

EXPLORING THE SILICON VACANCY CENTRE IN CVD GROWN NANODIAMOND FOR NEAR-RESONANT OPTICAL TRAPPING

By

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Except where acknowledged in the customary manner, the material presented in this thesis is, to the best of my knowledge, original and has not been submitted in whole or part for a degree in any university.

Matthew van Breugel

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Abstract

The focus of this thesis is the fabrication of diamond nanocrystals containing many Silicon Vacancy (SiV) centres. Firstly, we grow via chemical vapour deposition (CVD) a $200\text{--}\mu\text{m}$ thick diamond film on a silicon substrate. From this film, we produce diamond nanocrystals by means of ball milling. We characterize the physical and optical properties of the nanodiamond sample with a lab-built integrated confocal and atomic force microscope. We find that the fabricated nanodiamonds have an average size of $\sim 160\text{ nm}$ and contain SiV centres with a zero phonon line centred at 739 nm and an average inhomogeneous spectral line broadening of $\sim 12\text{ nm}$.

Secondly, we employ the fabricated nanodiamonds containing SiV centres to investigate a new type of optical trapping in liquid. This method exploits near-resonant dipole forces due to the atomic transition of the SiV centres and results in detuning-dependent attractive and repulsive forces in the vicinity of the atomic transition.

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1

Introduction

“I have a friend who’s an artist and has sometimes taken a view which I don’t agree with very well. He’ll hold up a flower and say “look how beautiful it is,” and I’ll agree. Then he says “I as an artist can see how beautiful this is but you as a scientist take this all apart and it becomes a dull thing,” and I think that he’s kind of nutty. First of all, the beauty that he sees is available to other people and to me too, I believe...I can appreciate the beauty of a flower. At the same time, I see much more about the flower than he sees. [...] Science knowledge only adds to the excitement, the mystery and the awe of a flower. It only adds. I don’t understand how it subtracts.”

Richard Feynman

Diamond is a unique material that possesses extreme mechanical, thermal, chemical, electronic and optical properties. In particular, nanoscale diamond (size ~ 100 nm) known in the community as nanodiamond has attracted increasing attention over the past few decades due to its enormous potential for applications in nanotechnology. In fact, beside the extraordinary material properties, diamond is also host to a large variety of colour centres — over 500 [1] — many of which are luminescent and possess unique optical and spin properties. Nanodiamond-based applications include uses as single photon sources and solid-state spin qubit registers for quantum computing, as high-resolution single-spin sensors, and as non-toxic biomarkers for life sciences.

The practical implementation of these applications relies heavily on the capability to control the properties of the nanodiamond material. For instance, for quantum technologies the diamond must be of ultra-high purity as spin coherence is crucial. For high-resolution sensing and biomedical imaging the critical aspects are the small size of the nanodiamond crystals and the optical stability of the colour centres they contain. The necessity to meet these requirements and thus realise many of the proposed technologies, has resulted in the

fast progress of diamond material science. Synthesis techniques have been developed to fabricate nanodiamond with improved purity [2] or containing specific colour centres [3].

1.1 Background & Scope

Nanoscale diamond materials include diamond films, particles and their assemblies. The system constituted by colour centres in nanodiamond, in particular, is quite attractive as it allows for the unique opportunity to study atom-like properties at room temperature. Defect centres in fact, behave as artificial atoms held within a stable environment provided by the diamond lattice. The Nitrogen Vacancy (NV) centre (Section 2.2.2) for instance, is arguably one of the most studied defects in diamond and is the prime example of the great potential nanodiamond-based technologies possess. The NV has been proposed and used for applications in the fields of quantum optics, quantum cryptography, hybrid quantum systems, high resolution sensing, and in life sciences as a biological label [2, 4–8].

1.1.1 Diamond NV Centre-based Applications

Quantum Information Technologies

Nanodiamond containing colour centres have been proposed and used as single photon sources [3]. This has opened up new avenues towards the development of future quantum technologies. The emission of a single photon is a non-classical state. The emitted photon is entangled with another property of the emitter, such as the electron spin.

The use of fluorescent diamond hosting colour centres as single photon sources is not limited to the field of quantum optics, but also to optical quantum information processing. In 2001 a new flavour of quantum computation known as optical quantum information processing was proposed. The paper stated that quantum computation could be achieved by the use of linear optics with only beam splitters, wave plates, mirrors and a single photon source [9]. This method has gained great popularity as experiments including diamond colour centres can be conducted at room temperature, unlike competing systems such as quantum dots that must be cooled to cryogenic temperatures.

In addition to being utilised as a single photon source in quantum computing, fluorescent nanodiamonds could be utilised as the basis for realising solid-state qubit registers [10, 11]. Specific fluorescent nanodiamonds meet DiVincenzo’s requirements for a qubit, the three major requirements being: that qubits can be initialised to an arbitrary value, that quantum operations can be performed faster than the coherence time of the system and that qubits can be read out easily [12]. With a classical analogy, these three requirements correspond to initialising a classical bit either into the 0 or 1 state, being able to manipulate the bit between these two states and the ability to read out which of the states the bit is in. The spin properties of the NV defect make it an ideal system to act as a room-temperature qubit. This is an advantage over similar artificial atom technologies like quantum dots. The

entanglement of two NV defects has been reported [13], demonstrating the viability of the technology.

Diamond Nanotechnologies for Sensing

Nanodiamonds containing fluorescent NV colour centres can act as a useful tool in high-resolution sensing techniques, particularly in high-resolution magnetometry. They serve as ultra-sensitive sensors where the intensity of magnetic fields at the nanoscale can be determined by measuring, directly, the Optically Detected Magnetic Resonance (ODMR) spectrum of the NV centres [14]. This sensing technique is based upon the hyperfine splitting of the electronic sublevels of the NV within the nanodiamond as they are influenced by a magnetic field. Specifically, the centre's electron spin is sensitive to magnetic fields as the Zeeman effect renders the sublevels of its ground state to be no longer degenerate. When a microwave field resonant with the ground state spin transition is applied, a change in the fluorescence intensity of the colour centre is observed and the intensity of the applied magnetic field can be directly derived [15, 16].

Diamond Nanotechnologies for Life Sciences

As a tool for biomedical imaging, fluorescent diamond nanocrystals are appealing due to their photostability, controllable surface chemistry and non-cytotoxicity. These properties make them a powerful alternative to other conventional methods like photobleaching dyes and toxic quantum dots. Moreover, the surface of a fluorescent nanodiamond can be readily functionalised with antibodies so that the nanodiamond bonds to the corresponding antigen, allowing specific protein targeting. The functionalised fluorescent nanodiamond can then be tracked as it moves in the biological environment. This has been demonstrated using a functionalised NV containing nanodiamond inside living cells [8].

Hybrid Quantum Systems

Diamond colour centres have also been proposed as suitable candidates for hybrid quantum systems which aim to combine advantageously the heterogeneous features of different classes of quantum systems. An example is that of cavity quantum electrodynamics (cQED), in which a quantum system (qubit) is strongly coupled to resonant photons in an electromagnetic cavity [17]. Similarly, in its mechanical analogue, a qubit can be coupled to a mechanical resonator with the resonant phonons acting as the equivalent of the cavity photons [18–20]. This is extremely intriguing as the control over spin-resonator hybrid quantum systems could offer the potential for long range spin-spin coupling for quantum information applications [21], while that over spin-phonon interactions could lead to the development of innovative high-resolution nanoscale sensors [15, 22, 23]. In this regard, diamond is a promising candidate as fluorescent nanodiamonds containing NV centres can be quite easily positioned relatively to other target photonic structures [24]. They however possess the drawback that their optical and spectral properties are not intrinsically best-suited for single photon technologies [25].

This is now triggering further interest in suitable alternatives. The spectrum of the NV shows a large phononic sideband, with only 4% of the centre's emission at room temperature being in its Zero Phonon Line (ZPL) at 637 nm (the wavelength corresponding to the primary electronic transition of the NV) [3]. Furthermore, the NV has a relatively long excited state lifetime of up to ~ 30 ns in nanodiamond [3]. In this respect, the negatively charged (SiV⁻) has superior spectral properties [26].

1.1.2 Potential of the Silicon Vacancy Centre

The exploration of the Silicon Vacancy (SiV) centre [27, 28] and of other centres such as Nickel- [29] and Chromium-based [30], has been driven by the pursuit of better material properties. In contrast to the NV, at room temperature the SiV emits light more efficiently ($\sim 80\%$) into its ZPL at 739 nm and also possesses a much shorter excited state lifetime of ~ 1 ns [3]. These two features make the SiV an exciting candidate to improve nanodiamond colour centre-based technologies, particularly as a single photon source in quantum computing, for biolabelling applications and for hybrid quantum systems [26]. Although this is not strictly relevant to this work, one of the current goals of our group is to employ SiV centres in diamond cavity quantum electrodynamics (cQED) experiments. We aim to place an isolated nanodiamond containing a single SiV centre in a Fabry-Perot type cavity consisting of a fibre-end mirror and an integrated planar dielectric distributed Bragg reflector (DBR) mirror.

Despite the aforementioned advantages, the realisation of SiV-based technology is still in its infancy. The spin properties of the SiV are not yet as well known as its optical properties and its electronic spin, its characteristics as a single photon source and spin coherence are still active areas of research [26, 31, 32]. Also, one of the main limitations yet to be overcome resides in the material science: fabricating single SiV colour centres in nanodiamonds is one of the challenges ahead, though improvements in diamond synthesis techniques are quickly advancing [33, 34]. In this context, one of the main objects of this thesis is the fabrication of nanodiamonds containing many SiV centres. Our Quantum Materials and Applications Group has strong expertise in the production and processing of fluorescent nanodiamond containing NV centres both for sensing and biological applications. My work on the fabrication of nanodiamonds containing many SiV centres builds on this expertise and goes beyond it. The premise comes from the extremely attractive idea for biosensing applications of combining quantum-based sensors with optical tweezers [35, 36].

1.1.3 SiV-Containing Nanodiamonds for Optical Trapping

Nanodiamonds have been proposed as high-resolution sensors for biological applications. In preliminary proof-of-principle experiments, they have been tracked within living cells by means of quantum-based fluorescence mechanisms [35] and manipulated in a liquid environment via optical tweezers [36]. While these two separate achievements are extremely promising, classical optical tweezers are limited in the size ($\sim$ hundreds of nm) of the nanodiamonds which can actually be manipulated. My work on the fabrication of nanodiamonds via chemical vapour deposition (CVD) addresses this aspect. At the end of this thesis, I

investigate the possibility of trapping nanodiamonds containing many SiV centres by means of optical tweezers that operate differently from classical optical trapping. This method exploits near-resonant dipole forces due to the atomic transition of the SiV centres and results in detuning-dependent attractive and repulsive forces in the vicinity of the atomic transition. I present our preliminary results and propose future developments towards the engineering of ideal nanodiamond sensors containing a single NV centre and many SiV centres which would possess both superior sensing and 3D-spatial manipulation capabilities.

1.2 Outline

The core subject of this thesis is the fabrication of nanodiamonds containing Silicon Vacancy centres. In addition to this, the thesis includes content pertaining to a novel method of trapping fluorescent nanodiamonds via the atom-like properties of incorporated colour centres.

In **Chapter 2**, we explore diamond, and in particular optically active defects that can form within the diamond host matrix. These defects are known as colour centres and possess favourable spin and optical properties. When these colour centres are found in nanoscale diamond particles, known as nanodiamonds, they prove a unique tool for many applications. We discuss two particular colour centres: the Nitrogen Vacancy and the Silicon Vacancy centres. The former initiated the development of the field and has expanded the horizons for diamond nanoscience over the past half century. The latter has been known for a much shorter period, but as it is further investigated it shows interesting properties that might outshine its predecessor in certain areas of research.

In **Chapter 3**, we examine the process of diamond synthesis and how colour centres can be incorporated into the diamond lattice. We discuss various methods and their respective advantages. We also discuss the process of milling diamond films into diamond nanocrystals (nanodiamonds), which is the method employed in this thesis for sample production.

In **Chapter 4**, we present the methods and results of our nanodiamond fabrication process, involving chemical vapour deposition growth and ball milling processes. We aim to fabricate nanodiamonds containing a high concentration of silicon vacancy centres. We show the results relevant to our samples, which have been characterised via confocal microscopy and atomic force microscopy.

In **Chapter 5**, we then consider optical trapping, focusing specifically on optical tweezers and atom trapping. Taking advantage of both classical and quantum regimes, we propose a new method of trapping nanodiamond particles by addressing their quantum properties. The construction of the experimental setup is outlined and further results analysed and presented.

Chapter 6 contains the conclusions and presents a premise for future work stemming from this research. There is great potential for this method of trapping to be conducted within biological cells and in combination with NV-containing nanodiamonds.

2

Diamond & Colour Centres

“Better a diamond with a flaw than a pebble without.”

Confucius

Here we review diamond as a material and in particular the colour centres that diamond can host. We then examine two such defects: the Nitrogen Vacancy and the Silicon Vacancy centres. They possess interesting spin-optical properties that continue to generate significant amounts of research, which is presented here alongside their applications.

The modern-day popularity of diamond can almost entirely be traced back to an extremely successful marketing campaign run by De Beers, a company which remains a leader in the world diamond trade. Their 1947 campaign is the origin of the slogan *A diamond is forever*, which is still well-known to this day, with diamond still considered both a sign of stature and an icon of popular culture. Diamonds are however much more than an elusive gemstone. Diamond has extraordinary properties ranging from mechanical, to electrical, optical and thermal. In addition, nanodiamond shows readily controllable surface chemistry and biological inertness [37–39]. With such a variety of unique properties diamond has been proposed and used in numerous applications and technologies (see Section 2.3).

Besides its outstanding macroscopic properties diamond also displays additional ones due to the lattice impurities it can host (mainly foreign atoms, lattice irregularities and combinations of both). Optically active defects are known as colour centres, renowned for their spin-optical properties. In the emergent field of nanotechnology, diamond containing colour centres has become a notable system, generating great interest since the turn of the 21st century. Some colour centres in diamond also possess favourable spin properties leading to further applications in, to mention just a few, quantum metrology as an ultra-high resolution sensor and in quantum information as a tool for quantum computation and quantum

cryptography. Further applications include uses as a non-toxic photostable marker in cell and biological environments.

2.1 Diamond

Diamond has been long known and utilised in machining and jewellery and it is now becoming the material of choice for cutting edge-technologies.

