. 6.1 and 6.2 as,

$$LG_p^\ell(\rho, \varphi, 0) = \frac{1}{\omega_0} \sqrt{\frac{2p!}{\pi(\ell+p)!}} \left[\frac{\sqrt{2}\rho}{\omega_0} \right]^\ell L_p^\ell \left[\frac{2\rho^2}{\omega_0^2} \right] \exp \left[-\frac{\rho^2}{\omega_0^2} \right] \exp[-i\ell\varphi] \quad (6.20)$$

and

$$HG_{nm}(x, y, 0) = \frac{1}{\omega_0} \sqrt{\frac{2^{-(n+m-1)}}{\pi n! m!}} H_n \left[\frac{\sqrt{2}x}{\omega_0} \right] H_m \left[\frac{\sqrt{2}y}{\omega_0} \right] \exp \left[-\frac{x^2 + y^2}{\omega_0^2} \right], \quad (6.21)$$

respectively. The phase $\phi(\mathbf{r})$ and amplitude $A(\mathbf{r})$ can be easily obtained from the above equations and inserted into Eq. 6.19 and finally in Eq. 6.15 to obtain the desired hologram, which will take the form,

$$\Phi = \text{mod} \left\{ J_1^{-1}[0.5819A(\mathbf{r})] \sin \left[\phi(\mathbf{r}) + 1.17\pi \left(x \frac{U}{\lambda f} + y \frac{V}{\lambda f} \right) \right], 1.17\pi \right\}. \quad (6.22)$$

Figure 6.2 (fourth row) shows examples of the holograms obtained as described above to generate LG_p^ℓ and HG_{nm} modes.

6.4 Experimental Implementation

6.4.1 Experimental setup

A schematic of the mode generation setup is shown in Fig. 6.4. The laser source, linearly polarized Verdi G Coherent laser ($\lambda = 532$ nm) was expanded using a telescope constituting a $10\times$ microscope objective and a lens L_1 of focal length $f = 100$ mm to approximate a plane wave. The expanded beam impinged onto a reflective spatial light modulator, Holoeye Pluto, with a resolution of 1920×1080 pixels and a pixel pitch of $8 \mu\text{m}$. Four separate holograms encoded on the SLM were used to generate LG_p^ℓ and HG_{nm} modes. Each mode was encoded with a unique carrier frequency, as explained in section 6.3, to place each mode at separate positions in the far field. The far field was obtained using a $2f$ configuration system, in which a lens of focal length $f = 250$ mm (L_2) was inserted halfway between the SLM and the detector, located at $2f$ from the SLM. All the modes were modulated in the 1^{st} diffraction order which was separated from the rest using a spatial filter. The mode quality of the generated modes was tracked using 2D image correlation, as will be explained in the next section.

6.4.2 Measurement of mode quality

The quality of the experimentally generated modes was quantified by correlating their intensity profile against their theoretical counterpart, represented by images A and B respectively. The 2D images correlation was computed as,

$$C = \frac{\sum_i \sum_j (A_{ij} - \bar{A})(B_{ij} - \bar{B})}{\sqrt{\sum_i \sum_j (A_{ij} - \bar{A})^2 \sum_i \sum_j (B_{ij} - \bar{B})^2}}, \quad (6.23)$$

where C , the correlation coefficient, is a dimensionless parameter that measures the similarity between two images, 0 for nonidentical images and 1 for identical images. A_{ij} and B_{ij} are the intensity values per pixel. $\bar{A}$ and $\bar{B}$ are the mean intensity values of A and B respectively.

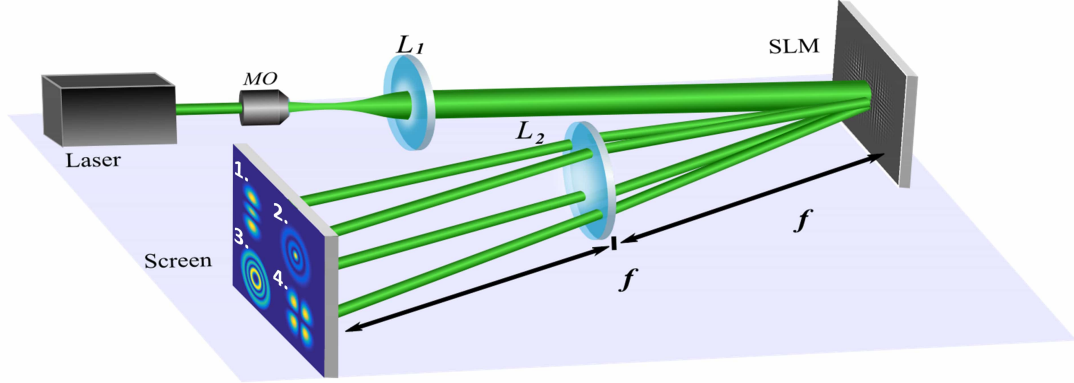


Figure 6.4: **Schematic representation of a mode generation setup.** A laser beam ($\lambda = 532$ nm) is expanded using a $10\times$ microscope objective (MO) and a collimating lens L_1 on to a reflective spatial light modulator (SLM) where a hologram generating LG_p^ℓ (2 & 3) and HG_{nm} (1 & 4) modes is displayed. The desired modes are generated in the focal plane of the Fourier lens L_2 (Screen) with unique spatial positions.

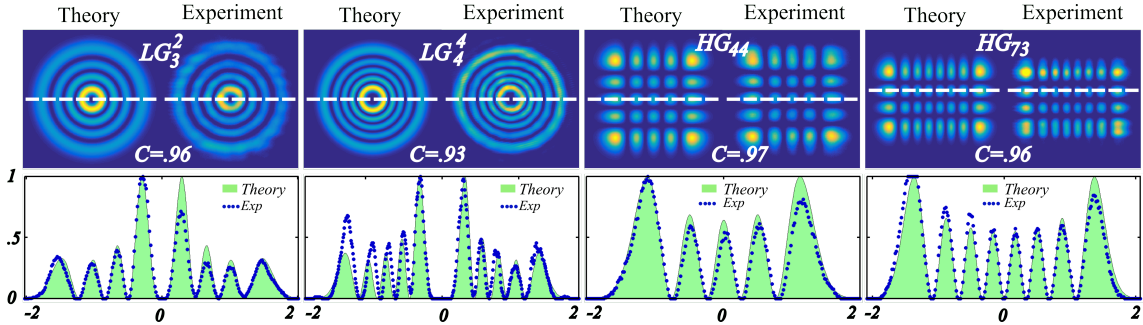


Figure 6.5: **Mode purity measurements using correlation.** Experimental and theoretical intensity profiles of LG_p^ℓ and HG_{nm} modes with corresponding correlations values C (top row). Cross-sectional intensity profile along the dashed line comparing theory and experiment (bottom row). Notice how the correlation values decrease as the mode complexity increases.

A straightforward correlation measurement of the generated modes provides information about their quality as a function of their structure complexity. Figure 6.5 (top) shows the transverse intensity profile of the modes LG_3^2 , LG_4^4 , HG_{44} and HG_{73} generated through complex amplitude modulation. Their corresponding correlation coefficients are $C = 0.96$, $C = 0.93$, $C = 0.97$ and $C = 0.96$. A cross-sectional plot of the mode's intensity profile, illustrating the intensity variations across the beam, is also shown in Fig. 6.5 (bottom). Figure 6.5 also exposes that HG_{nm} modes possess higher correlation values than LG_p^ℓ .

A comparison of the mode quality between the two beam shaping techniques,

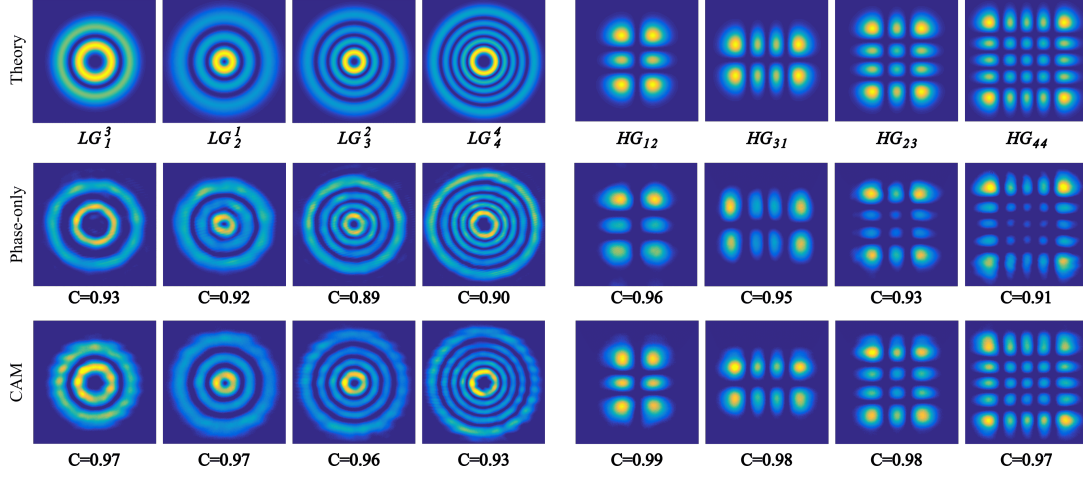


Figure 6.6: **Comparison of beam generation techniques.** The top row shows the theoretical intensity profile of LG_p^ℓ (left) and HG_{nm} (right) modes. Second and third row show experimental intensity profiles of phase only and complex amplitude modulation (CAM), respectively. Notice that CAM allows for higher correlation values.

phase-only and complex amplitude modulation (CAM), was also performed. Figure 6.6 shows the theoretical (top) intensity profile of the modes LG_1^3 , LG_2^1 , LG_3^2 , LG_4^4 , HG_{12} , HG_{12} , HG_{31} , HG_{23} and HG_{44} along with their corresponding experimental profiles generated through phase-only (Fig. 6.6 center row) and CAM (Fig. 6.6 bottom row). As expected, the correlation values decreases as the complexity of the modes increases. Moreover, the correlation values are always higher for modes generated through CAM.