2.1.1 Lattice Structure

The diamond lattice consists of carbon atoms arranged in a tetrahedral crystal structure [40]. Carbon has a $1s^2 2s^2 2p^2$ electronic configuration, so there are four valence electrons in its outer shell. In diamond, carbon forms sp^3 -hybrid orbitals. Each carbon atom bonds covalently to its four neighbours, forming a strong periodic structure (Figure 2.1a), which is the key to diamond's extreme properties.

2.1.2 Physical Properties

Diamond has extreme physical, thermal and optical properties. It is the hardest known naturally occurring material and is remarkably resistant to deformation. This is ideal for its applications in the cutting, grinding and polishing industry. It has exceptional electronic and thermal properties, such as high thermal conductivity, which make it suitable for high-power, high-frequency, high-temperature and high-voltage electronics. It possesses a notably high refractive index of ~ 2.4 and can also appear coloured as a result of lattice defects. Traditional uses of diamond in optics include windows for infrared instrumentation and radiation detectors. Additionally, a new range of applications are being proposed and realised exploiting the spin-optical properties of colour centres in diamond.

2.2 Defects in Diamond

Diamond is host to over 500 optically active defects over the range of 170 nm to 20 μm in the electromagnetic spectrum [1]. These defects can be classified as intrinsic, extrinsic or a combination of both, some giving rise to interesting optical properties (Section 2.2.2 and Section 2.2.3).

2.2.1 Intrinsic & Extrinsic Defects

Intrinsic defects are irregularities of the diamond lattice. There are different types of intrinsic defects, all of which can occur naturally or be artificially introduced via irradiation. Of these defects we note three specific types: lattice sites shared by an additional carbon atom [42], lattice sites that are missing a carbon atom [43, 44] and lattice sites with broken bonds [45, 46].

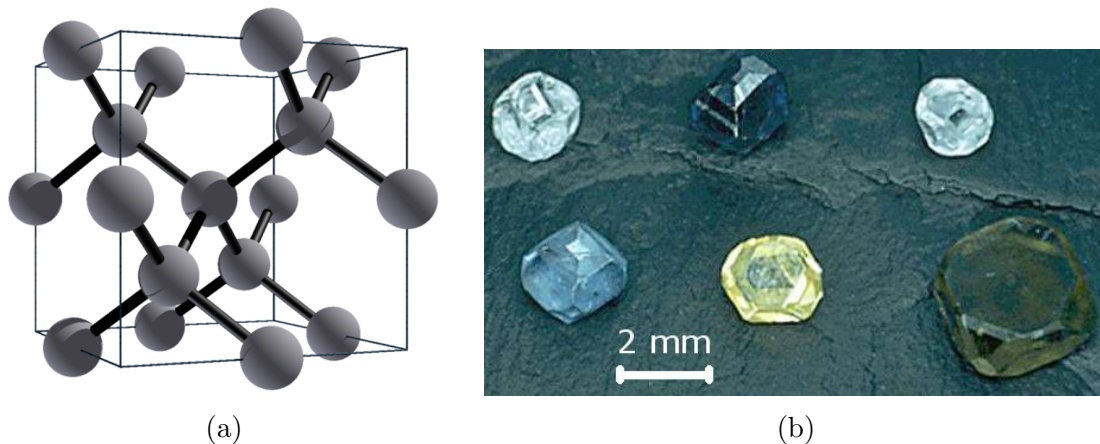


Figure 2.1: **Diamond structure and appearance.** (a) Diagram of the diamond lattice (two interpenetrating face-centered cubic (fcc) Bravais lattices) grey spheres represent carbon atoms. (b) Synthetic diamonds of various colours, each containing different colour centres which give them their characteristic nuances [41].

Extrinsic defects are a result of the incorporation of foreign atoms in the diamond matrix. There are two types of extrinsic defects: substitutional and interstitial. The former is the replacement of carbon at a lattice site by a foreign atom, while the latter is the presence of a foreign atom between lattice sites [40]. Both intrinsic and extrinsic defects give rise to the characteristic colouring of naturally-occurring diamond.

2.2.2 The Nitrogen Vacancy Centre

The Nitrogen Vacancy (NV) centre has attracted considerable attention over the past decade and is one of the most studied defects in diamond. NV centres are formed by the removal of two neighbouring carbon atoms from the diamond lattice, with one atom site hosting a nitrogen atom, and the other site left vacant, orientated along the $\langle 111 \rangle$ direction in the lattice [47, 48], as shown in Figure 2.2a. The NV can be found in either its neutral charge state NV^0 , or its negatively charged state NV^- . The NV^- exhibits unique spin and optical properties, because of that from here on the abbreviation ‘NV’ will refer specifically to the NV^- state, unless specified otherwise.

We are particularly interested in the case of single NV hosted in diamond. A single NV behaves as an artificial atom — an emitter with a discrete anharmonic energy level structure. This structure is retained at room temperature due to the host diamond matrix. The observation of single NV centres alone implies several properties: a favourable optical absorption cross-section, a relatively short excited state lifetime, good quantum efficiency of the optical cycle and the absence of long-lived dark state that shelves the fluorescence [49].

The NV has defined energy levels with optically active transitions and its own spectral fingerprint (Figure 2.2b). A notable feature of the NV photoluminescence spectrum is the Zero Phonon Line (ZPL) at 637 nm, corresponding to the energy difference between the ground and excited state [50], and followed by a large phononic sideband to the red of the ZPL. We note that a secondary ZPL is also optically active in the infrared region at 1042 nm [51] (Figure 2.3a).

The electronic structure (Figure 2.3a) is at the core of almost every aspect of the NV. There are six electrons associated with the NV, five from the intrinsic nitrogen atom and one additional electron from elsewhere in the lattice (usually from a neighbour nitrogen) [3]. Most of the charge density ($\sim 72\%$) is at the three nearest neighbour carbon atoms surrounding the vacancy, a small fraction ($\sim 0.2\%$) is at the nitrogen and the rest ($\sim 28\%$) is spread over the lattice [52]. The electronic structure features ground and excited triplet states, 3E and 3A_2 , which are separated by the aforementioned optical transition at 637 nm. The 3A_2 ground triplet state has a zero field magnetic resonance at ~ 2.88 GHz [53, 54], which is in the microwave regime. In the absence of a magnetic field, the ground state $m_s = \pm 1$ sub-levels are degenerate, though the presence of a magnetic field can lift the degeneracy due to the Zeeman effect and therefore can become resonant both slightly above and slightly below 2.88 GHz. This trait makes the NV excellent for spin and magnetic sensing [15, 16, 55–57]. However, the optical properties of the NV are by no means ideal. For instance, the NV^- centre possesses a relatively low emission rate (intrinsic spontaneous emission lifetimes up to ~ 30 ns) and a relatively broad (~ 200 nm) intrinsic emission spectrum with only 4% of its fluorescence into its ZPL [3].

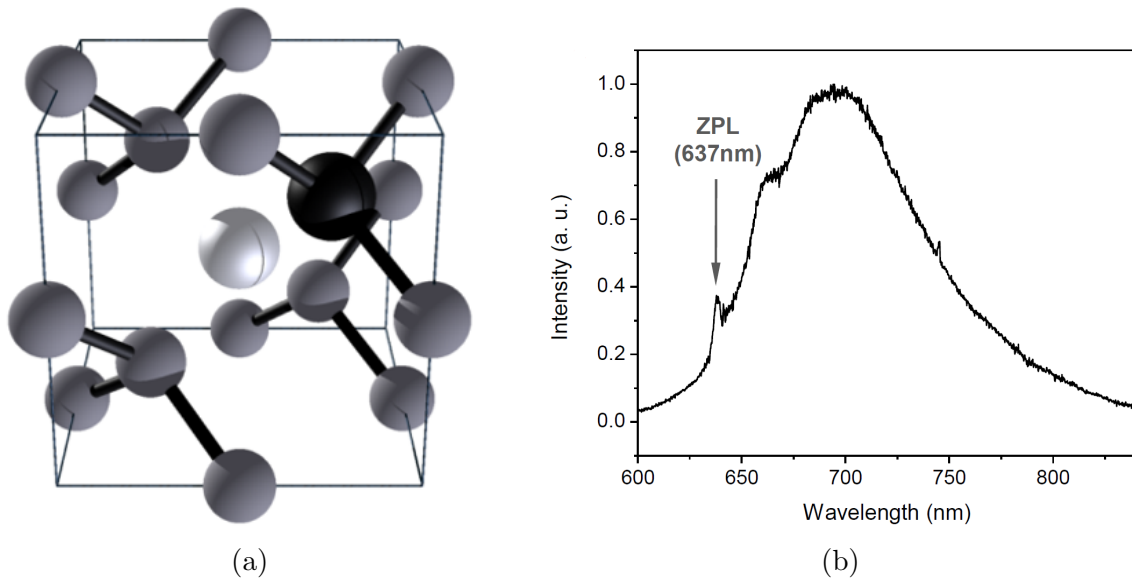


Figure 2.2: NV centre structure and photoluminescence spectrum. (a) Diamond lattice containing an NV colour centre, grey spheres represent carbon atoms, the white sphere represents a vacancy (an empty lattice site) and the black sphere represent a nitrogen atom. (b) Spectrum of the NV^- colour centre at room temperature showing the ZPL and the large phononic sideband, under excitation with 532-nm pump [58].

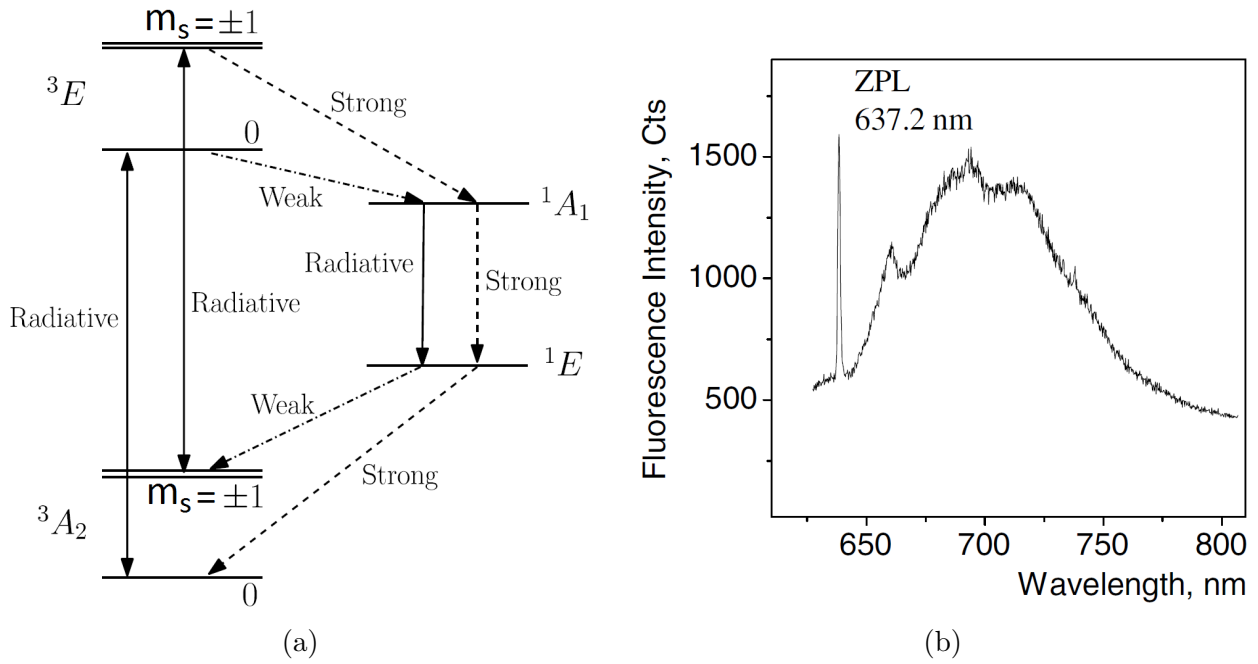


Figure 2.3: **NV centre electronic structure and low-temperature photoluminescence spectrum.** (a) The electronic structure of the NV⁻ colour centre [59, 60]. Radiative transitions are marked with solid arrows, whereas dark transition are marked with dashed arrows. The radiative transitions between the 3E and 3A_2 triplet states correspond to 637 nm. The 3A_2 ground triplet state has a zero-field magnetic resonance at ~ 2.88 GHz [53, 54] and the $m_s \pm 1$ states are degenerate in the absence of a magnetic field. The radiative transfer from the 1A_1 state to the 1E state is the origin of the secondary ZPL at 1042 nm. (b) Low-temperature ($T = 1.8$ K) spectrum of the NV [14].

2.2.3 The Silicon Vacancy Centre

Unlike the NV, the Silicon Vacancy (SiV) emits over 80% of its fluorescence into its ZPL [34], making it the brightest yet discovered colour centre in diamond [28]. As such, the SiV has generated significant research over the past few years because of its appealing optical properties. In the SiV defect, two neighbouring carbon atoms are removed from the lattice along the $\langle 111 \rangle$ direction; both these lattice sites remain vacant, while a silicon atom is located between them [61–63] (Figure 2.4a). The SiV displays what is known as the split-vacancy configuration. Although the NV spin properties remain better understood than those of the SiV, the optical properties of the SiV have the potential to surpass those of its predecessor.

Like the NV, the SiV can exist in either a neutral charge state, SiV⁰, or a negatively charged state, SiV⁻. Theory calculations indicate that the origin of the strong 739-nm fluorescence originates from the SiV⁻ state of the colour centre [61]. The neutral charge state of the SiV (SiV⁰) shows a ZPL at 946 nm [64]. As to now, the SiV⁰ has however attracted less attention in comparison to its negatively charged counterpart (SiV⁻); henceforth from now on, the

more interesting SiV^- will be referred simply as SiV, unless differently stated. There are eleven electrons associated with the SiV colour centre: six in the dangling bonds from the surrounding carbon atoms of the host matrix, four from the silicon atom and one additional electron that has been trapped by the defect [64]. Investigation into the configuration of the electronic structure of the SiV is still ongoing.

The electronic structure of the SiV is revealed by the spectrum taken at 4 K [31] (Figure 2.5b). The spectrum has four distinct peaks, indicating four separate optical transitions, the strongest at 739 nm being the ZPL. The four transitions occur as a result of doubly-split ground and excited states [65, 66] (Figure 2.5a). The excited state lifetime of the SiV is an order of magnitude smaller than that of the NV, making the SiV a more efficient emitter. The excited state lifetime of the SiV is on the order of ~ 1 ns [3, 33, 67, 68], whereas for the NV the excited state lifetime is on the order of ~ 20 ns [3, 69–71].

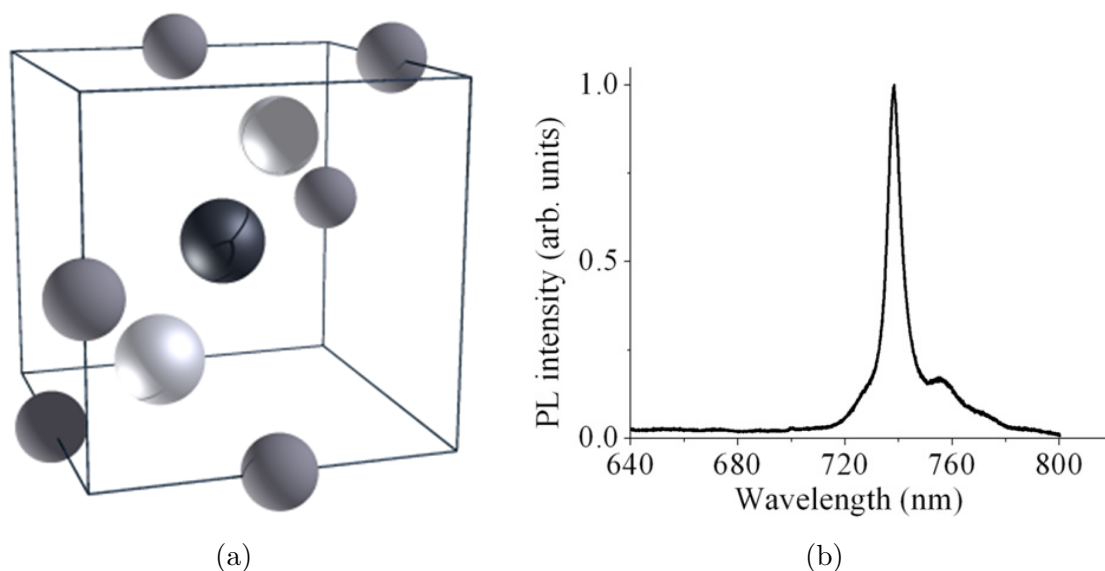


Figure 2.4: **SiV centre structure and photoluminescence spectrum.** (a) Diamond lattice containing a SiV colour centre, the grey spheres represent carbon atoms, the white spheres represent vacancies (empty lattice sites) and the black sphere represent a silicon atom. (b) Spectrum of the SiV^- colour centre showing the ZPL at ~ 739 nm [3].

Another advantage of the SiV over the NV is its stability in ‘ultrasmall’ nanodiamonds (size < 10 nm). The NV is theoretically predicted to become unstable in nanodiamond with a size less than 2 nm, though this is yet to be directly observed as artificially fabricated NV containing nanodiamonds have not been reduced further than 5 nm without the annihilation of the NV centre [73]. Density functional theory (DFT) simulations indicate that the SiV is stable at nanodiamond sizes smaller than that of the NV — down to at least 1.1 nm [74]. SiV fluorescence has been observed from nanodiamonds discovered in meteorites [75–77], with photostable emission observed for crystals as small as 1.6 nm [74].

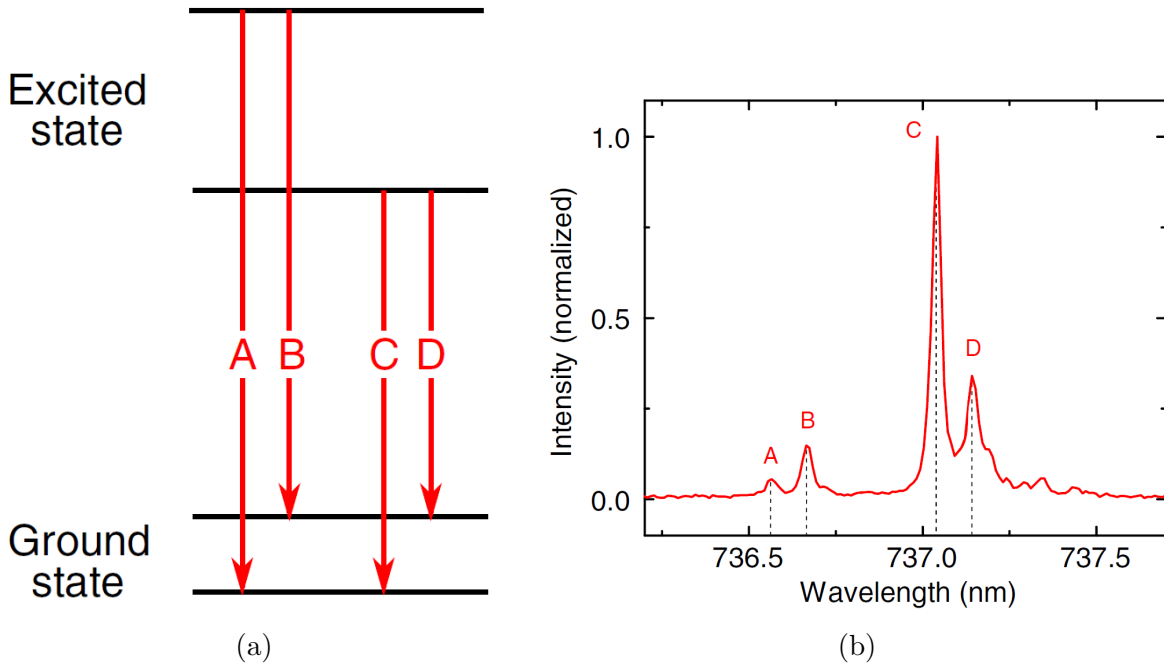


Figure 2.5: **SiV centre electronic structure and photoluminescence spectrum.** Adapted from [31]. **(a)** Configuration of the electronic structure of the SiV. Optical transitions are marked ‘A’ through ‘D’, corresponding to their location in the SiV spectrum. **(b)** Normalised spectrum of the SiV taken at 4 K under excitation with 700-nm pump, with transition ‘A’ through ‘D’ annotated. Perturbations in the spectrum towards redder wavelengths of transition ‘D’ are attributed to ^{29}Si and ^{30}Si isotopes [31, 65, 72].

There has been limited investigation into the effects of lattice strain on the SiV. Those conducted show slight alteration of the fine structure at low temperature [66, 67]. For the NV, the fine structure of the ZPL is very much influenced by strain within the lattice causing a shift of the ZPL and of the relative position of the energy levels [78].

2.3 Applications of Colour Centres

There are several applications in which fluorescent nanodiamonds have a strong presence, all of which draw on the atom-like properties of the colour centre. The NV demonstrated its viability as a photostable single photon source [4, 79, 80] shortly after the first single NV was observed [49]. As a photostable single photon source, NVs do not photobleach [4] and exhibit blinking only when reduced to sizes on the order of 5 nm [73]. Due to this property, the NV is a viable tool for quantum cryptography [5, 6] and may become a suitable candidate system for room-temperature optical quantum information processing [9]. Current investigations also indicate the possibility of utilising the NV as an electrically-driven single photon source [81].

The NV is able to act as a solid state qubit, satisfying each of DiVincenzo’s qubit requirements [12, 82, 83]. It can be initialised into a known state, which can then be manipulated

and read out. This has led to the NV being used in fundamental quantum experiments concerning non-classical states, such as Bell state violation [84]. The spin coupling of two NVs has been demonstrated [10]. This holds great promise towards the development of scalable NV-based multi-qubit systems [7].

The NV has the ability to act as a nanoscale sensor, for instance, in high-resolution sensing of magnetic fields. In the presence of a magnetic field, the 3A_2 $m_s = \pm 1$ ground state of the NV becomes non-degenerate. The threshold above which this non-degeneracy appears is $4 \text{ nT Hz}^{-1/2}$ [2] and the degree of the Zeeman splitting can be readout via Optically Detected Magnetic Resonance [85], in both bulk diamond [86] and nanodiamonds [73]. The effectiveness of nanodiamond-based high-resolution sensing has been recently demonstrated by detecting the magnetic field of single spins [56, 57].

Fluorescent nanodiamonds also find applications in biological sciences. Nanodiamonds are able to transit into living cells because of their biological and chemical inertness [39], and their reduced size. Therefore, fluorescent nanodiamonds containing NV centres have been proposed as bio-markers. Combined with the fact that they are photostable emitters, NV centres can be optically detected within living cells. Either in addition with magnetic field measurements or as a stand-alone tool, these nanodiamonds can be tracked in 3D as they travel within living cells [8]. Recently, in addition to tracking nanodiamonds, quantum coherence measurements as well as monitoring of the orientation of single NVs has been conducted in living human HeLa cells [35].

In this regard, the SiV centre is holding even greater potential than the NV centre. Its ZPL at 739 nm is within the near-infrared window of biological tissues. This is a regime of low-absorption in comparison to other optical wavelengths (Figure 2.6). This makes the SiV a favourable system that has great promise for biological applications, with some preliminary investigations recently conducted in neural precursor cells [87].

In Section 1.1, we briefly outlined our overall objective of trapping nanodiamonds hosting SiV centres via addressing their ZPL dipole. Combining the fact that the ZPL is within the near infrared biological window and that the groundwork for intercellular nanoscale magnetic field measurements has been developed, it is feasible to devise an experiment taking advantage of this. If a nanodiamond could be fabricated to contain a high concentration of SiVs and only a single NV, it could act as a nanoscale magnetic field sensor whose position within a living cell could be manipulated as desired. The premise of such an experiment should act as a strong motivation to pursue this idea in future research.

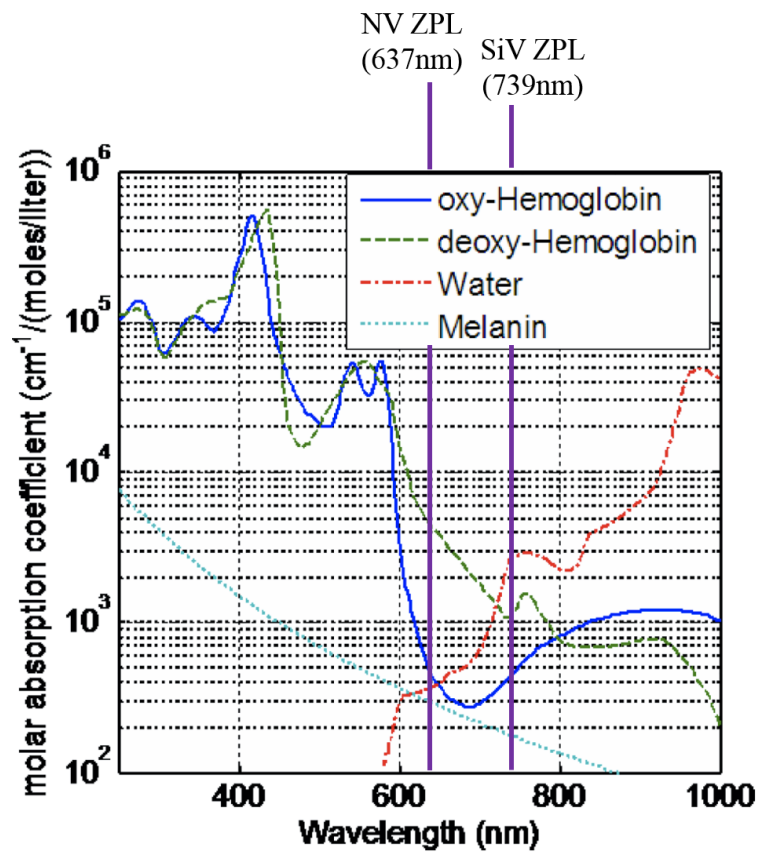


Figure 2.6: Molar absorption coefficients as a function of wavelength for **common biological substances** [88]. Two components of blood, oxy-hemoglobin and deoxy-hemoglobin, are shown, as well as melanin, a component of the skin, and water. The positions of the respective NV and SiV ZPLs are marked and correspond to regions of low molar absorption in oxy-hemoglobin and deoxy-hemoglobin.

3

Diamond Synthesis & the Incorporation of Colour Centres

“You will not believe me even when I tell you, so it is fairly safe to tell you. And it will be a comfort to tell someone. I really have a big business in hand, a very big business. But there are troubles just now. The fact is... I make diamonds.”

H. G. Wells, The Diamond Maker

In this chapter methods of diamond synthesis including high pressure high temperature, chemical vapour deposition and detonation are reviewed. Further to this, methods used to incorporate colour centres in diamond material are also discussed in addition to the presentation of a method to mill diamond material down to nanoscale particles.

3.1 Introduction to Diamond Synthesis

The scientific progress leading to the artificial synthesis of diamond spanned over 250 years, developed by many small steps and often with large periods without any advancement being made. Once it was realised that diamond is composed purely of Carbon [89], effort was put into the development of methods to artificially mimic the conditions of high pressure and high temperature under which diamond is formed in nature. These conditions happen to be found beneath the surface of the Earth between 150 km and 200 km below the crust [90].