6.5 Discussions

Digital holography has emerged as a powerful technique for light beam shaping, prompted by the advent of computer controlled devices such as spatial light modulators. The advantages of light beam shaping through digital devices has been fully exploited in a wide variety of applications[219–221]. In particular, the modulation of light beams has enabled applications in fields such as optical imaging, optical tweezers and optical communications to mention just a few. In this tutorial we presented a complete description of this technique, while guiding the reader through all the steps involved in the process. First, we introduced two basis sets of spatial modes, Laguerre-Gaussian and Hermite Gaussian, that provided with the modes to exemplify the mode modulation principle. Incidentally, each mode set forms a complete orthogonal solution set of the paraxial wave equations in cylindrical and Cartesian coordinates, respectively. Next, we outlined step by step the process of digital hologram generation to produce these modes. Moreover, since most optical fields requires the shaping of both, amplitude and phase degrees of freedom for an accurate reproduction, we outlined two commonly used techniques to perform such modulations. The first comprises the generation of phase-only holograms whereas the second one consists in the generation of holograms where the amplitude modulation is embedded in the phase to generate a complex amplitude modulation hologram. Of

these two techniques, complex amplitude modulation reproduces optical modes with higher qualities. Even though its implementation is challenging, several approaches have being derived over the years to outline its implementation. Here we only focused on one of these methods, described in the text, which produces spatial modes with high quality.

Chapter 7

Optical imaging of NV^- color centers

7.1 Introduction

It is now evident from the PL intensity measurements that NV centers were successfully fabricated in the specified regions A–D in proximity to the diamond surface; as well as the optical knowledge to manipulate a single beam of light from a coherent laser source. We now shift our attention to photo-induced imaging techniques to characterize and identify the exact location of the NV centers in the diamond, with interest centered around isolated NV centers which can then be probed for statistical and coherence characteristics of a single photon source. In this chapter, we firstly give a brief background on light microscope imaging, particularly of photoluminescence materials. Secondly, we introduce a homebuilt confocal light microscope imaging system and highlight its fundamental mechanism for improved resolution and contrast. Lastly, we provide the component description and analysis of the homebuilt confocal microscope setup that was used for the high resolution imaging of the sample to ascertain the presence of NV centers.

7.2 Confocal fluorescence microscopy

The microscopic imaging of extremely small particles such as molecules and atoms (i.e., objects that are off-range in terms of the working resolution of the human eye) has become essential in several research topics, ever since the inception of microscope devices in the early 1600s. Legend has it, since the days of Hans Lippershey and Zacharias Janssen of Middleburg, Holland [222]. Microscopes allow us to venture into the microscopic world of small objects, limited mainly by one important parameter: the resolution of the imaging device. In microscopy, resolution is defined as the ability to resolve the minimum distance between two objects during any optical imaging process [223]. The resolution of a microscopic imaging system is limited due to the diffraction limit where the spatial resolution is of the order of the wavelength of the light used for excitation, introduced by Abbe [224] in 1873. The process is

described by the following mathematical expression,

$$\begin{aligned} d_{min} &= \frac{\lambda}{\text{NA}_{obj}} \\ &= \frac{\lambda}{n \sin \alpha}, \end{aligned} \quad (7.1)$$

where d_{min} is the minimum distance in a periodic grating that can be resolved, λ is the wavelength of the propagating light waves, NA_{obj} is the numerical aperture of the illuminating objective, which is defined as the sine of the half aperture angle α multiplied by the refractive index n of the medium placed in between the objective front lens and the cover slip.

Many optical techniques have been developed over the years to overcome the diffraction limit and achieving super-resolution where objects closer than the diffraction limit can be resolved in the optical far field. However, some of these techniques are limited to certain types of sample surfaces while imaging only over 1 and 2 dimensional structures. These techniques include the scanning transmission electron microscope [225], the atomic force microscope [226], the scanning near field optical microscope [227] and the scanning tunneling microscope [228].

Here, we investigate the confocal laser scanning microscopy which is a noninvasive, optical resolution and contrast increasing microscopy imaging technique [223]. The scanning confocal microscope was introduced by Marvin Minsky in the late 1950s, who was a postdoctoral fellow at Harvard University at the time [229]. Following this remarkable and pioneering work, many scientific fields relying on optical imaging experienced a surge in growth and development. Like many non-contact conventional microscopy, the imaging process can operate in air, vacuum or liquid environment [223]. However, unlike the conventional wide-field fluorescence microscopy with specimen images that often appear to be blurred, confocal imaging affords the user with highly resolved and detailed image information of a specimen, even in the atomic scale. This is possible by exciting a thin cross-section of the specimen and blocking out light that is not from the focal plane of the microscope, as seen in Fig. 7.1. Additionally, it also possible to construct three-dimensional (3D) images of the specimen by assembling a series of in-focus thin slices taken along the z-axis.

7.2.1 Description

Schematic illustrating the principle of confocal microscopy is depicted in Fig. 7.1. Confocal microscopy is essentially a point-by-point image construction procedure where light is focused at a point sequentially across a specimen and then collected sparingly. By illuminating a single point at a time, a user avoids most of the unwanted light that obstructs imaging when the whole specimen is illuminated at the same time. During the imaging process, light intensity from the focal point of the objective lens is highest at the focal plane, i.e, a thin cross-section of the specimen is imaged. However, other regions ($z \neq \text{focal plane}$) within the specimen are also illuminated by out of focus light. Hence, the detected light will include the in-focus light from the focal plane and the out of focus light from the other regions which then obscure the signal generated from the specimen.

With a confocal setup, the reflected light that is out of focus is impeded by a confocal pinhole aperture placed before a detector which implies that only focused

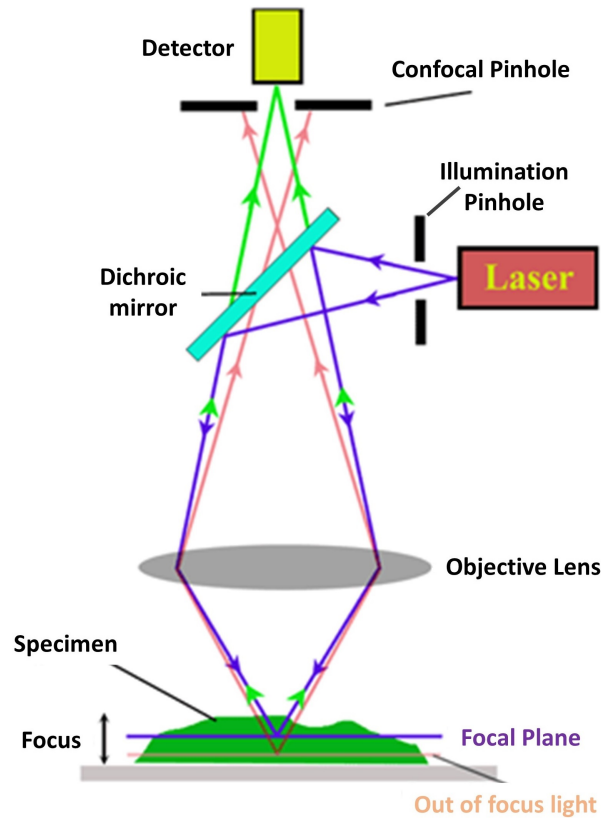


Figure 7.1: **Schematic of a typical confocal microscope system.** Excitation beam (purple) from a laser source enters a confocal system through an illumination pinhole and is reflected by a dichroic mirror onto an objective lens that focuses the beam onto a specimen. The scattered light is reflected back through the lens where only the excited light (green and pink) is allowed to pass through the mirror while the background light is reflected. The confocal pinhole blocks out of focus light (pink) and allows only light (green) from the focal plane to go through to a detector [230].

light is detected, as seen in Fig. 7.1. The light that eventually passes through is detected by a detection system where an image is reconstructed. The illumination pinhole aperture also reduces the effect of in-focus and out of focus light combining at the confocal aperture by imaging at the focal plane of the objective lens the pinhole aperture placed in front of a laser source. The combination of the two pinhole apertures significantly reduces the blurriness that is typical of conventional wide-field images. The focal plane located at the specimen and the pinhole placed before the detector are known as conjugate planes, hence the name “confocal” pinhole (as shown in Fig. 7.2), i.e., the pinhole is a conjugate to the focal point of the objective lens.