3.1.1 High Temperature High Pressure

The High Pressure High Temperature method, abbreviated HPHT, is based upon the phase transition of carbon from graphite to diamond. This transition takes place at pressures above 5 GPa, and temperatures above 1500 °C (Figure 3.1). The first phase diagram of Carbon

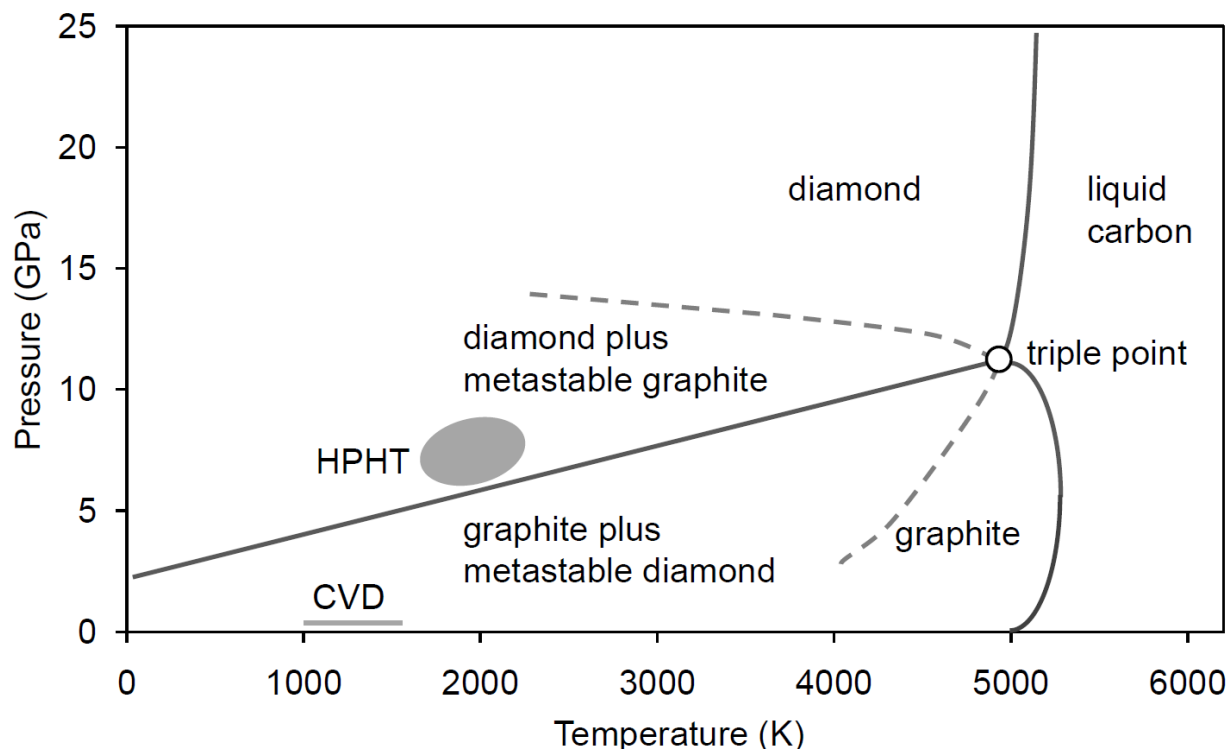


Figure 3.1: **Phase diagram of carbon.** The regions for HPHT and CVD diamond synthesis are marked [58].

was compiled in 1938 [91] and was constructive to the development of diamond synthesis techniques.

This was first achieved in 1953 and since then multiple technologies for HPHT diamond synthesis have been born [92–94]. Anvils exert pressure on a core reaction cell, which is also being heated. Carbon containing materials are placed inside the reaction cell. The cell also contains a solvent metal, typically iron or nickel, and a high-purity carbon source, typically graphite. The solvent metal acts as a transport agent for the dissolved carbon in order to reach the seed diamonds and also reduces the required minimum external pressure for reaching the target conditions.

The HPHT process is still used in industry today, due to its low cost and relatively high throughput. However, it does not allow for much customisation in the synthesis process. In 2005, half a century after the HPHT method was invented, another method of diamond synthesis that could produce large single crystal diamonds became popular: chemical vapour deposition [95].

3.1.2 Chemical Vapour Deposition

The chemical vapour deposition method, abbreviated CVD, allows for a high level of control and hence customisation over the growth process of artificial diamonds. The CVD method became popular in 2005 because of its ability to produce large single crystal diamonds.

In the early days of CVD synthesis, the method suffered from slow growth rates, though over time, both the understanding of the growth dynamics and of the synthesis techniques were improved [96–99], and in 1981 the CVD method could achieve growth rates of up to $1\text{ }\mu\text{m/hour}$.

In contrast to the HPHT method, the CVD method takes place at a much lower pressure, and a slightly lower temperature — therefore occurring in a separate region of the carbon phase diagram (Figure 3.1). CVD diamonds are grown on a substrate with the carbon atoms provided via a hydrocarbon gas, typically methane (CH_4). The process takes place inside a reaction chamber, where temperature and pressure are controlled. The substrate for the diamond growth (typically silicon, quartz, sapphire or iridium), is seeded with nanodiamonds. The prepared substrate is placed inside the reactor and the chamber’s pressure reduced to around 10 Torr. A mixture of gas is pumped into the chamber, including methane (CH_4), hydrogen (H_2) and oxygen (O_2). The methane acts as the source of the carbon atoms required for synthesising the diamond; the hydrogen and oxygen facilitate the etching of the graphite that tends to form around the core diamond during the process. The gases are then heated either via a hot filament or a microwave source. Once the gases reach $800\text{ }^\circ\text{C}$, they ionise into free radicals, and a plasma is formed above the substrate. Inside the plasma, the free radicals recombine and begin to form diamond around the nanodiamond seeds. As the process continues, the diamond growth spreads and coalesces to form a diamond film across the substrate.

A schematic of a microwave-assisted CVD reactor is shown in Figure 3.2. The diamond samples used in this thesis were grown at the OptoFab node of the Australian National Fabrication Facility which operates a Seki A5250 CVD reactor, shown in Figure 3.3a, with corresponding hardware shown in Figure 3.3b. In this particular setup, the substrate holder can be swapped out to be either a ‘heating’ stage or a ‘cooling’ stage, allowing for a slight change in the growth conditions.

3.1.3 Detonation

The formation of diamond by detonation was first observed in 1961, but reached great popularity only in very recent years [101, 102]. The premise is to detonate explosives, which contain carbon in their reactants in a chamber with an inert material, such as water or argon. The detonation of the explosives generates high pressure and high temperature within the chamber, generating the right conditions for carbon to form diamond. These conditions are reached only for less than a microsecond as the shock wave passes. The result is the formation of diamond nanocrystals, and due to the short duration which the growth conditions exist, the formed nanodiamonds display a very narrow size distribution. The nanodiamonds synthesised by this method, known as detonation nanodiamonds, are typically around 5 nm in size and no bigger than 10 nm .

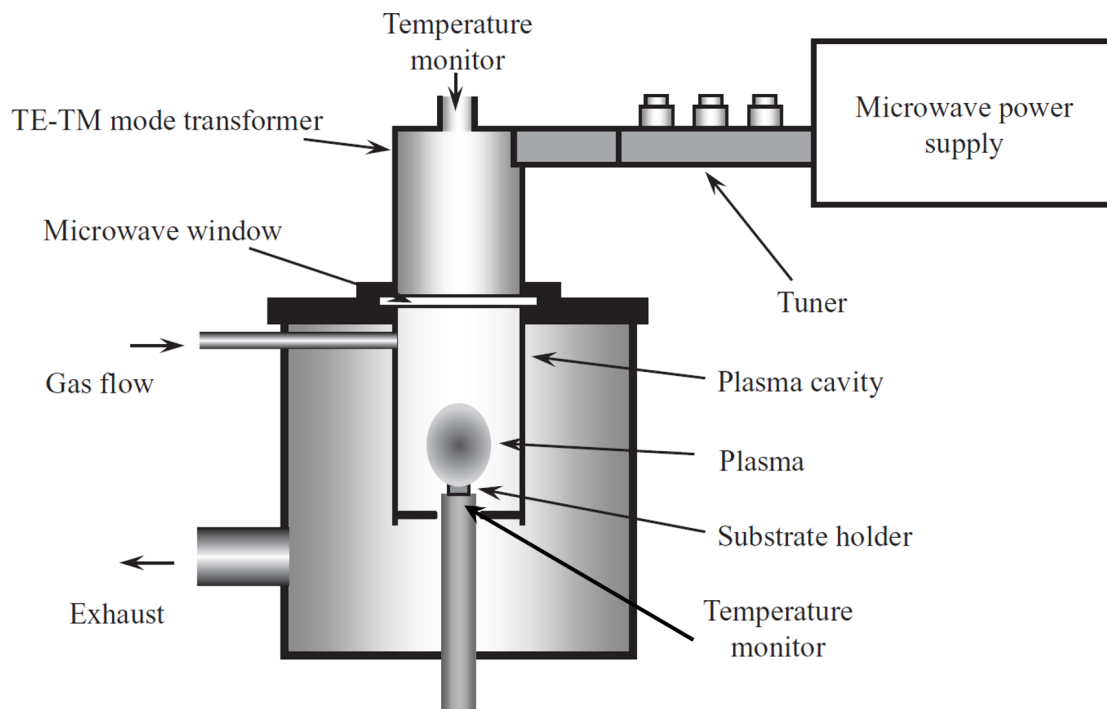


Figure 3.2: **Schematic diagram of a microwave-assisted CVD reactor**, adapted from [100]. A plasma is shown inside the reactor, resulting in diamond growth on the substrate.

3.1.4 Other Methods

There are numerous other methods of artificial diamond synthesis including laser ablation [103], autoclave synthesis from supercritical fluids [104], chlorination of carbides [105], ion irradiation of graphite [106], electron irradiation of carbon onions [107] and ultrasound cavitation [108]. High Temperature High Pressure, Chemical Vapour Deposition and Detonation still remain the mainstream methods of diamond synthesis due to the extensive research that has been put into those methods and the work that has gone into making them more efficient.

3.2 Incorporation of Colour Centres

As it is, the synthesis of diamond alone is only half the story of the process. Various methods for enhancing the amount of colour centres present in diamond samples exist. The complexity of these methods varies widely, from relatively simple processes to ones requiring multiple steps and very elaborate procedures. We discuss a selection of the most relevant for this thesis.

3.2.1 Irradiation

Enhancement of colour centres via irradiation is carried out in conjunction with annealing [50]. One possibility involves focusing an electron beam onto the sample to bump carbon

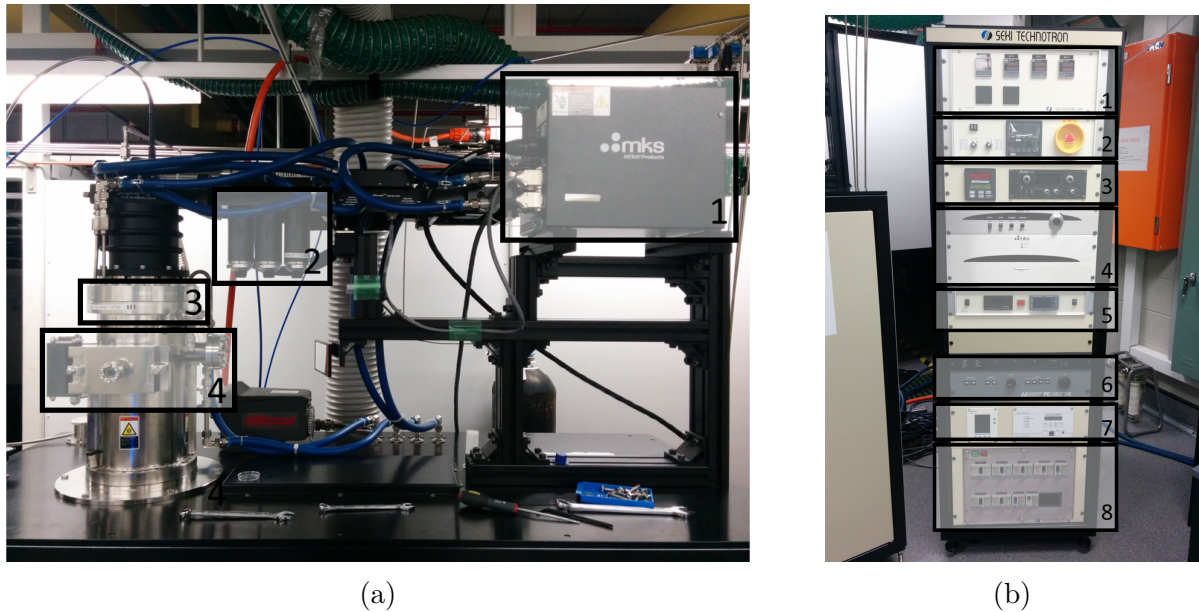


Figure 3.3: **CVD reactor.** (a) Seki A5250 CVD reactor operated by the OptoFab node of the Australian National Fabrication Facility on campus at Macquarie University. Several components are highlighted: **1:** 2.4 GHz 5 kW microwave source. **2:** Microwave tuners. **3:** Microwave window. **4:** Reaction chamber. (b) Drivers for the CVD reactor. **1:** Mass flow controllers readout and control, which govern the amount of gasses injected into the reaction chamber. **3:** Plasma temperature indicator and reaction chamber pressure readout and control. **4:** Microwave source readout and control.

atoms out of their sp^3 lattice position and create vacancies within the diamond lattice. For this method to be successful, the diamond sample must already contain the foreign atoms required for the targeted type of colour centre — typically nitrogen, for which this method is popularly used [109].

3.2.2 Ion Implantation

Used in conjunction with annealing [110], this method implants foreign atoms into the diamond lattice [111–113]. Ions are accelerated and bombard the host matrix, becoming implanted at depths dependent on the acceleration energy. Subsequent annealing favours the generation of colour centres [114, 115]. The method also allows for both the density and locations of implanted ions to be controlled to a certain degree [115, 116] — an advantage which has been used to create the first single SiV centres in diamond [33]. Atoms that have been successfully incorporated in the diamond lattice via ion implantation include xenon, nickel, boron and silicon [117–120]. Due to the ability to create an abundance of silicon atoms in the CVD growth process, and their affinity to be incorporated in the diamond lattice, the CVD growth method is usually preferred for the inclusion of SiV centres in diamond.

3.2.3 Incorporation via CVD Growth

The inclusion of colour centres via the CVD growth method is undertaken by introducing the desired dopant into the reaction chamber where the diamond is grown. This can be achieved by either choosing the appropriate substrate or by introducing a dopant into the reaction chamber. For NVs the inclusion occurs because of the abundance of nitrogen in the atmosphere — even though the CVD reaction chamber is reduced to low pressure there is enough residual nitrogen remaining inside the chamber to result in NV colour centre formation [109]. Note that the parameters inside the reactor can be controlled to manipulate to concentration of NVs generated [121]. In the case of SiVs, the source of the silicon atoms is the etching of the silicon substrate by the plasma in the reaction chamber [122, 123] or the etching of the quartz walls of the CVD reaction chamber [124] (again, the parameters can be controlled to reduce the chance of this occurrence). Hence, the use of a silicon substrate in CVD diamond synthesis will readily result in the creation of SiV colour centres. SiVs incorporated in diamond via this method predominantly form as complete units [64], however for NVs this is not the case and the concentration is commonly enhanced via the migration of vacancies by annealing.

3.2.4 Bottom-up Approach

Recently, a new method for incorporating previously unseen colour centres in diamond has been reported. The method utilises a ‘bottom-up’ approach to include europium colour centres in both bulk diamond and nanodiamonds [125]. Lanthanides such as europium have unique spin-optical properties, including narrow optical transitions and long spin coherence times. These make them good candidates for quantum information processing and quantum metrology. Simulations indicate that europium vacancy defects would be able to form inside the diamond lattice, however attempts to force europium atoms into the lattice via ion implantation were unsuccessful. A bottom-up method was then developed that would preserve the atomic transition of the europium atom. Bulk diamond, and later nanodiamonds, are first oxidised to create a negatively charged surface. A positively charged polymer (polyallylamine hydrochloride) is then assembled on the surface, which is subsequently treated with a europium complex (tri-(2,6-pyridine dicarboxylic acid)). The bulk diamond (or nanodiamond) is then placed in a CVD reactor and diamond growth conditions generated. The method was successful in creating europium vacancies within the diamond lattice and maintaining the atomic transitions of the europium atom (Figure 3.4).

3.2.5 Annealing

Annealing is the process of heating a diamond sample in vacuum, resulting in the mobilisation of vacancies within the diamond lattice. Once above $\sim 850^\circ\text{C}$, vacancies become mobile in the lattice [126], diffusing through the host matrix. This is a desirable effect as when a vacancy arrives at a site where it can form a colour centre, i.e. adjacent to a nitrogen or silicon atom, it is energetically favourable for the vacancy to form colour centres such as NVs [127] and likely SiVs. The process has the desired effect of enhancing the concentration of colour centres in the diamond sample.

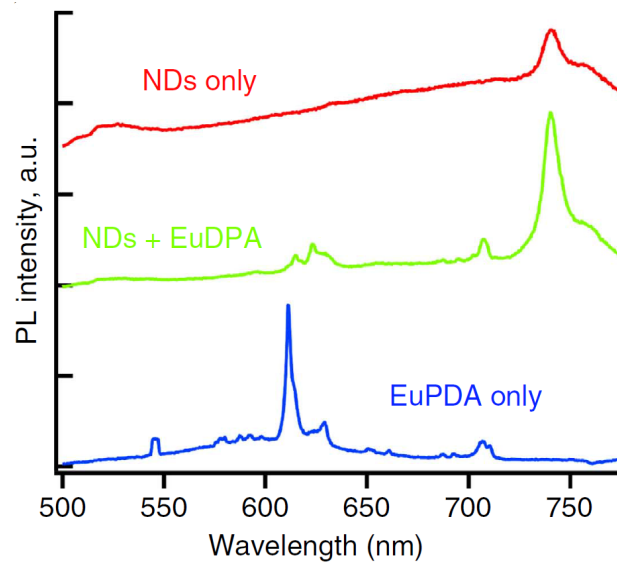


Figure 3.4: **Photoluminescence spectrum of nanodiamonds hosting europium vacancy complexes.** Successful inclusion of europium vacancy complexes in nanodiamonds via a bottom-up approach [125]. It can be observed that the optical transition of the Europium atom has been maintained.

3.3 Milling of Diamond to Nanodiamond

Nanoscale diamond materials, typically on the order of 100 nm, incorporate both diamond films and diamond particles. In this work, we have and will usually refer to nanoscale diamond particles as nanodiamonds. We aim to produce nanodiamonds containing a high concentration of SiV colour centres, as the resonant trapping effect for diamond nanoparticles containing SiV centres is proportional to the number of centres per single nanocrystal. For this to be achieved via the use of the facilities available to us, a diamond film was grown on a silicon substrate. The film was then milled to the desired size scale via the use of a planetary ball mill.

In order to produce nanodiamonds, one must either select a top-down or a bottom-up approach. The former method requires the conversion of diamond films or bulk diamond into nanodiamond, while the latter relies on the diamond being grown to the desired size. A top-down method was chosen for this research, drawing on available resources and expertise. The OptoFab node of the Australian National Fabrication Facility operates a Fritsch Pulverisette 7 planetary ball mill, which is used for our top-down approach. The milling machine has two separate counter-balanced canisters (Figure 3.5b) that operate simultaneously throughout the milling process. Each canister is filled with two components: the material which is to be milled, and the grinding balls which undertake the physical milling process.

The interaction between the material and the grinding balls is complex [128]. However, the underlying actions inside the chamber can be summarised as follows: the canisters rotate in opposite directions to the disk which they are sunken into, see Figure 3.5a, creating the

unique kinematics of the planetary ball mill. Via this movement, the sample is ground by impact, shearing and frictional forces resulting from ball-to-ball and ball-to-wall collisions, which are in turn a result of centrifugal and Coriolis forces generating the kinetic energy of the grinding balls [129]. Hardmetal tungsten carbide canisters and tungsten carbide (WC) grinding balls are used. As diamond has a hardness greater than that of WC, contamination of diamond samples prepared in this way with WC is expected [130].

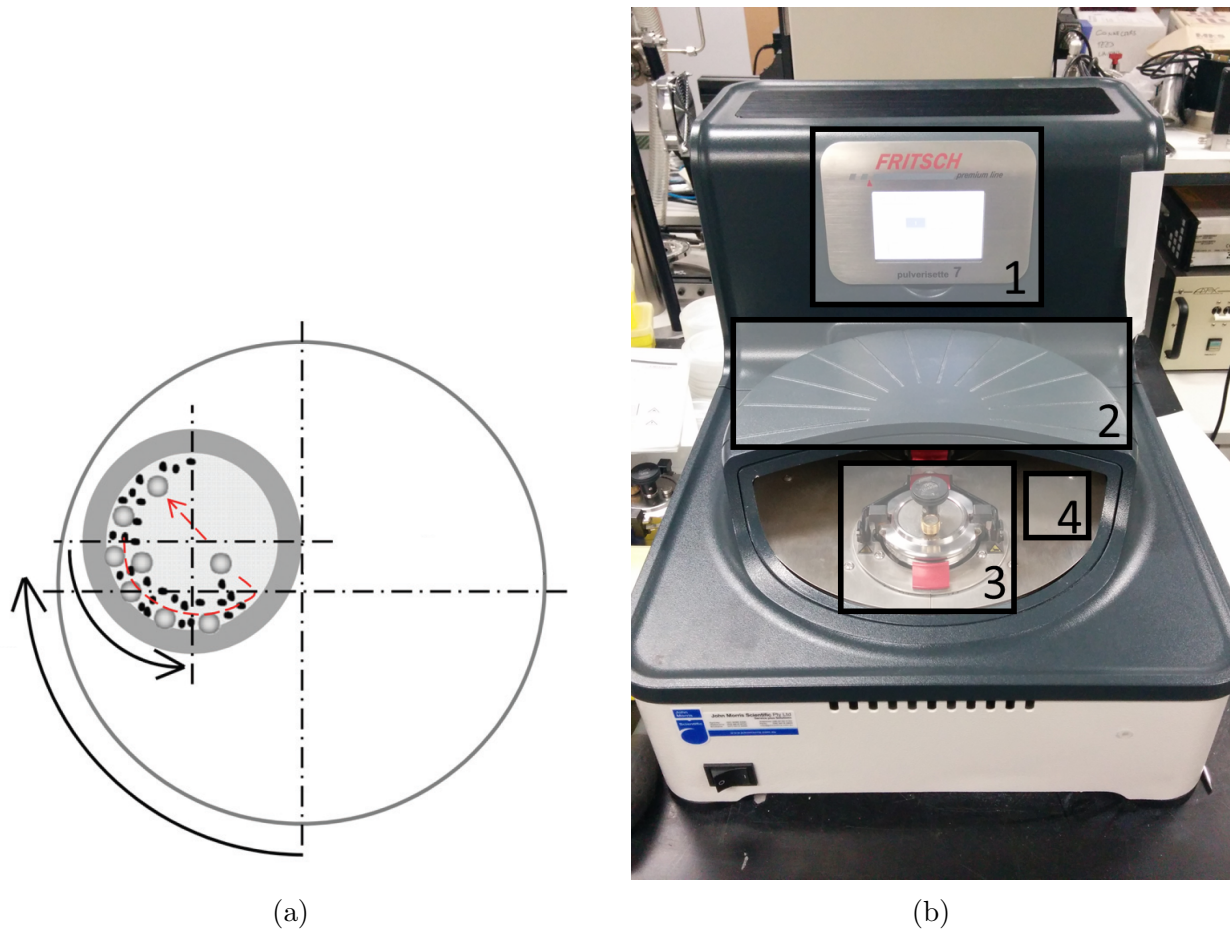


Figure 3.5: **Planetary ball milling machine.** (a) A top-down schematic of a milling chamber in a planetary ball mill, adapted from [131]. Black arrows indicate the motion of both the milling chamber and the sun disk, while the red dashed arrow indicates the motion of the milling balls and particulates being milled. (b) Fritsch Pulverisette 7 planetary ball mill operated by the OptoFab node of the Australian National Fabrication Facility, on campus at Macquarie University. Several components are highlighted; **1:** Touchscreen control panel for operation. **2:** Safety cover (retracted). **3:** Grinding canister (one of two). **4:** 'Sun' disk. The canisters rotate around the centre of the sun disk (hence 'planetary' ball mill), and in the opposite rotational direction.

4

Growth and Characterisation

“The true delight is in the finding out rather than in the knowing”

Isaac Asimov

This chapter summarises the results of our experimental efforts on diamond growth, milling and characterisation of nanodiamonds containing SiV centres. I present the fabrication process of two separate samples, **Sample A** and **Sample B**. Between these two cases, the seeding process, growth conditions and growth durations were altered and the milling of **Sample A** undertaken.

For **Sample A** our aim was to fabricate nanodiamonds on the order of 100 nm containing a high concentration of SiV colour centres — this was done to establish a reliable protocol for future work and diamond synthesis. In the case of **Sample B** our aim was to fabricate nanodiamonds from a sample prepared under a different set of growth conditions — however, due to delays this sample was unable to be milled. We analyse the effectiveness of each step and, where necessary, comment on options whereby the chosen path could be improved. We utilise the facilities discussed in Chapter 3: Seki A5250 CVD reactor and Fritsch Pulverisette 7 planetary ball mill, in addition to a NT-MDT Ntegra Atomic Force Microscope (AFM) combined with a lab-built confocal microscopy setup.

4.1 Substrate Preparation

Our aim is to fabricate ‘bright’ nanodiamond samples, containing many fluorescent SiV centres. Growing diamond material on a Silicon substrate via CVD is known to be one of the most efficient ways of incorporating SiV centres in diamond film due to plasma etching of the substrate [122]. We use a silicon wafer (1 inch diameter) as the substrate, which provides an abundance of silicon atoms (see Section 3.2.3). Prior to seeding, both silicon wafers were cleaned with acetone. To characterise the surface of the substrate, an AFM scan of the

surface was taken (Figure 4.1). The measurement reveals that there exists some curvature extending radially in the wafer, though we note that there is a minimal 500 nm rise over 40 μm of wafer. We also see that there are small feature on the surface of the substrate on the order of 50 nm, which are however negligible with respect to the diamond growth process.

The cleaned substrates were then seeded with 4-nm detonation nanodiamonds — these act as seeds over which new diamond material growth can take place. The same high-concentration seeding solution of detonation nanodiamond in water has been used for both **Sample A** and **Sample B**. In the case of **Sample A**, the sample was spin-coated. The seeding solution was first sonicated for 10 minutes, then 20- μL of solution was pipetted onto the substrate. A 20- μL solution of detonation nanodiamond in water was pipetted onto the the centre of the substrate surface. The substrate was then secured and spun at 1200 rpm for 30 seconds. This produced a spiral pattern on the surface of the substrate (Figure 4.2a). We decided to exploit this unusual surface pattern to investigate the diamond growth both in the seeded and unseeded regions.

In the case of **Sample B**, different substrate preparation procedures were followed. Again the seeding solution was sonicated for 10 minutes and 20- μL of it were placed onto the substrate but, this time, left to dry at an angle (Figure 4.2b). The solution deposited on the substrate did not spread uniformly, showing regions with a greater concentration of deposited nanodiamonds than others. It is straightforward to identify the region of the substrate which is seeded with the nanodiamond particles.

To verify the size of the seed detonation nanodiamonds an AFM scan of a seeded silicon substrate was undertaken. The data shows that prior to spin coating the seed nanodiamond had agglomerated into ~ 15 -nm clusters. The agglomeration however, can be assumed inconsequential for the growth of a diamond film as this is on the order of microns.

4.1.1 Growth Conditions

To investigate the influence of the temperature of the substrate on the growth of the diamond film, heating and cooling stages were used within the CVD reactor. For **Sample A** a cooling stage was used to decrease the temperature of the substrate. Conversely, for **Sample B** a heating stage was used, to raise the temperature of the substrate.

Once the substrate was placed in the CVD reaction chamber, the pressure was reduced by a system of vacuum pumps. Once the decreased pressure was achieved, the system was ramped up and the plasma reaction was initiated by the generated microwaves (Section 3.1.2). The procedure that leads to the formation of the plasma spans for approximately 20 minutes; the specific details can be found in Appendix A. The effect of using the two different stages is to investigate their respective effects on the growth rate of diamond material within the reactor in different conditions.

Along with the type of stage, the key contributing factors that will have the most influence on the thickness of the film produced are i) the percentage of CH_4 in H_2 of the gas mix, ii) the growth duration and iii) the temperature of the substrate (this being directly influenced by the utilised stage). These key growth conditions are listed in Table 4.1.