Now, since confocal imaging is a point-by-point illumination process, this implies that at each point there are a few emitted photons to collect at a time to give accurate information. Hence, every point must be illuminated for a long time to collect enough light for precise measurements. This means that the amount of time needed to create a confocal image is extended. A solution for such a predicament would be to use a highly intense light source (in the order of mW). Additionally, in order to construct a complete confocal image of a specimen, a computer is attached to the detector and builds up an image one pixel at a time. The created image is of

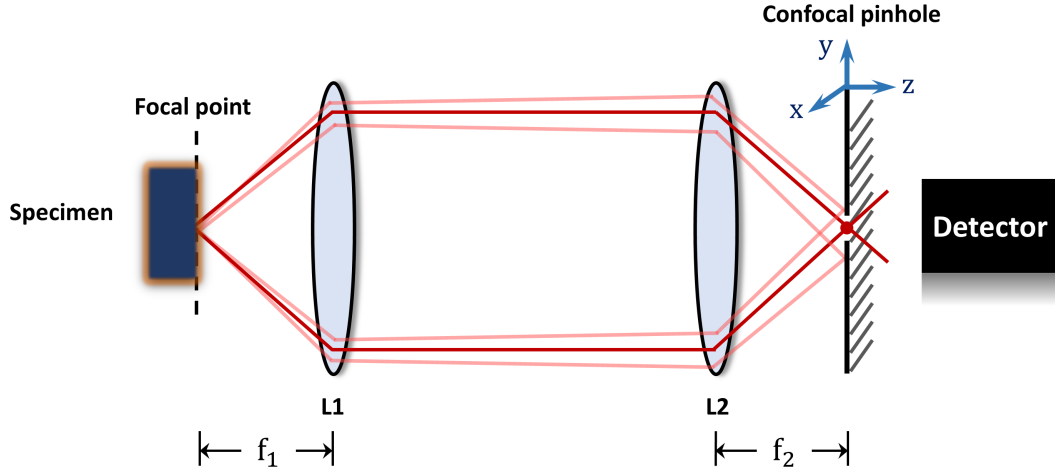


Figure 7.2: **Schematic of conjugate planes.** A combination of the focal point of the lens and a pinhole placed before the detector. The pinhole is dubbed as a “confocal” pinhole because it is conjugate to the focal point of the lens.

a thin two-dimensional (2D) region of the specimen, i.e., optical sectioning.

7.2.2 Experimental setup

Confocal setup

The schematic of the homebuilt scanning confocal setup is shown in Fig. 7.3. A linearly polarized Verdi G Coherent laser source ($\lambda = 532 \text{ nm}$) was directed and impinged onto a reflective SLM (detailed description in Chap. 6) aligned to modulate horizontally polarized light. This is where a diffraction grating with unique propagation angles is digitally programmed to manipulate the spatial positions of the outgoing beam at the local plane of the Fourier lens (L1), imaging the SLM plane (at the focal plane of the microscope objective, Fig. 7.3 (B.)) by a $4f$ system consisting of lenses L1 and L2 with focal length of $f_{1,2} = 750 \text{ nm}$. The resultant beam is then directed into an optical cage system where the beam is expanded using a telescope of lenses L3 and L4 with focal lengths $f_3 = 150 \text{ nm}$ and $f_4 = 300 \text{ nm}$, respectively. The focal length of the telescope lenses are chosen such that the beam undergoes a $2\times$ magnification in order to completely fill the entrance pupil of the objective, which ensures a tightly focused beam with a sufficient intensity gradient for illumination. The expanded excitation beam is reflected by a longpass dichroic mirror, into an inverted infinity-corrected microscope objective ($100\times$ oil immersion Nikon N100 $\times$ -PFO, NA 1.3) with 0.16 mm working distance and 200 mm tube lens focal length.

The dichroic mirror (DMLP567R) reflects light with a short wavelength ranging from 380 nm – 550 nm for ultraviolet and green light; and transmits light with longer wavelengths, ranging from 584 nm – 800 nm for red and near infrared light. The objective focuses a beam on a diamond sample that is placed on a 3-axis stage. The stage is programmed to move linearly in the xy -direction with increments corresponding to the scanning distance limited by the possible diffraction range of the beam that fully enters the back pupil of the objective; and also moves in the z -direction for the optical sectioning of the diamond sample. The light from the

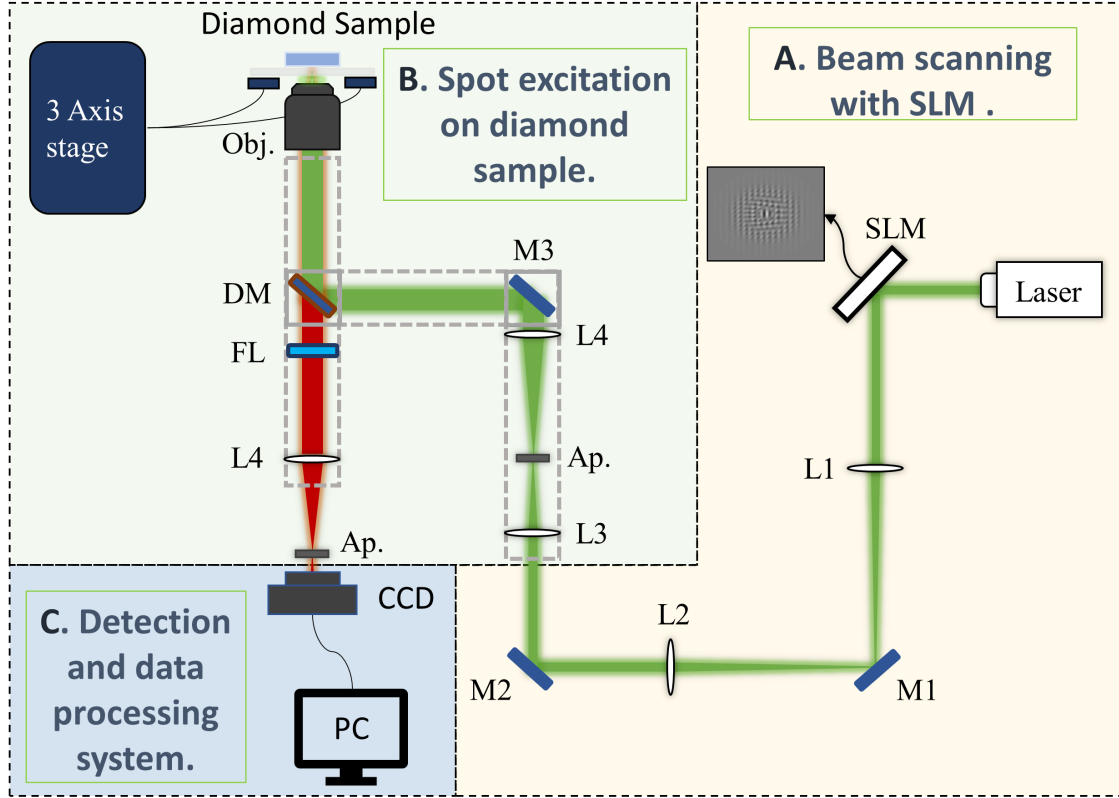


Figure 7.3: **Schematic of a confocal fluorescence microscopy.** **A.** A laser propagates and impinges onto a reflective SLM screen that can be modulated to modify the propagating angle of the laser beam. **B.** The generated modes are directed into a confocal imaging configuration system where the diamond sample is excited. **C.** The resultant fluorescence is detected by a CCD camera where the results are processed by a computer.

sample is collected by the same microscope objective and is transmitted through the same dichroic mirror and filtered by a premium bandpass filter (CWL= 635 nm) with a full width at half maximum (FWHM) of 10 nm, specifically suited for the ~ 637 nm emission of NV^- centers. The light is then focused onto a CCD camera by lens L4 with focal length of 200 nm. The CCD camera captures the images generated by each scan and the data is stored in a computer for data analysis and processing.

Scanning

The scanning process implemented by Minsky [229], was to move the stage rather than the beam to avoid the complications of realignment of the optics. The setup used by Minsky [229], could only take a single image every 10 s. Recent developments in optics and electronics have drastically improved the functionality of confocal microscopes (i.e., improved speeds, image quality and storage of the generated images) while keeping the key operation of the first design intact: the point-by-point illumination with the pinhole apertures.

In this project, we took full advantage of the capabilities of the SLM device which was able to modify the direction of the propagating beam at specified angles by modulating the transfer function with a linear phase imposed grating, as clearly described in Chap. 6. The SLM was programmed to move the beam laterally in