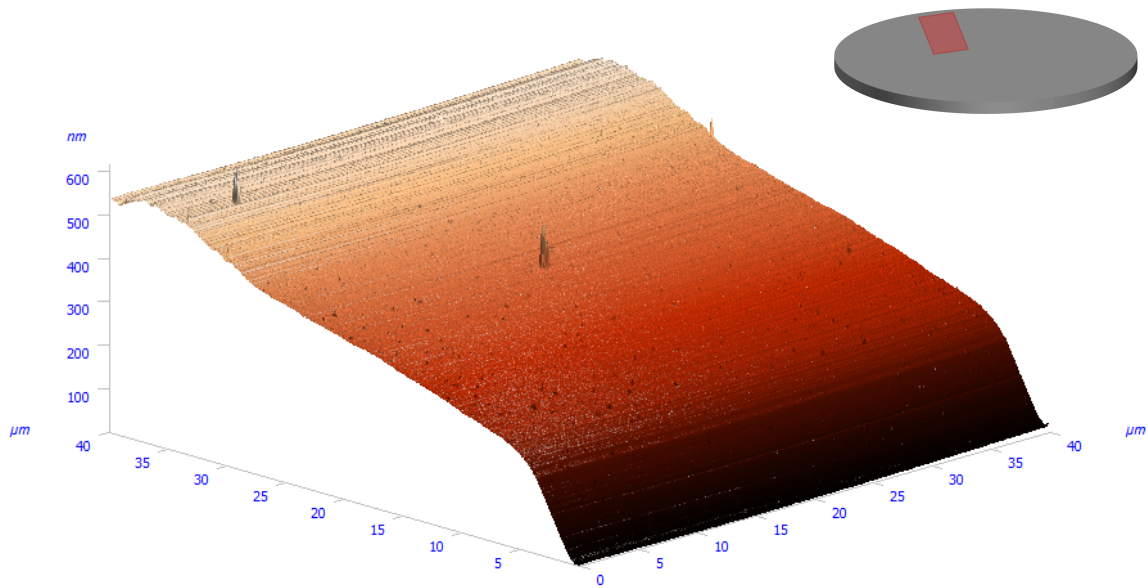
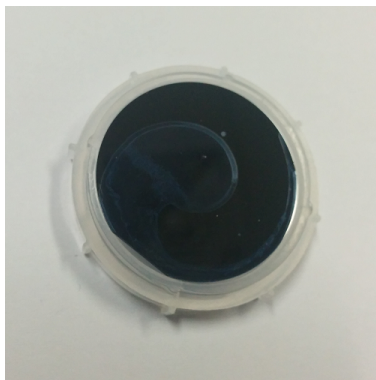
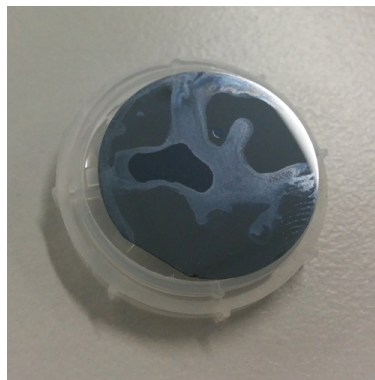


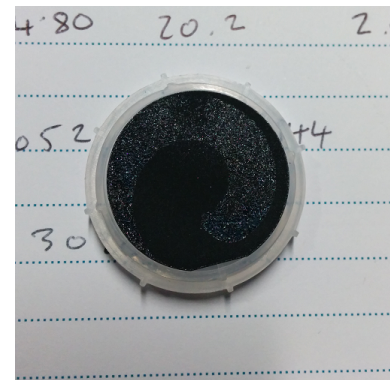
Figure 4.1: **AFM scan of a silicon wafer substrate.** A slight curvature of the substrate surface of 500 nm over 40 μm and features on the surface on the order of 50 nm are noticeable. The inset sketch of a silicon wafer shows the not-to-scale approximate region of the AFM scan. The curvature extends radially, increasing from the centre outward. Lines running along the gradient of the substrate are an artefact of the scan data.



(a)



(b)



(c)

Figure 4.2: **Substrate preparation.** Seeded substrates of Sample A and Sample B. (a) Sample A substrate seeded by spin coating 20 μL of detonation nanodiamond solution at 1200 rpm for 30 seconds. (b) Sample B substrate where 20 μL of detonation nanodiamond solution was dispersed and left to dry at an angle. (c) Image recorded of Sample A after diamond growth. We can observe that the region where the substrate was seeded has resulted in a greater diamond growth when compared to that of the unseeded region.

Table 4.1: Key conditions relating to the growth rates of **Sample A** and **Sample B**.

	Sample A	Sample B
Deposition duration	75 hours	48 hours
Type of stage	Cooling	Heating
Substrate temperature	144 °C	519 °C
CH ₄ in H ₂	4.2 %	4.2 %

4.1.2 Surface Characterisation & Treatment

Utilising the growth conditions in Table 4.1 we were able to fabricate diamond films (Figure 4.2c). We observe that the spiral pattern from the seeding process remained, hence displaying two well-separate regions of grown diamond material. The region of substrate that was seeded yielded a uniform growth, in contrast with the unseeded region which shows a non-uniform diamond growth. This peculiarity motivated us to conduct a more detailed analysis via the use of a scanning electron microscope (SEM).

The SEM analysis revealed some interesting properties about the growth of **Sample A**. First, we examine the seeded region (Figure 4.3a). We see that the seeding and growth conditions have resulted in the growth of a polycrystalline diamond film. Within the polycrystalline film we also observe that fractures have formed (Figure 4.3b). We believe that this is a result of the strain induced by the lattice mismatch between the growing diamond and the silicon substrate — specifically, the fractures appear as the diamond film relaxes after growth. In latter stages of the nanodiamond fabrication process the ‘film fracturing’ became a desirable feature; we will revisit this in due course (Section 4.1.3).

At the boundary between the seeded and unseeded regions, a striking difference is noticeable (Figure 4.3c & Figure 4.3d). The polycrystalline film that has grown over the seeded region of the substrate quickly degrades into an agglomeration of large diamond granules at the boundary of the unseeded region. It is likely that during the spin coating process, some seed nanodiamonds broke free from the body of water solution and scattered out of the seeded region, likely with some density gradient. The nanodiamonds, now separated by much larger distances than those within the seeded region act as well-isolated seeds for the diamond growth. As the reactions continue within the chamber, diamond material in the unseeded region takes longer to coalesce with its nearest neighbours, resulting in the large diamond granules that we see (Figure 4.3c & Figure 4.3d).

In areas of the unseeded region hence, we observe isolated diamond crystal structures of various sizes (Figure 4.3e & Figure 4.3f). The sizes of these crystals span from less than 10 μm to well over 100 μm . The various sizes of the isolated diamond crystals suggests different growth rates. We infer that these isolated diamond crystals are the result of diamond material being scattered over the substrate during the deposition process, becoming themselves new seeds at random times during growth.

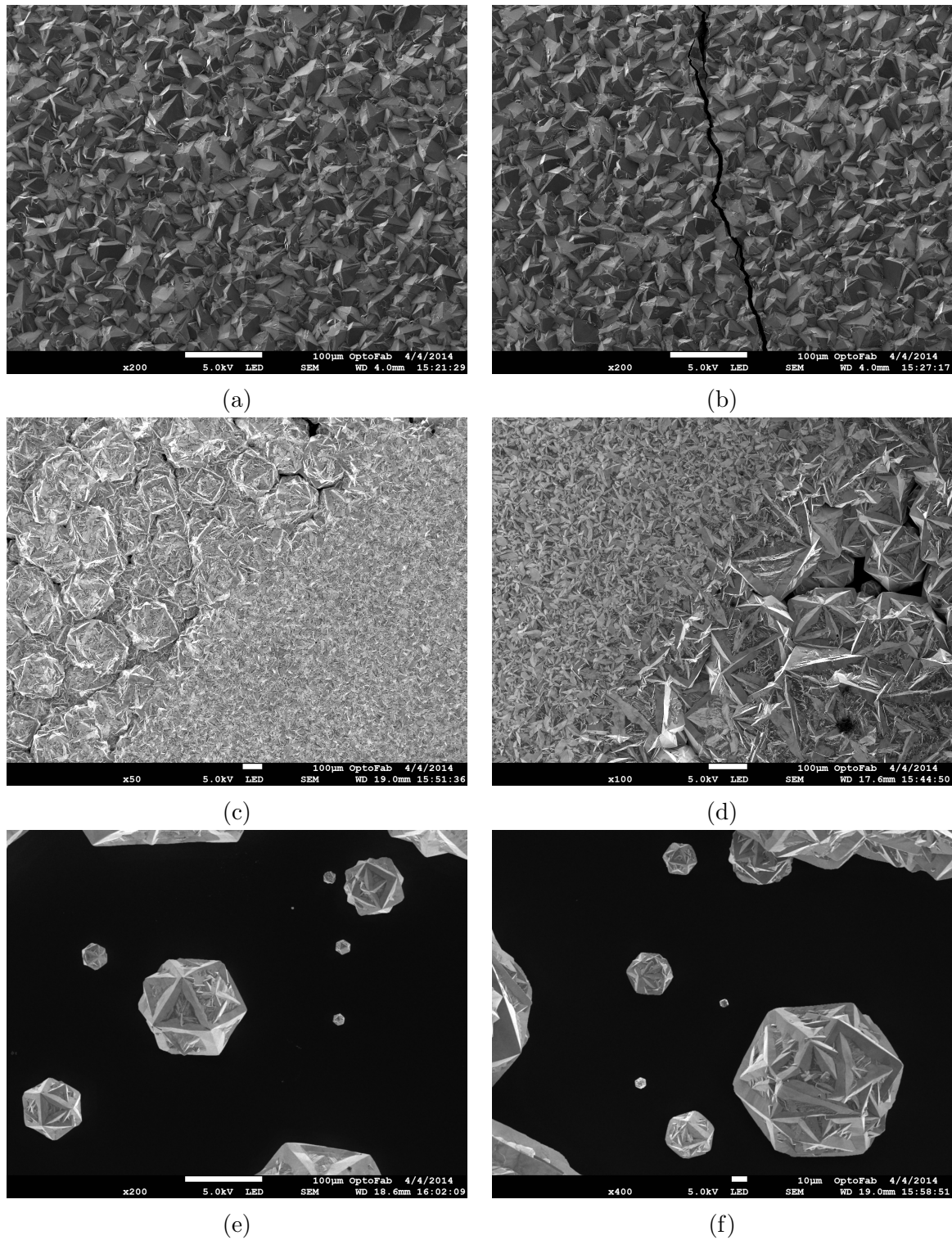


Figure 4.3: **SEM sample characterisation.** SEM images of Sample A. (a) Polycrystalline diamond film that has grown on the seeded region of the substrate. (b) A fracture that has formed in the polycrystalline film, likely due to different strains between the diamond lattice and the silicon substrate. (c, d) Boundaries of the seeded and unseeded regions, showing the transition from polycrystalline growth to large agglomerates that have taken a longer time to coalesce. (e, f) Isolated diamond crystals of various sizes.

The surface of **Sample A** was then characterised via Raman spectroscopy (Figure 4.4). The diamond peak can be seen at 1332 cm^{-1} , along with another small peak at $\sim 1530\text{ cm}^{-1}$. This latter feature corresponds to the approximate location of the G-band, indicating the presence of a layer of graphite over the diamond sample [37]. To remove this graphite layer, the sample was air-oxidised at 600°C for 10 minutes. Air oxidation has been shown to reduce the size of nanodiamonds by removing carbon atoms from their surface [132]. The air-oxidisation process would remove the sp^2 carbon layer first, and subsequently proceed with the removal of some sp^3 diamond carbon (the rate measured in HPHT nanodiamonds is $\sim(10\pm 1)\text{ nm/hr}$ at 600°C [132]). During the air-oxidisation process, carbon atoms (either sp^2 - or sp^3 -phase) bond with oxygen in the atmosphere, producing carbon dioxide (CO_2) and detaching from the surface. Raman spectroscopy subsequent to oxidation showed the reduction of the G-band, indicating that the air-oxidisation treatment was successful in the removal of graphite from the surface of **Sample A**. **Sample B** was air-oxidised as well, at 600°C for 10 minutes.

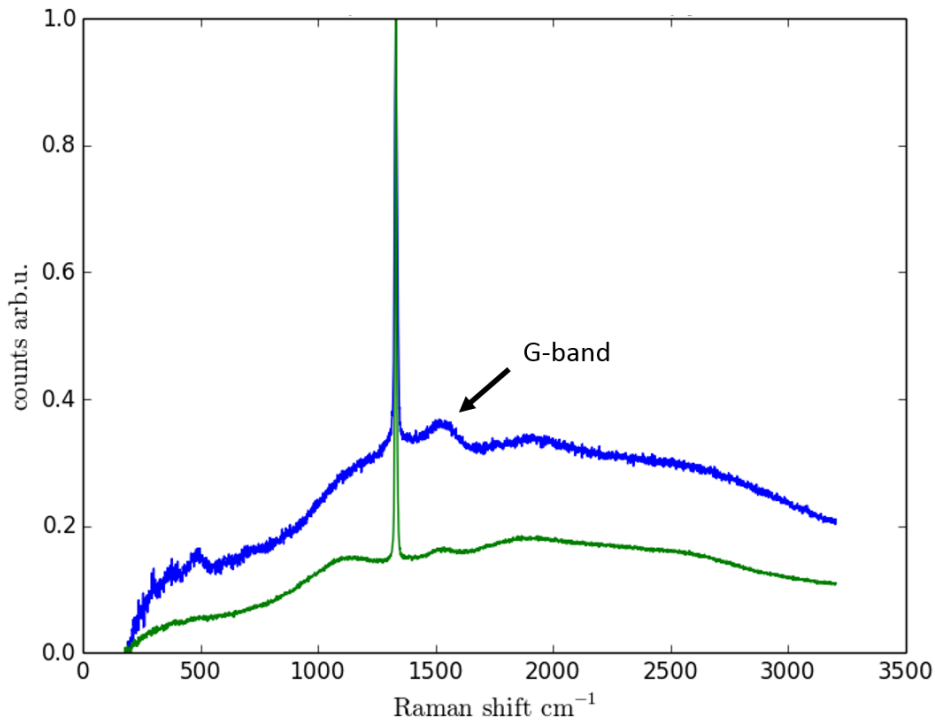


Figure 4.4: **Sample Raman spectroscopy.** Normalised Raman spectroscopy of **Sample A** before (blue) and after (green) air-oxidisation at 600°C for 10 minutes. The data has been normalised to the peak of the ZPL and a linear gradient has been subtracted from the fluorescence data to remove the background signal. The diamond peak at 1332 cm^{-1} is clearly observable and evidence of graphite on the surface is given by the presence of the characteristic G-band fluorescence at $\sim 1530\text{ cm}^{-1}$. After air-oxidisation the signal from the G-band is reduced as well as the overall background fluorescence of the sample.

4.1.3 Film Thickness

To quantify the thickness of the fabricated films a Veeco Wyko NT9800 Optical Profiler was used. Though for this measurement to be successful, a suitable ‘step’ between the substrate and the diamond film had to be found. In Figure 4.3 we observed fracturing of the diamond film of **Sample A** in the SEM investigation of the sample surface. We applied force to facilitate the fracture of the diamond film and separate it from the substrate surface, leaving areas where the step between the diamond and the substrate was clearly visible. In the case of **Sample A** this was achieved by utilising a razor blade and manually applying force between any large fractures that could be seen by eye. This task required multiple attempts due to the high strength of the diamond, though was successful in achieving the desired outcome. In the case of **Sample B**, the same method was followed, with the process being easier in this case. In fact, approximately one day after the sample was grown, the difference between the strain of the diamond film and the substrate was sufficient for the sample to fracture and for a large portion of the film to separate from the surface of the substrate. We attributed this to the different nature of the seeding process (Section 4.1.2) which encourages a sharper transition between seeded and unseeded areas on the substrate.