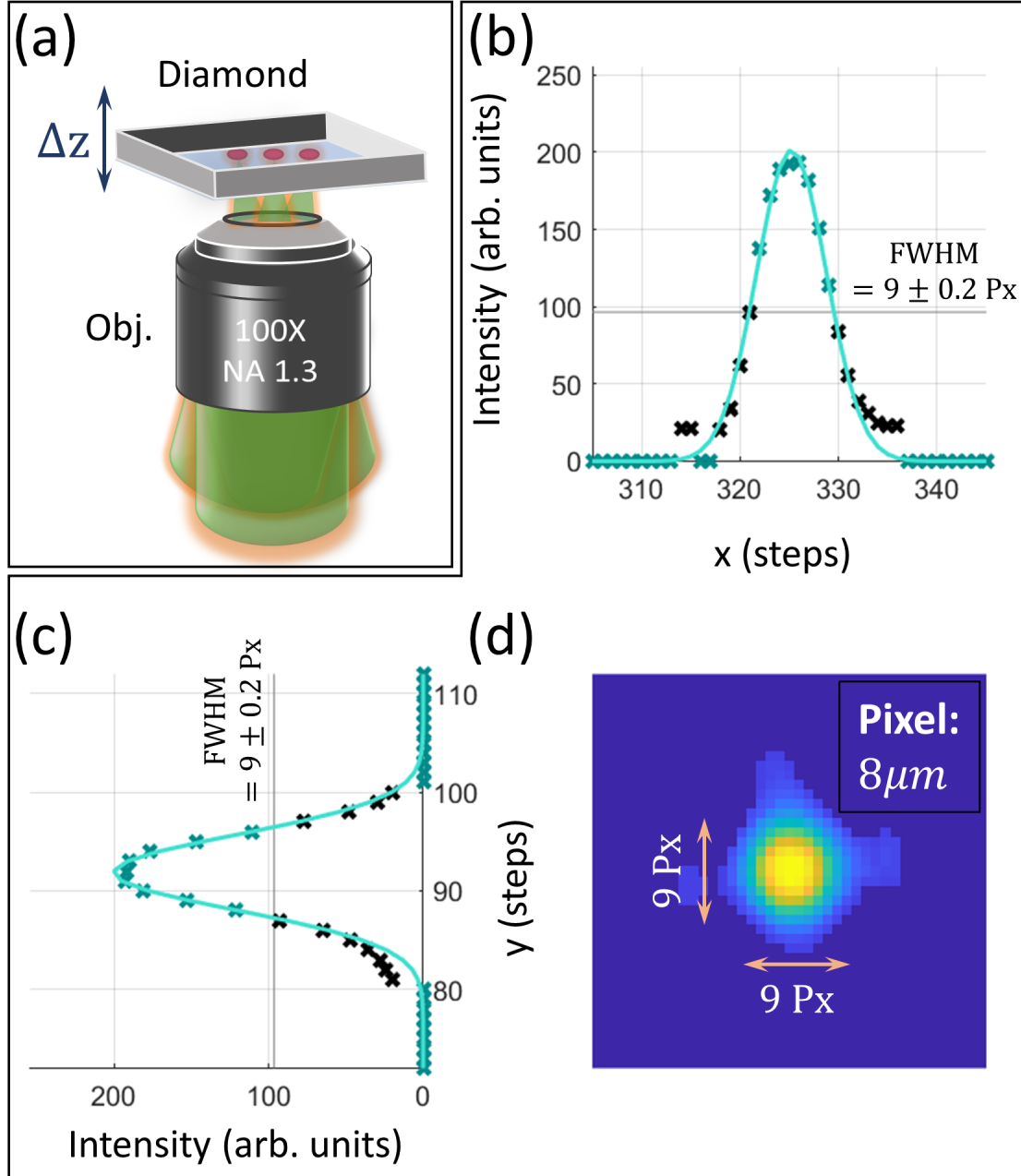


Figure 7.4: **Confocal scanning process with SLM.** (a) Schematic of a confocal scanning process. A modulated beam provides optical excitation in a small NV center active area of the sample at a time (NB. not multiplexing). (b)–(c) Horizontal and vertical cross-sections at $x \approx 98$ and $y \approx 98$, through maximum which are fitted with a Gaussian. The FWHMs (half width at $1/e^2$) are 9 pixels, respectively, which corresponds to a beam waist of $\sim 0.72 \mu m$. (d) Excitation beam focused through a microscope objective (100 $\times$, NA= 1.3). The beam size is about 9 pixel $\times$ 9 pixel on proximity to the diamond surface.

the xy -direction with increments corresponding to the average size of the beam at the focal plane of the objective. The size of the beam was averaged over the scanning area that corresponded to a grating range, where each subsequent beam perfectly fitted in an xy -array without overlapping or leaving any spaces in between the corresponding beam positions. The grating range was about 38 pixel $\times$ 28 pixel

($27.36\text{ }\mu\text{m} \times 20.16\text{ }\mu\text{m}$) with an average beam waist of $\sim 0.72\text{ }\mu\text{m}$ with laser powers of about 20 mW–100 mW. Moreover, stage scanning was also implemented for the optical sectioning of the diamond sample with a z – range of about $20\text{ }\mu\text{m}$ over 6 planes. The z – stack scan was appropriately arranged such that $z_{min} = -16\text{ }\mu\text{m}$ and $z_{max} = 4\text{ }\mu\text{m}$ when the beam was focused at the top of the diamond surface while $z_{min} = -4\text{ }\mu\text{m}$ and $z_{max} = 16\text{ }\mu\text{m}$ when the beam was focused at the bottom of the diamond surface, as oriented in Fig. 7.4 (a). A 3-axis stage, equipped with differential micrometer drives was computer controlled for all optical sectioning processes. The focal plane ($z = 0\text{ }\mu\text{m}$) of the objective was manually adjusted by hand before every z – stack process. A 2D scan was carried out for the green laser beam on the diamond surface with no filter, mainly to average out the beam size across the grating range. The 3D scan with the z – stack was also carried out with a filter (FL in Fig. 7.3) to ascertain any NV center activity within the diamond surface. The process also required no realignment of optics where the SLM along with the 3-axis stage and the CCD camera were a fully functional automated scanning system for confocal imaging. The time it took for each scan is closely associated with the refresh rate of the SLM (60 Hz) and the frame rate of the detection device (CCD-24.7 fps), i.e., it took less than 20 ms to acquire information from one image point, which pales in comparison to what was implemented by Minsky [229].

Data processing

Every imaged point was detected by a Thorlabs (DCC1240C) CCD camera and automatically stored in a computer to be processed and analyzed. 2D scans for the excitation (green) beam were carried out without a filter to determine the full width at half maximum (FWHM) ratio from the horizontal (FWHM_x) and vertical (FWHM_y) cross-sections, as depicted in Fig. 7.4 (b-d). The generated images were processed using a Matlab (R2018b) custom made script. Intensity profiles along the x and y directions of a single beam spot were also generated. The images with low intensity (< 50) and minimum noise were ignored for any processing. The cross-sections for each beam spot were fitted with a Gaussian and stored after each scan. Note that this is determined by the spot size of the reflected excitation laser on the diamond sample, which is the same as the collection spot because the same objective for excitation and collection of light was used. All the stored images for the beam spot were integrated together to affirm the combined image dimensions.

Excitation beam 3D scans were also carried out with a filter for z -stack processing. The process was performed on both NV center inactive and active areas in order to yield a suitable noise to background ratio and also to optimize performance. The data for each z -position was analyzed by using a red, green and blue (RGB) visualization process for multidimensional data. This is because the excitation green beam in this case is filtered out, and the red fluorescence from the NV centers is not visible enough to be detected with a naked eye. However, the FWHM analysis of the generated beam spots provided with adequate information that was utilized to define a mask that scans the grating range around the grain boundaries (NV center active region) of the reference diamond, with results for a certain spot shown in Fig. 7.6–7.11 in this case. Now, each generated image was analyzed for intensity profiles where the images with low intensity (< 50) were ignored. The RGB images were loaded from FWHM intensity information, and the images were plotted and stored in a computer.

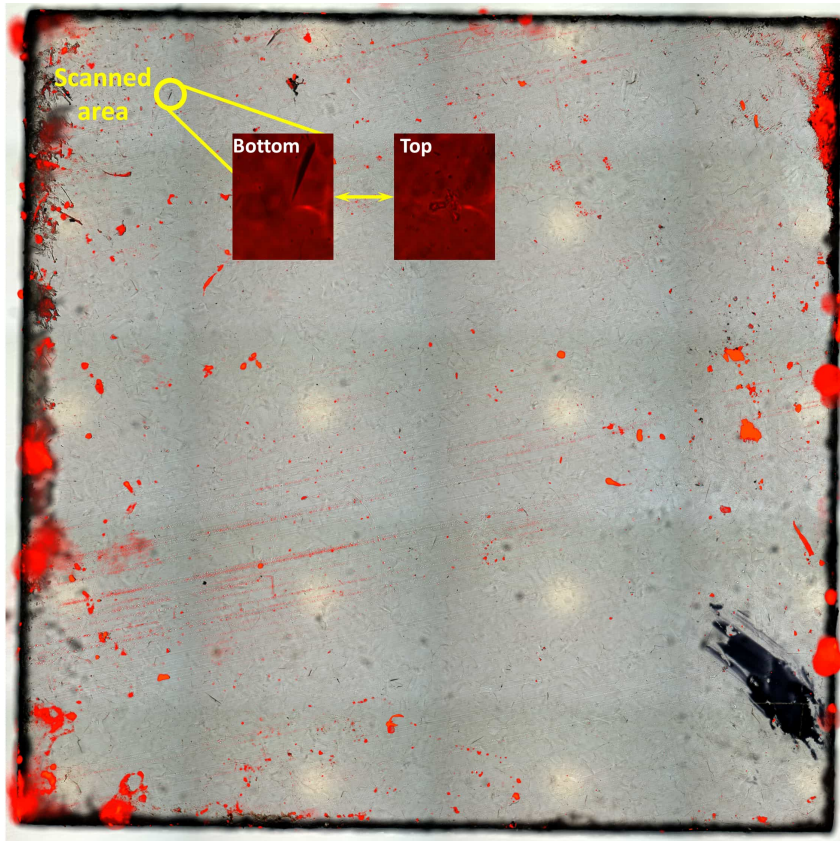


Figure 7.5: **Wide-field fluorescence microscopy.** A bright-field image overlapped with a fluorescence image of the reference diamond taken by a $10\times$ objective. The bottom scan clearly shows the mark from the bright-field image while the top scan shows the opposite side of the same position.

7.2.3 Results

Figure 7.5, depicts a wide-field microscopy image of the reference diamond taken by a commercial light microscope device (Olympus BX 63 OM/FM). The image is a combination of a bright-field image and red fluorescence image of the reference diamond sample (N.B. not all the visible red patches are NV centers but dirt on the surface of the diamond). The image assists in determining the grain boundaries associated with NV center activity. Confocal microscope z -scans were carried out on several regions around the grain boundaries. The z -stack results are depicted below, when the diamond sample is scanned at the top for one particular region circled in yellow in Fig. 7.5. Figures 7.6–7.11, depict the yield from the RGB intensity plots, showcasing very intense activity in the red color range, while the green and blue colors show no activity. This is very much associated with NV centers since the confocal setup is optimized to detect only light of wavelength of about ~ 637 nm. The NV center activity is within the grating range with area of $27.36\ \mu\text{m} \times 20.16\ \mu\text{m}$. The resulting light intensities from $z = 4\ \mu\text{m}$ to $z = -16\ \mu\text{m}$ exhibit similar NV center activity in all the 6 z -planes, i.e., $16\ \mu\text{m}$ below the diamond surface and $z = 4\ \mu\text{m}$ above the surface. The same experimental process was repeated for the investigated diamond. The results showed no indication of NV center activity for all implanted regions. This is mainly due to the low sensitivity of the CCD device used to record the fluorescence from a limited number of NV^- centers.

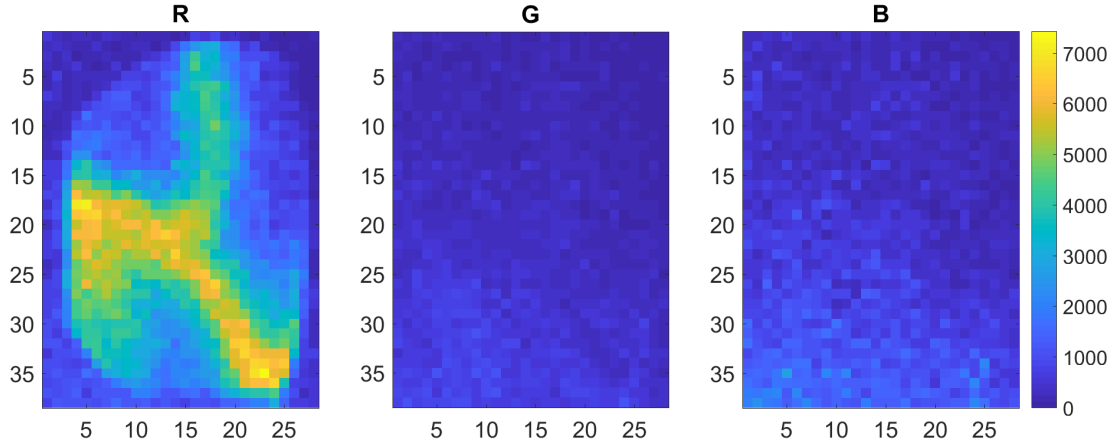


Figure 7.6: **Confocal microscopy scan of NV center active region.** RGB intensity plots of a NV center active region ($38 \text{ pixel} \times 28 \text{ pixel}$). The scan is focused at $z = 4 \mu\text{m}$ above the diamond sample.

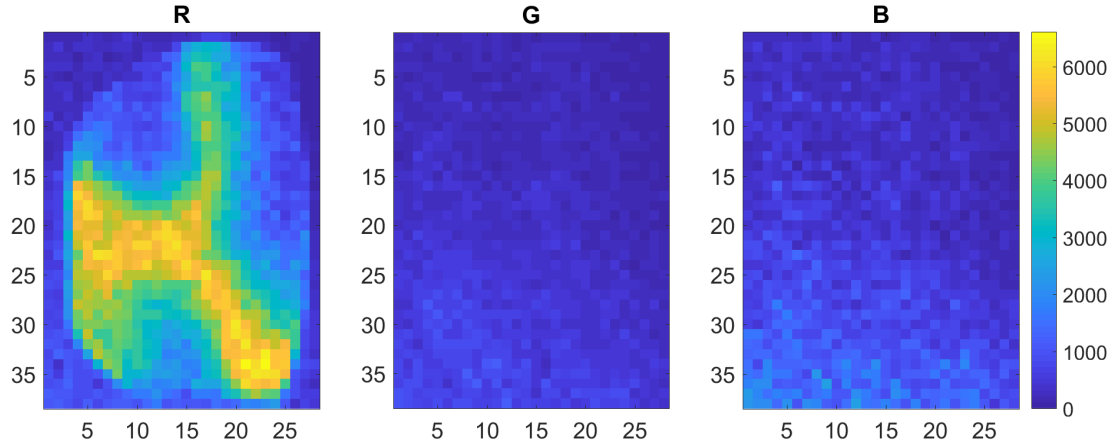


Figure 7.7: **Confocal microscopy scan of NV center active region.** RGB intensity plots of a NV center active region ($38 \text{ pixel} \times 28 \text{ pixel}$). The scan is focused at $z = 0 \mu\text{m}$ in proximity to the diamond sample.

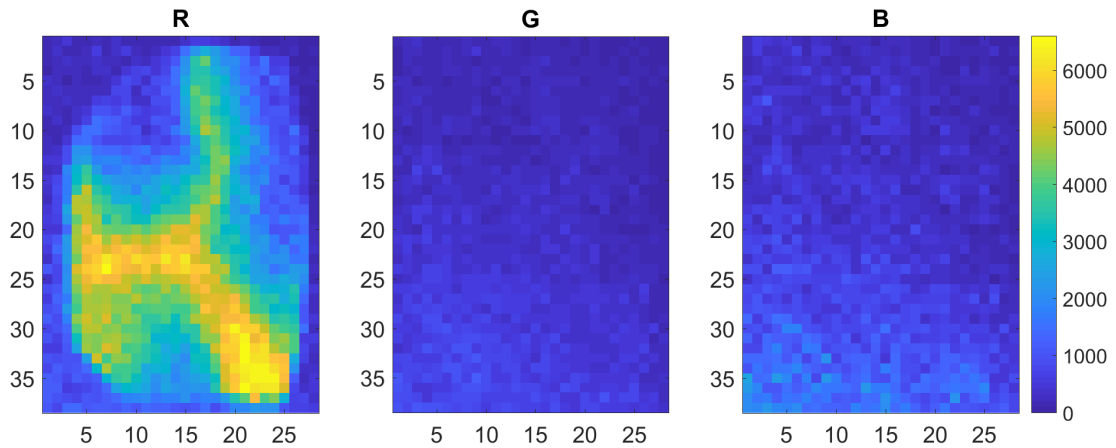


Figure 7.8: **Confocal microscopy scan of NV center active region.** RGB intensity plots of a NV center active region ($38 \text{ pixel} \times 28 \text{ pixel}$). The scan is focused at $z = -4 \mu\text{m}$ within the diamond sample.

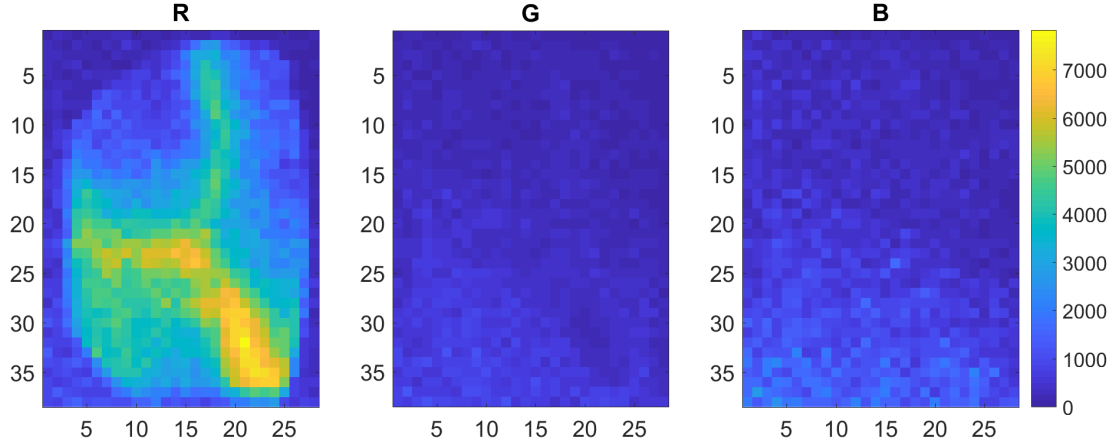


Figure 7.9: **Confocal microscopy scan of NV center active region.** RGB intensity plots of a NV center active region (38 pixel $\times$ 28 pixel). The scan is focused at $z = -8\mu\text{m}$ within the diamond sample.