Once diamond flakes were separated from the substrate, areas where the fracture occurred were located and suitable substrate-diamond film steps identified. Measurements of the step height were then taken with the optical profiler and the film thickness determined (Table 4.2). From this information and the growth duration, we derived the samples growth rates assuming a linear growth as a first order approximation. The growth rates of **Sample A** and **Sample B** differ, which is attributed to the type of stage that was used within the CVD reactor. From the data, we derive that the cooling stage results in a faster growth rate than the heating stage. This is a result of the heating stage providing energy to the system — a slower but speculatively smoother growth is expected in contrast to using the cooling stage where no additional energy is added.

Table 4.2: Film thickness and growth rates of **Sample A** and **Sample B**.

	Sample A	Sample B
Film thickness	$(208 \pm 5) \mu\text{m}$	$(74 \pm 5) \mu\text{m}$
Growth rate	$(2.77 \pm 0.07) \mu\text{m/hr}$	$(1.54 \pm 0.09) \mu\text{m/hr}$

4.1.4 Milling

The sample was milled in a Fritsch Pulverisette 7 planetary ball mill as discussed in Chapter 3. A ‘dry’ milling method was employed in contrast to a ‘wet’ milling method (where the sample is milled in a water solution containing the grinding media) as the former allows for easier separation of the sample from the grinding media. A 20 –mL tungsten carbide (WC) milling chamber was selected, as WC ranks at 9 on the Mohs scale. Tungsten carbide balls of 1.0–mm diameter were selected as the grinding media (Glen Mills Inc. 7409-001000) to facilitate the milling of **Sample A** to nanoscale particles.

The milling chamber was packed with 80 g of grinding media and 85.3 mg of diamond material. As explained previously (Section 3.3) the mill contains two separate chambers

which must be balanced for safe operation. The second chamber was packed with 80 g of grinding media and 85.9 mg of aluminium oxide to balance the sun disk.

Care had to be taken to ensure that neither of the milling chambers exceeded 100 °C to reduce the risk of an explosion. Milling runs were limited to 5 minutes at 1100 rpm, and a lab-built cooling system including the use of a desk fan to cool the chambers after each run, was employed.

In between each milling run, a sample was taken for analysis. The milling chamber was opened and 15 milling balls of the grinding media removed. To maintain the weight of the chamber and hence balance the sun disk, whenever an amount of grinding media was removed, that same amount was replaced by new grinding media. The extracted grinding media was then placed into a vial and 1.5 mL of deionised water (Milli-Q) added. The vial was then sonicated for 60 minutes to detach diamond material from the surface of the grinding media. The sample was then pipetted into a new vial to separate the solution from the grinding media. The vial was then left to settle so that any large micron-sized particles would sediment to the bottom of the vial. The sample was typically left to settle for one day, then was once again pipetted into a new vial taking care not to transfer any sediment that had formed. The sample was then analysed using dynamic light scattering (DLS). For **Sample A** this process was repeated until DLS measurements (Malvern Instruments Zetasizer Nano ZS) indicated particle sizes of (120 ± 25) nm (Figure 4.5).

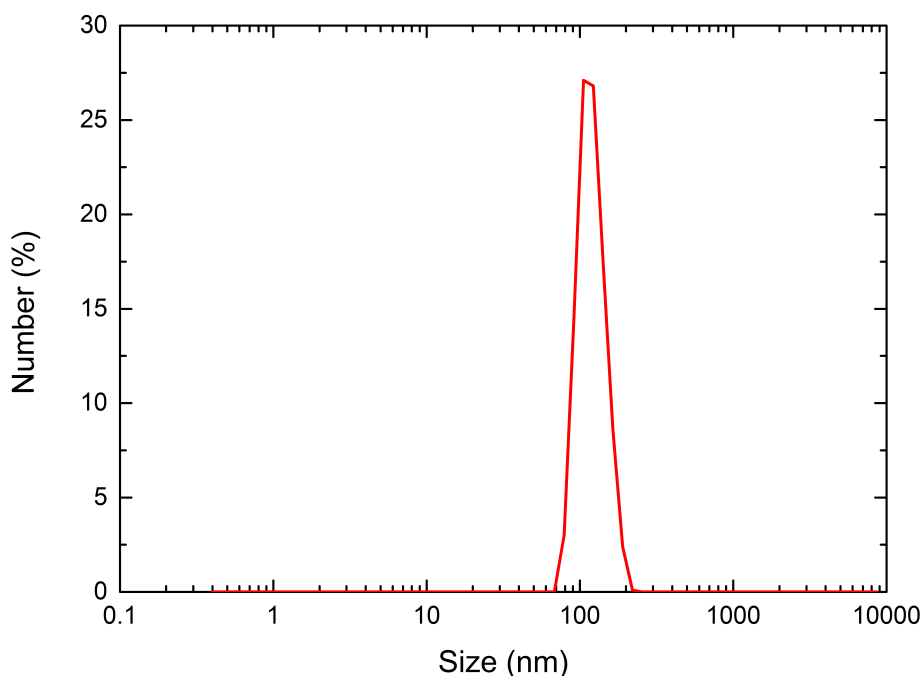


Figure 4.5: **Sample DLS measurement.** Dynamic light scattering (DLS) measurement of **Sample A**. Measurement data indicated a mean particle size of (120 ± 25) nm.

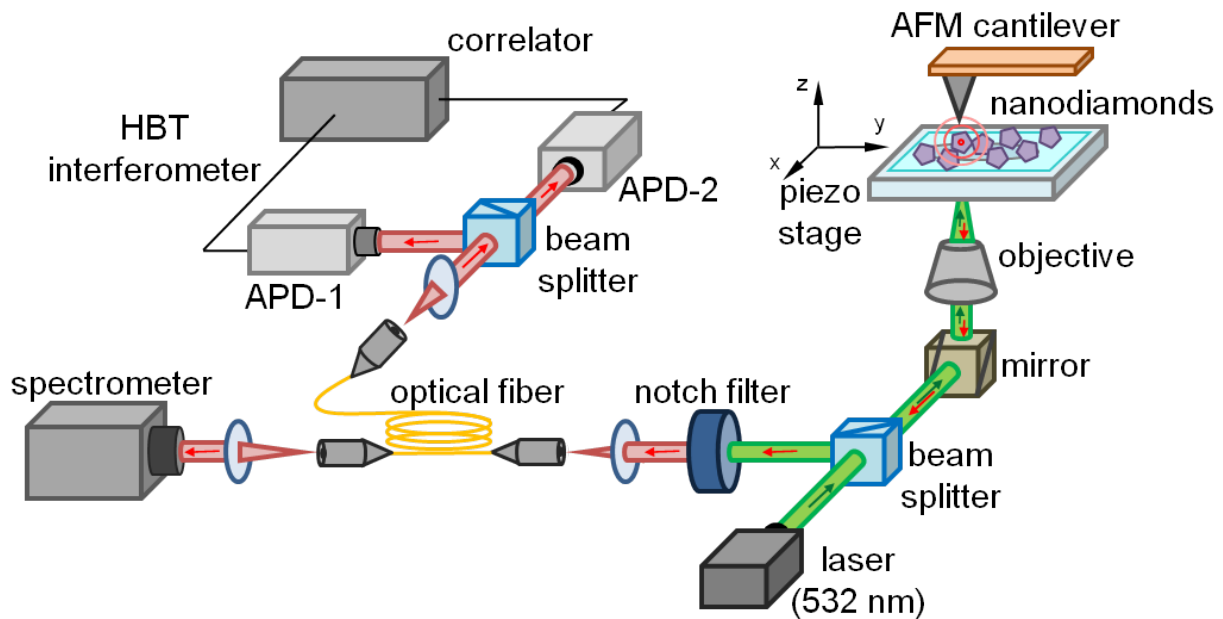


Figure 4.6: **Experimental setup.** A schematic representation of the combined confocal microscopy and atomic force microscopy setup adapted from [133]. A green laser is focused through the confocal setup onto the sample. The fluorescence from the nanodiamonds is collected by the microscope objective, filtered and directed to either a spectrometer or a Hanbury-Brown and Twiss (HBT) interferometer. An AFM above the sample measures the size of the diamond nanocrystals over the same region.

4.2 Nanodiamond Sample Characterisation

After the solution of nanodiamond in water was obtained as described above, the nanodiamond sample was characterised. This was achieved by the use of a lab-built setup (Figure 4.6). The configuration was originally designed to characterise NV containing nanodiamond samples, allowing for combined confocal microscopy and atomic force microscopy (AFM) to be undertaken. We utilised this setup, after making appropriate modifications, to take measurements of our nanodiamond samples containing SiV centres.

4.2.1 Sample Preparation

The sample was prepared in three steps. First, the solution was sonicated for 60 minutes to detach any aggregations of nanodiamond that had formed in the solution. Next, a $\sim 3 \mu\text{L}$ droplet of the solution was placed on a glass coverslip using a pipette. The coverslip was then heated at 50°C to evaporate the water, leaving behind the nanodiamonds on the coverslip. Once on the coverslip, the van der Waals forces are strong enough for the nanodiamonds to remain in place on the coverslip surface.

4.2.2 Confocal Microscopy

Once the sample was prepared, a combined confocal and high-resolution AFM scan was taken over a $40 \times 40 \mu\text{m}^2$ region (Figure 4.7). Fluorescence was clearly observed, and the spectra of several nanodiamonds recorded. The first observed fluorescence from a nanodiamond was fed into the spectrometer and showed the strong characteristic emission of SiV centres (Figure 4.8).

The spectra of 50 nanodiamonds was then recorded to build statistics for the ZPL location and its full width at half maximum (FWHM). The data was extracted by fitting a curve constructed of a Lorentzian and three Gaussians (Figure 4.8). The Lorentzian was fitted to the ZPL, while the Gaussians were fitted to other features of the spectrum. This data was used to build the histograms in Figure 4.9. The results are also summarised in Table 4.3.

The combined confocal and AFM setup is shown in Figure 4.6. A green laser beam (wavelength 532 nm, solid-state CW Compass 315M, 100 mW maximum output power) is focused through the confocal setup onto the sample (laser power measured at the sample $\sim 100 \mu\text{W}$). The sample of fluorescent diamond nanocrystals is placed on a transparent cover slip mounted on a piezoelectric stage. The fluorescence from the nanodiamonds is collected by the microscope objective, filtered (a notch filter is used to cut out the excitation wavelength) and directed to either a spectrometer or a Hanbury-Brown and Twiss (HBT) interferometer, where two avalanche photodiodes (APDs) work in coincidence to evaluate the second-order correlation function $g_2(f)$ revealing when required the presence of a single emitter (this was never the case in this experiment). An AFM above the sample measures the size of the diamond nanocrystals over the same region as the confocal scan.

4.2.3 Atomic Force Microscopy

The data from the combined confocal and high-resolution AFM scan (Figure 4.7) was analysed using a MATLAB script specially developed for this task. Approximately 200 nanodiamonds were examined and their height data recorded (Figure 4.11). The average crystal size determined to be $(162.5 \pm 22.3) \text{ nm}$ (Table 4.3). This value is greater than the $(120 \pm 25) \text{ nm}$ indicated by DLS measurements (Figure 4.5), however, is within the range of the uncertainties. Due to the sub-nanometer sensitivity of the AFM equipment this data is believed to be more reliable than the DLS measurement data.

Table 4.3: A summary of the key nanodiamond characterisation results of **Sample A**

	Sample A
Average location of the ZPL	$(739.1 \pm 0.8) \text{ nm}$
FWHM of the ZPL	$(12.8 \pm 3.1) \text{ nm}$
Crystal Size	$(162.5 \pm 22.3) \text{ nm}$

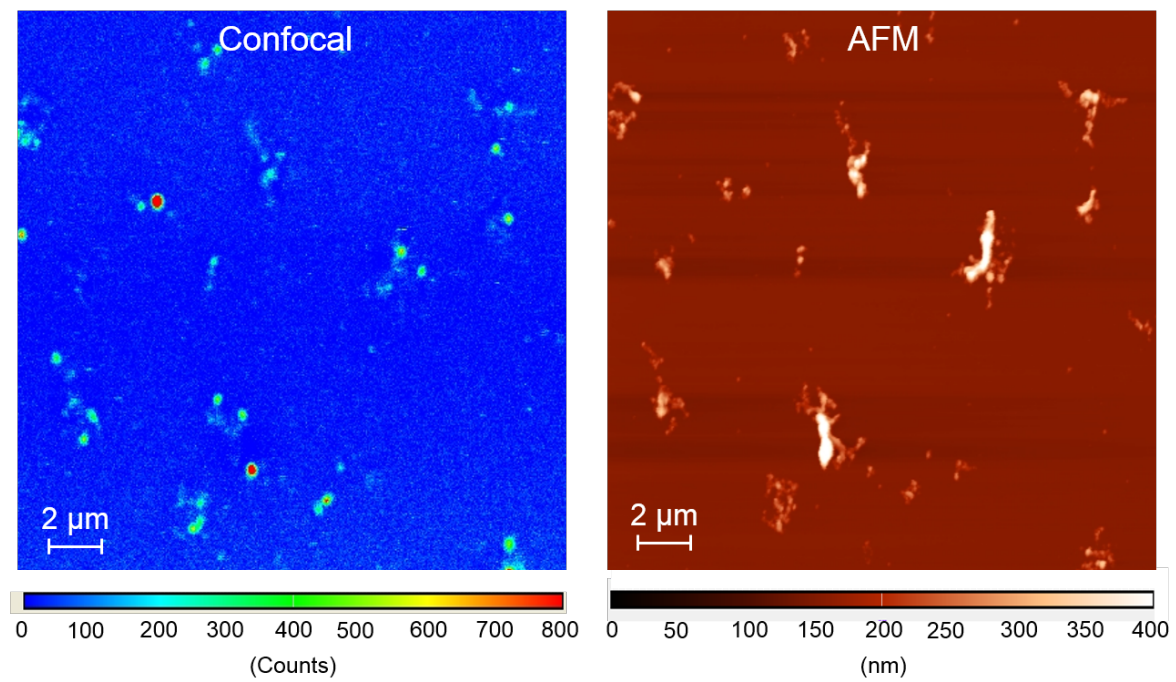


Figure 4.7: **Sample confocal and AFM measurements.** A region of the $40 \times 40 \mu\text{m}^2$ sample showing combined confocal and high-resolution AFM scans. The data shows that there are correlations between fluorescence from the confocal scan and features on the coverslip surface, indicating that the fluorescence is originating from nanodiamonds containing SiV centres.