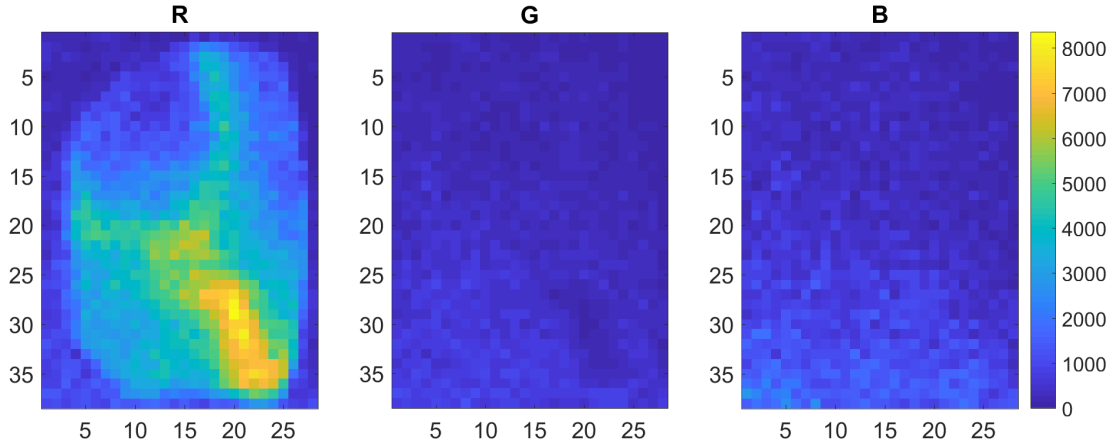


Figure 7.10: **Confocal microscopy scan of NV center active region.** RGB intensity plots of a NV center active region (38 pixel $\times$ 28 pixel). The scan is focused at $z = -12\mu\text{m}$ within the diamond sample.

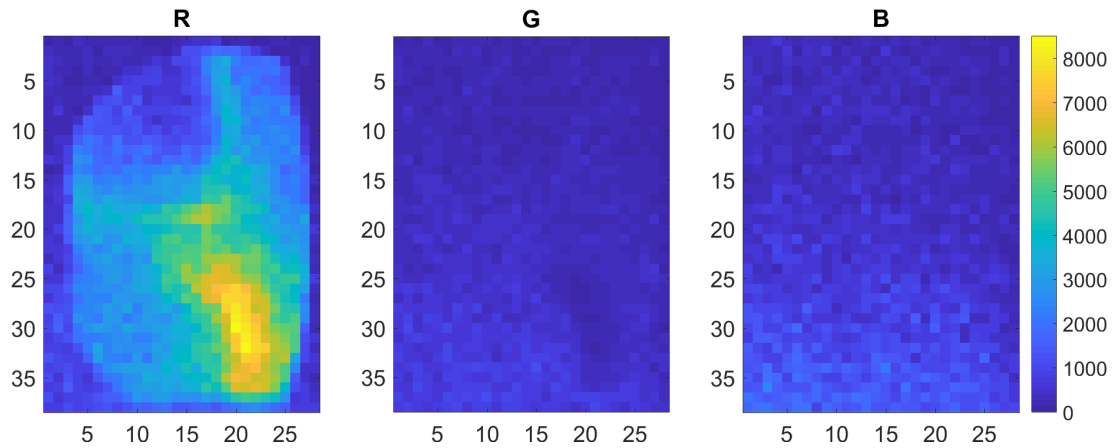


Figure 7.11: **Confocal microscopy scan of NV center active region.** RGB intensity plots of a NV center active region (38 pixel $\times$ 28 pixel). The scan is focused at $z = -16\mu\text{m}$ within the diamond sample.

7.2.4 Discussions

A confocal fluorescence microscope was built and optimized to detect fluorescent light with wavelength of about 637 nm. The reference diamond sample with NV center active regions around the grain boundaries was used to investigate whether the homebuilt setup was fully optimized for confocal imaging. Commercial imaging assisted in identifying suitable grain boundary regions for potential scanning. The RGB intensity plots from a selected boundary region (shown in Fig. 7.5) showcased very intense activity in the red color range, which is attributed to NV center activity. The RGB results presented above from a CCD detector system may not be well-resolved and infers that the grating area of about $27.36 \mu\text{m} \times 20.16 \mu\text{m}$ is congested with coupled NV centers. For well-resolved confocal images with improved signal-to-noise ratio, detection systems such as photon multiplier tubes (PMTs) or avalanche photodiodes (APDs) are excellent options for determining the spatial distribution of isolated NV centers across a diamond sample. These detector devices are more suited for confocal processes, due to their fast signal detection capabilities while also generating very low noise values which result in a high dynamic range.

Furthermore, certain regions within the grating range seem to experience photon saturation due to high effective illumination intensity ($P \geq 20 \text{ mW}$, $I \geq 25 \times 10^9 \text{ W/m}^2$), which decreases the resolution of the confocal microscope [231]. The resolution of the confocal microscope can also be deterred by fast acquisition times at excessively high illumination intensities. However, both properties can be adjusted by pre-programming the SLM device and manually reducing the laser power such that the home-built confocal setup works optimally. Beam shaping is also known to affect the resolution of confocal microscopes. Other authors have reported resolution enhancement with radially polarized LG modes [232]. There has also been a reported 20 % resolution improvement with Bessel-Gauss beams as compared to conventional Gaussian beams [233]. Data acquisition processes can also be improved by the simultaneous generation of multiple light beams (i.e., mode division multiplexing) without compromising the acquisition time from each illuminated spot. This is another excellent feature of the SLM device. The reader can refer to a detailed tutorial on multiplexing by Rosales-Guzmán et al. [234].

Chapter 8

Summary, Conclusion and recommendations

8.1 Summary

Throughout this dissertation the aim was to investigate the emission properties of NV centers fabricated in a relatively pure type IIa diamond sample. Our experimental approach in Chap. 4, for NV center fabrication involved a constant low energy ion implantation process for doping N and C ions in 8 preselected regions A→B and 1→4 (see Fig. 4.8 (c)), respectively, with ion fluence increasing chronologically. The ion fluence ranging from 5×10^9 ions/cm² – 5×10^{12} ions/cm² was chosen to avoid graphitization of the sample and to ascertain a high probability of creating isolated NV centers, while the low energy assured that the created NV centers are in proximity to the diamond surface. The results were conclusive, as NV centers with both charge states (NV⁰ and NV⁻) were successfully created only at N implanted regions. Interestingly, the ZPL of NV⁰ centers close to the diamond surface far exceeded that of NV⁻ centers, indicating the low fabrication of the desired NV⁻ centers relative to the NV⁰ centers after ion implantation. The photochromic effect between the charge states was also evident after thermal treatment (at 800 °C for 30 min) of the sample, where the NV⁻ centers dominated the PL activity, indicating a significant increase in NV⁻ centers while the PL activity of NV⁰ centers diminished. The mobility of vacancies during the annealing process also resulted in the appearance of three unimplanted regions near the relatively high implanted regions (C–D and 4).

A home-built optical setup was also introduced in Chap. 7, in order to locate individual NV centers embedded in both the reference and investigated diamond samples. Firstly, a commercial light imaging setup was used to identify the grain boundaries associated with the reference diamond sample (polycrystalline CVD diamond). The home-built optical setup was configured into a confocal imaging system to detect fluorescent light with wavelength of $635 \text{ nm} \pm 10 \text{ nm}$. The optical sectioning capability of the confocal setup was exploited on the diamond samples with a $20 \text{ }\mu\text{m}$ z -resolution spanning over six planes where $z_{min} = -4 \text{ }\mu\text{m}$ and $z_{max} = 16 \text{ }\mu\text{m}$ when scanning from the bottom of the sample or $z_{min} = -16 \text{ }\mu\text{m}$ and $z_{max} = 4 \text{ }\mu\text{m}$ when scanning from the top of the sample. Each z -scan had a similar grating area of about $27.36 \text{ }\mu\text{m} \times 20.16 \text{ }\mu\text{m}$ with beam steps corresponding to the size of the beam spot on the surface of the sample focused at the focal plane of the microscope objective. NV⁻ center emission activity was observed around a selected grain boundary region

for the reference diamond when excited with a He–Ne green laser with a wavelength of 532 nm. The generated RGB intensity profiles indicated activity only in the red color region for NV^- centers. The investigated diamond sample was also scanned, showing no activity for NV^- centers.

Before the optical imaging of NV^- centers, mode modulating techniques were also studied in Chap. 6, to gain insight into the operational flexibility of a computer-controlled beam modulating device known as an SLM. Mode modulating applications were intricately demonstrated with the generation of LG and HG modes of different orders. The SLM along with a 3-axis stage, was a cardinal component in the step-by-step confocal scanning process, where it was possible to largely automate the confocal optical setup such that the manual realignment of optical elements was entirely avoided. The SLM was used as a digitized diffractive element to manipulate the beam direction of the propagating laser beam in order to excite subsequent positions on the diamond surface limited only by a pre-programmed grating range, while the 3-axis stage was used to navigate the 20 μm z -scanning range described above.

8.2 Conclusion

NV centers were successfully created in three of the N ion implanted regions (B $\rightarrow$ D), in proximity to the diamond surface. The low ion fluence used for region A didn't have any effect in the matrix structure of the diamond nor the creation of NV centers in the diamond sample, even after thermal annealing. The fabrication of NV centers in regions B and C was with minimum damage to the diamond structure, where both spectra appeared to be similar to that of the unimplanted region with the ZPLs of both the charge states of the NV center the only exceptions. The damage incurred in region D was clearly evident, with the spectrum exhibiting deformation between the ZPLs for NV^0 and NV^- centers, affecting the 2nd order diamond Raman. After ion implantation, both charge states showcased similar PL activity in region B, while NV^0 centers dominated in regions C and D. After thermal annealing, the ZPLs of both charge states in regions B and C was affected while the structural deformation in region D was also reduced. The NV^- center dominated the PL activity as compared to NV^0 , after annealing. The C implants also had no effect both in the integrity of the sample nor the fabrication of NV centers after ion implantation and thermal annealing. However, after annealing three unimplanted regions appeared close to regions C–D (N implants) and 4 (C implants). The limited PL activity in regions B and C indicate minimum created NV^- centers with a high probability of isolated NV centers.

The automated z -scan of the reference diamond sample was fairly successful, with NV^- center activity in all the six planes around a preselected grain boundary region established by the generated RGB intensity plots. However, due to the low sensitivity of the CCD detection system that was used, it cannot be easily concluded that the NV^- centers excited in the reference diamond are mostly isolated, which is a crucial requirement for any successful characterization of the photon distribution of the fluorescent light emitted from an individual NV^- center to be considered a SPS. A detector with a fast photon count rate and a high dynamic range would be suitable to identify the spatial distribution of NV^- centers across the diamond samples. A z -scan on all the implanted regions of the investigated diamond was also

carried out, indicating no NV^- activity, mostly probably due to the low sensitivity of the detection system used.

We can now conclude that the ion implantation process in diamond with limited fluence and low energy, accompanied by heat treatment, is crucial to the optimization of well-controlled nitrogen doping for limited NV center creation in proximity to the diamond surface, howbeit, not yet conclusive for isolated centers. The photoluminescence intensity analysis carried out on the surface of the investigated diamond sample correlates with the predicted vacancy concentration and ion range by the SRIM program. The low ion fluence and ion energy ensured that the created centers were close to the diamond surface without unrecoverable structural damage taking place. Thermal annealing also showed favorable outcome on the sample by maintaining equilibrium of the diamond matrix after ion implantation. The confocal imaging setup was effective in demonstrating NV^- activity in N rich diamond samples (reference diamond) with limited confocal resolution, however, less effective in N limited diamond samples (investigated diamond). An improvement in the detection component of the confocal system will go a long way in establishing a highly sensitive confocal setup, detecting even individual centers. With this accomplishment, it will be possible to integrate diamond-based NV centers into light characterization optical setups to substantiate the single photon properties associated with NV^- centers.

8.3 Future recommendations

There is still plenty of work in the fabrication of suitable distribution of NV centers across a diamond sample. By annealing an ion implanted diamond sample in temperature cycles ranging from $600^\circ\text{C} - 2000^\circ\text{C}$, it is also possible to establish a rate at which individual NV^- centers are created using thermal treatment. The affirmation of the single photon emission attribute related to NV^- defect centers in diamond for QIP applications requires the ingenuity of an HBT interferometer setup consisting of a 50 : 50 beam splitter, two single photon counting detectors and an electronic coincidence counter (refer to Appx. D), in order to characterize the emitted fluorescent light from the centers. However, to implement such an intricate quantum configuration, the imaging of individual NV centers is paramount. Hence, the confocal resolution demonstrated in this dissertation must be significantly improved. Further studies in the possible advancement of the confocal resolution can be carried out by adjusting the refresh rate of the SLM device to match the acquisition time of the detection system, while also exploiting the excellent properties of high order LG modes and Bessel-Gauss modes (i.e., with a long depth of field and a tight focal spot), for step-by-step excitation. Mode multiplexing can also be introduced to compare the confocal resolution of successive single spot excitation against a simultaneous $m \times n$ array of single spot excitation ($m, n = 1, 2, 3, \dots$). This can reduce the combined time for data acquisition and processing without compromising on the resolution of the generated confocal images. With solid-state based SPSs in conjunction with ever advancing optical techniques, quantum information processing experiments can be carried out en route to establishing reliable quantum based devices.

Appendices

Appendix A

Publication

- Rosales-Guzmán, C., Bhebhe, N., Mahonisi, N. and Forbes, A., 2017. Multiplexing 200 spatial modes with a single hologram. *Journal of Optics*, 19(11), p.113501.

Appendix B

Conferences attended and Presentations

- CoE-SM / AMSEN Annual Student Presentations: 28 April 2017, University of the Witwatersrand, Johannesburg, South Africa.
- South African Institute of Physics (**SAIP2017**) 62nd annual conference: 3-7 July 2017, Stellenbosch University, Cape Town, South Africa. **Poster** presentation: *Controlling the spatial distribution of multiplexed modes*.
- CoE-SM / AMSEN Annual Student Presentations Workshop: 04 April 2018, University of the Witwatersrand, Johannesburg, South Africa. **Poster** presentation: *Controlling the spatial distribution of multiplexed modes*.
- South African Institute of Physics (**SAIP2018**) 63rd annual conference: 25-29 June 2018, University of the Free State, Bloemfontein, South Africa. **Poster** presentation: *Single photon emission from NV defects in diamond*.
- Siegman International School of Lasers 63: 28 July-04 August 2018, Technical University of Denmark, Island Of Hven, Backafallsbyn, Sweden. **Poster** presentation: *Characterization of NV⁻ centers embedded in diamond*.
- CoE-SM / AMSEN Annual Student Presentations Workshop: 21 May 2019, University of the Witwatersrand, Johannesburg, South Africa. **Poster** presentation: *Characterization of NV⁻ centers embedded in diamond*. **Oral** presentation: *Fabrication of NV centers in diamond for quantum information processing*.
- South African Institute of Physics (**SAIP2019**) 64th annual conference: 08-12 July 2019, Protea Hotel Ranch Resort, Polokwane, South Africa. **Poster** presentation: *Fabrication of NV centers in diamond*. DPCMM award for best poster presentation.

Appendix C

Simulated output for ion and target vacancy production

SRIM output data files with information regarding the simulation of the impact of injected nitrogen ions inside a diamond matrix with energy 7 keV. The detailed information of the parameters involved in the simulation is shown in the TDATA.txt file. The damaged incurred inside the diamond because of the energetic ions interacting with the target vacancies is shown in the VACANCY.txt file. The distribution of the ion projectile is also provided in the RANGE.txt file along with the range straggling in the projected range. Both the VACANCY.txt and RANGE.txt files included tabulated data (not shown here) which were analyzed to provide suitable plots for analysis purposes.

TDATA.txt file

```
===== N (7) into Layer 1 =====
SRIM-2008.03
=====
Data of TRIM Calculation
=====
Ion = N ( 7) Ion Mass= 014.0030
Energy = 7000000.E-06 keV
Ion Angle to Surface = 5 degrees
===== TARGET MATERIAL =====
Layer # 1 - Layer 1
Layer # 1 - Bottom Depth= 1.E+03 A
Layer # 1- Density = 17.64E22 atoms/cm3 = 3.52 g/cm3
Layer # 1- C = 100 Atomic Percent = 50 Mass Percent
=====
Target energies for target atom = C
Displacement = 50 eV, Binding = 3 eV, Surface = 7.41 eV
=====
Depth Range of Tabulated Data= 000000.E+00 - 100000.E-02 Angstroms
=====
Total Ions calculated = 005000
Average Range = 10605.E-02 Angstroms
```

Average Straggling = 41499.E-03 Angstroms

Average Vacancy/Ion = 35930.E-03

=====
Total Backscattered Ions= 4

Total Transmitted Ions = 0
=====

See files SRIM Outputs*.txt for tables :

TDATA.txt – Details of the calculation.

RANGE.txt – Final distribution of Ions/Recoils

VACANCY.txt – Distribution of Vacancies

VACANCY.txt file

=====
N (7) into Layer 1
SRIM-2008.03
=====

Ion and Target VACANCY production

See SRIM Outputs\TDATA.txt for calc. details

=====
See file : SRIM Outputs\TDATA.txt for calculation data

Ion = N Energy = 7 keV

=====
TARGET MATERIAL =====

Layer 1 : Layer 1

Layer Width = 1.E+03 A ;

Layer # 1- Density = 17.64E22 atoms/cm3 = 3.52 g/cm3

Layer # 1- C = 100 Atomic Percent = 100 Mass Percent

=====
Total Ions calculated =5000.00

Total Target Vacancies = 36 /Ion

Total Target Displacements = 37 /Ion

Total Target Replacement Collisions = 2 /Ion

!!!! NOTE : 2nd Column below is number of Primary Knock-Ons
!!!! (PKO are number of Target Atoms Recoiling from the Ion.)
=====

Table Units are >>>> Vacancies/(Angstrom-Ion) <<<<
=====

RANGE.txt file

=====
N (7) into Layer 1
SRIM-2008.03
=====

ION and final RECOIL ATOM Distributions

See SRIM Outputs\TDATA.txt for calculation details

=====
See file : SRIM Outputs\TDATA.txt for details of calculation

Ion = N Energy = 7 keV

===== TARGET MATERIAL =====

Layer 1 : Layer 1

Layer Width = 1.E+03 A Layer # 1- Density = 17.64E22 atoms/cm3 = 3.52 g/cm3

Layer # 1- C = 100 Atomic Percent = 100 Mass Percent

=====

Total Ions calculated =5000.00

Ion Average Range = 106.0E+00 A Straggling = 415.0E-01 A

Ion Lateral Range = 290.9E-01 A Straggling = 369.2E-01 A

Ion Radial Range = 449.3E-01 A Straggling = 251.3E-01 A

=====

Transmitted Ions =; Backscattered Ions =4

(These are not included in Skewne- and Kurtosis below.)

Range Skewne- = 000.0724 &= $[-(X-Rp)^3]/[N*Straggle^3]$

Range Kurtosis = 002.6529 &= $[-(X-Rp)^4]/[N*Straggle^4]$

Statistical definitions above are those used in VLSI implant modelling.

=====

=====

Table Distribution Units are >>>> (Atoms/cm3) / (Atoms/cm2) <<<<

=====

Appendix D

Optical characterization of NV^- centers with a $g^{(2)}(\tau)$ function

In order to experimentally characterize the fluorescence from an individual NV^- center, the use of the Hanbury-Brown and Twiss interferometer is paramount. The HBT interferometer allows us to classically measure the intensity fluctuations of the second-order time intensity photon correlation function, $g^{(2)}(\tau)$, given by the following mathematical expression,

$$g^{(2)}(\tau) = \frac{\langle : \hat{I}(t) \hat{I}(t + \tau) : \rangle}{\langle : \hat{I}(t) : \rangle^2}, \quad (\text{D.1})$$

where $\hat{I}(t)$ is a quantum operator representing the intensity of a light field proportional to its electromagnetic energy flow incident on a detector. Eq. D.1, implies a correlation measurement of a detected photon at time $t + \tau$ after a single photon has been detected at time t . The ' $\langle \rangle$ ' notation represents time averaging while ' $::$ ' represents normal ordering of measurement events. Information about the intensity fluctuation of the light source is obtained when $\tau \rightarrow 0$. For a single photon emitter, $g^{(2)}(0) < 0.5$, expressing Eq. D.1 as,

$$g^{(2)}(0) = \frac{\langle \hat{a}^\dagger(t) \hat{a}^\dagger(t) \hat{a}(t) \hat{a}(t) \rangle}{\langle \hat{a}^\dagger(t) \hat{a}(t) \rangle^2}, \quad (\text{D.2})$$

where $\hat{a}$ and $\hat{a}^\dagger$ are creation and annihilation photon operators, respectively. The intensity operator $\hat{I}(t)$ is proportional to $\hat{a}^\dagger(t) \hat{a}(t)$, where the photon operators satisfy the commutation rule,

$$[\hat{a}, \hat{a}^\dagger] = \hat{a} \hat{a}^\dagger - \hat{a}^\dagger \hat{a} = 1 \quad (\text{D.3})$$

Now, since the number of photons registered on a photon counting detector is proportional to the intensity fluctuation, the photon distribution of photons can also be measured with the $g^{(2)}(\tau)$ function, which is the probability of registering an event with two photons within a certain given time interval, and is given by the following expression,

$$g^{(2)}(0) = 1 + \frac{\Delta n^2 - \langle n \rangle}{\langle n \rangle^2}, \quad (\text{D.4})$$

where n represents the number of photons detected at two available photo counting detectors. An ideal photon source emits a well defined number of photons at a

given time, and hence there is no fluctuation in the photon number distribution (i.e., $\Delta n=0$), then Eq. D.4 becomes,

$$g^{(2)}(0) \geq 1 - \frac{1}{\langle n \rangle}. \quad (\text{D.5})$$

A single photon source has an average photon count of 1 since there will be no coincidental photon counts on both detectors (see Fig. D.1 (b)), which implies that the $g^{(2)}(0)$ function should be zero. However, because of the dark counts associated with detectors as well as stray photons, the minimum condition for SPSs is $g^{(2)}(0) \leq 0.5$. The lack of any coincidental events at $\tau = 0$ is known as antibunching. Classical light (bunching) and coherent light (random) will have $g^{(2)}(\tau) \geq 1$ and $g^{(2)}(\tau) = 1$, respectively. Thus, light can be classified by their photon distribution as being classical, coherent or single photon source.

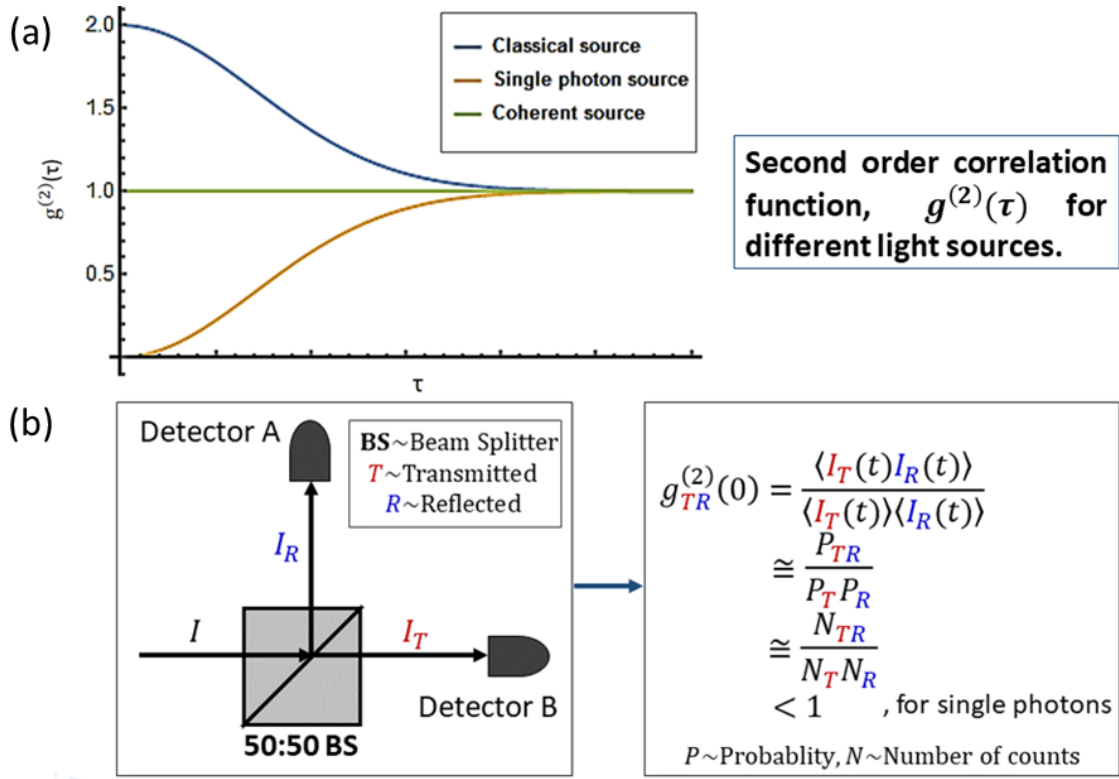


Figure D.1: **Second order correlation function ($g^{(2)}(\tau)$)**. (a) Second-order correlation characteristic curves for classical, coherent and single photon sources. (b) $g^{(2)}(\tau)$ function depicted via a beam splitter with reflected and transmitted intensities describing the probability of a single event.

Figure D.1 (a), shows the $g^{(2)}(0)$ curves of statistic events for the above mentioned sources where from top to bottom each source has bunched, random and antibunched stream of photons, respectively. The classification of light sources is given by the following as $\tau \rightarrow 0$,

- Classical source: $g^{(2)}(0) = 2$,
- Coherent source: $g^{(2)}(0) = 1$,
- Single photon source: $g^{(2)}(0) = 0$,

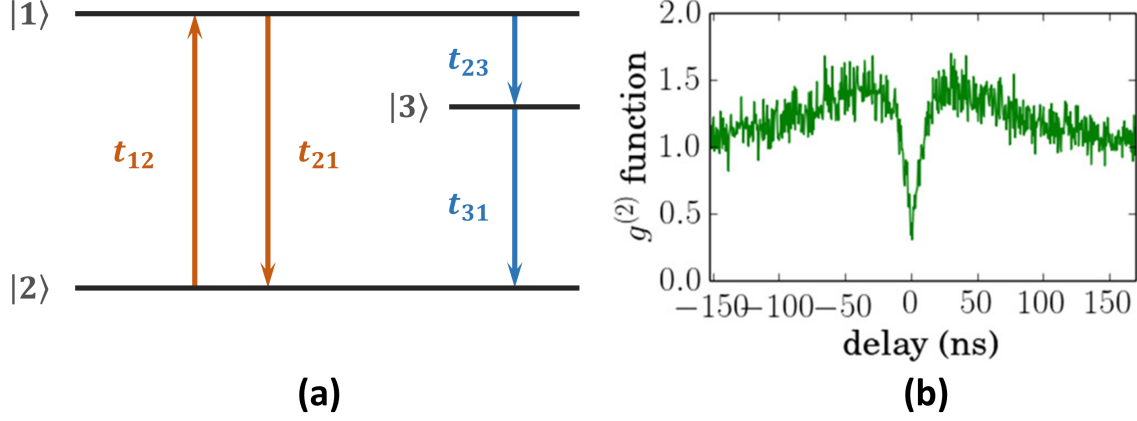


Figure D.2: **An emission and excitation three-level system.** (a) A Jablonski diagram with excitation and emission rates k_{ij} (where $i, j = 1 - 3$) for ground state $|1\rangle$, excited state $|2\rangle$ and a metastable state $|3\rangle$. (b) $g^{(2)}(\tau)$ function with antibunching effect at $\tau = 0$ together with a bunching at finite time delay [235].

In Fig. D.2 (a), the photophysics of NV centers is modeled with a Jablonski diagram consisting of a three-level system for NV centers with a metastable state ($|3\rangle$), which justifies the bunching effect at finite time delays superimposed into an antibunching curve, as seen in Fig. D.2 (b). The excitation and emission states, t_{12} and t_{21} , respectively, are radiative transitions. Non-radiative transitions for the shelving level state are represented by t_{23} and t_{31} . Berthel et al. [235], details explicitly the photodynamics of NV centers for both charge states with an HBT interferometer at varied powers, affecting the quantum efficiency of individual centers.

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