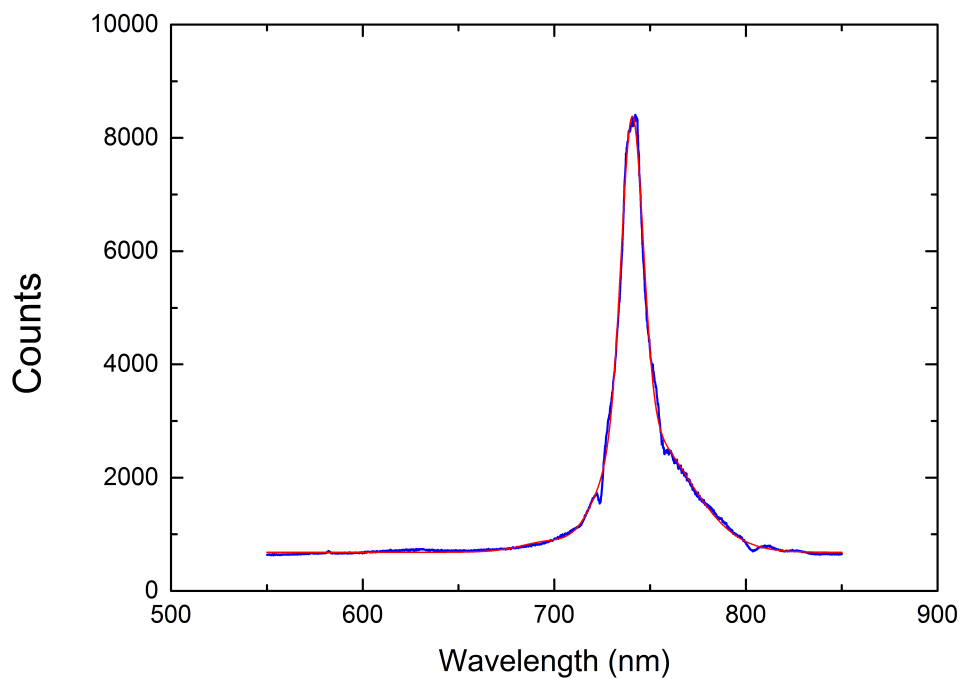
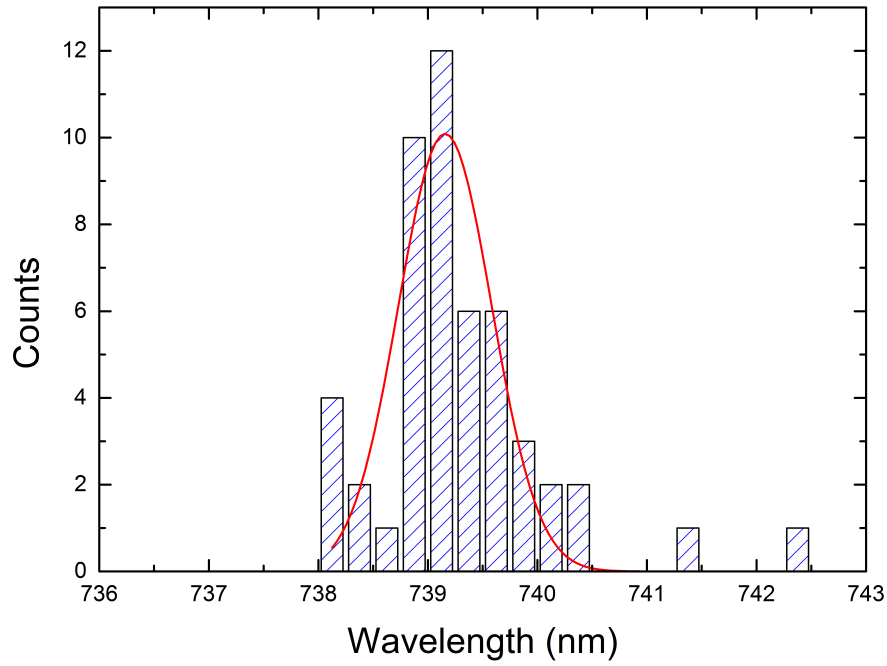
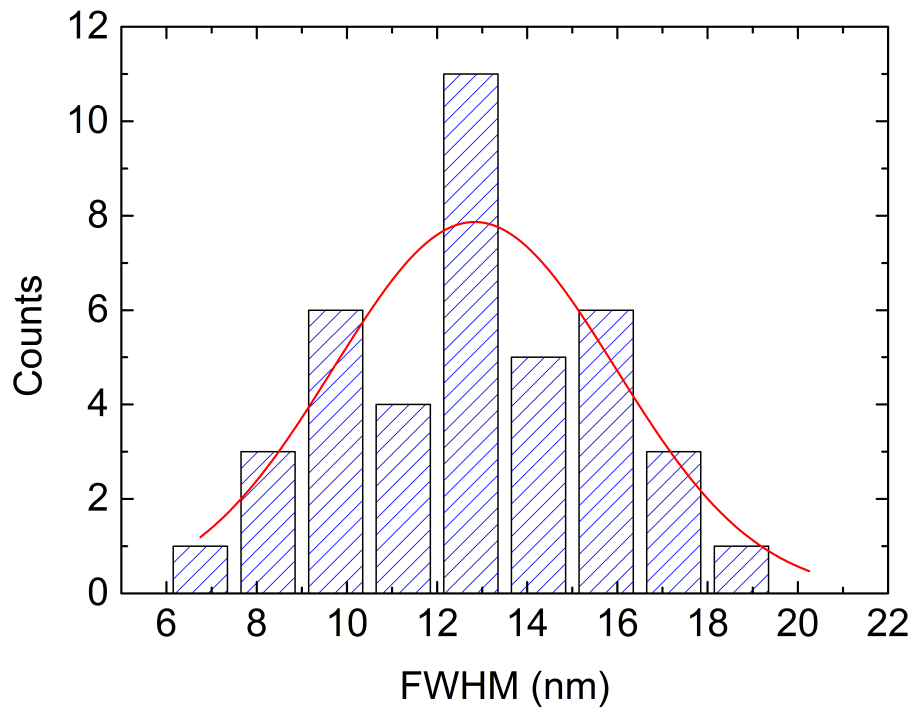


Figure 4.8: **Photoluminescence spectrum of the grown nanodiamond sample containing SiV centres.** Observed spectrum of SiV fluorescence from a nanodiamond prepared from **Sample A** (blue), with the ZPL located at 739 nm. A fit (red) comprising a Lorentzian and three Gaussians was applied to extract ZPL location and FWHM data.



(a)



(b)

Figure 4.9: **Sample ZPL characterisation.** Fluorescence characterisation data of Sample A recorded for ~ 50 nanodiamonds. (a) Location of the SiV centre ZPL — the peak of the fitted Gaussian is located at 739.1 nm. (b) Full width at half maximum of the ZPL fluorescence — the peak of the fitted Gaussian corresponds to 12.8 nm.

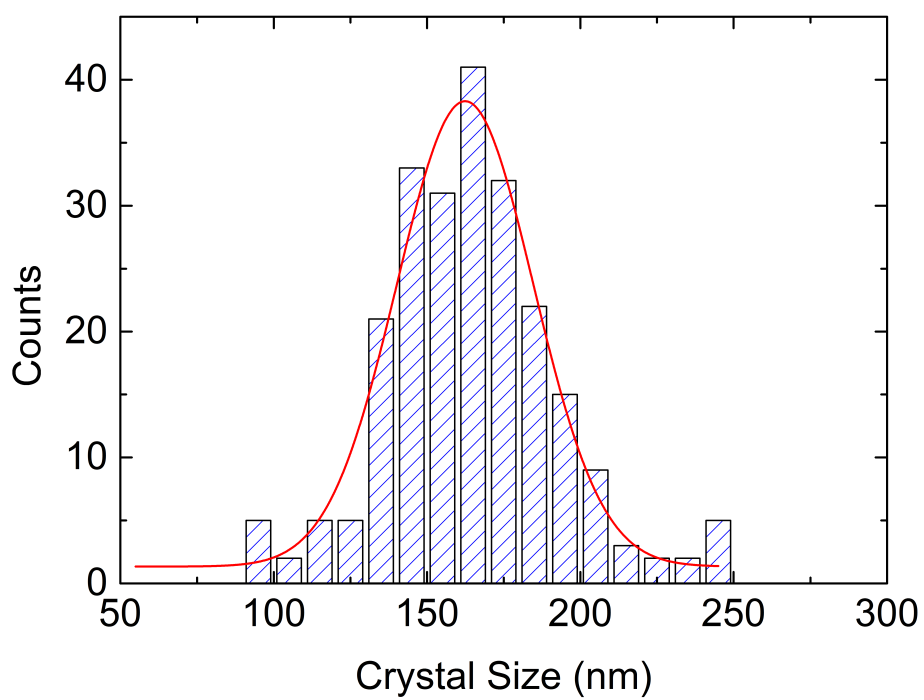


Figure 4.10

Figure 4.11: **Sample size measurement and characterisation.** Distribution of crystal sizes for **Sample A** — the peak of the fitted Gaussian corresponds to a crystal size of (162.5 ± 22.3) nm.

5

Optical Trapping of SiV Nanodiamonds

“If we knew what we were doing, it wouldn’t be called research, would it?”

Albert Einstein

In this chapter we use our in-house fabricated nanodiamonds containing SiV centres to investigate a novel regime of optical trapping: the combination of conventional optical tweezers with atomic dipole trapping. The SiV centre behaves as an artificial atom, therefore nanodiamonds containing many SiV centres are expected to exhibit a collective atom-trapping-like effect due to the SiV centres in the nanodiamond host. In the following chapter, we will refer to this additional effect as near-resonant optical trapping.

5.1 Background

In 1970 Ashkin observed that particles roughly $1\,\mu\text{m}$ in size could be trapped via laser light [134]. This resulted in the development of two distinct major research fields: optical tweezing of dielectric nanoparticles in liquid (predominantly in biological contexts) and dipole trapping of neutral atoms. Ever since, these fields have evolved independently. Classical optical tweezers rely on the bulk polarisability of micron- or nano-sized particles. The trapping strength depends on the refractive index contrast between the medium and the trapped particle. Using only conventional far-field optics, this limits the size of trapped nanodiamonds to $\sim 100\,\text{nm}$ [36]. Below this size limit the forces exerted are no longer strong enough to trap nanodiamonds efficiently.

Conversely, atomic dipole trapping is based on the near-resonant polarisability of single atoms [135]. The manipulation of neutral atoms using optical trapping has led to significant breakthroughs in quantum technologies such as atomic clocks, optical lattices and quantum simulation [136–138]. Here we combine the two regimes of optical trapping in one and the same system.

5.2 Theoretical Description

We first present a very brief discussion of the theoretical background behind optical trapping. We summarise the main ideas and formulas necessary to understand our experimental results.

Exposing a polarisable particle to laser light, i.e. to a time-varying electric field, induces a dipole moment which in turn is associated with a polarisation energy in the external field. Following the semiclassical treatment [139], we denote the expectation value of the induced dipole moment of the particle by $\langle D_\epsilon \rangle$ and write

$$\langle D_\epsilon \rangle = \epsilon_0 \alpha \mathbf{E} + c.c. \quad (5.1)$$

Here, α is the (complex) polarisability of the particle, which is directly related to its refractive index, and $\mathbf{E}$ is the time-varying electric-field vector. If the light field (or electric field) exhibits a spatial variation, the particle experiences a force of the form

$$\mathbf{F} = \langle D_\epsilon \rangle \nabla \mathbf{E}(\mathbf{r}, t) \quad (5.2)$$

If we substitute the complex value for the polarisability

$$\alpha = \alpha' + i\alpha'' \quad (5.3)$$

and write the electric field as

$$\mathbf{E}(\mathbf{r}, t) = \mathcal{E}(\mathbf{r}, t) + \mathcal{E}^*(\mathbf{r}, t) \quad (5.4)$$

with

$$\mathcal{E}(\mathbf{r}, t) = \frac{\mathbf{E}_0(\mathbf{r})}{2} e^{i\phi(\mathbf{r})} e^{-i\omega t} \quad (5.5)$$

we obtain the following expression for the force (with terms oscillating at twice the optical frequency are neglected)

$$\mathbf{F} = \epsilon_0 \alpha' \frac{\mathbf{E}_0}{2} \nabla \mathbf{E}_0(\mathbf{r}) - \epsilon_0 \alpha'' \frac{\mathbf{E}_0^2}{2} \nabla \phi(\mathbf{r}) \quad (5.6)$$

The first term is the so-called gradient or dipole force $\mathbf{F}_{grad}$, while the second term is called the scattering force $\mathbf{F}_{scat}$

$$\mathbf{F} = \mathbf{F}_{grad} + \mathbf{F}_{scat} \quad (5.7)$$

The gradient force results from the real part of the polarisability, whereas the scattering force is due to the imaginary or absorptive part of α . Due to the strongly damped motion of the particle in the liquid environment, we can safely neglect the influence of the scattering force for the rest of this chapter. The remaining dipole force can be written as the gradient of a conservative potential

$$\mathbf{F}_{grad} = -\nabla U_{grad} \quad (5.8)$$

5.2.1 Classical Approach

Without going into details, we simply state the expression for the classical dipole potential, U_{cl} , for a nanosized particle trapped in a Gaussian beam [140]

$$U_{cl} = \frac{2\pi n_m R^3}{c} \left(\frac{m^2 - 1}{m^2 + 2} \right) \frac{2P}{\pi w_0^2} \quad (5.9)$$

Here n_m denotes the refractive index of the surrounding medium, while m is the ratio of the refractive index of the trapped particle, n_p , to the refractive index of the surrounding medium, $m = n_p/n_m$. The quantity R denotes the radius of the trapped particle, c is the speed of light in vacuum, P is the incident power and w_0 the beam waist. The classical potential strongly depends on the ratio between the refractive index of the trapped particle and the surrounding medium but overall is only a slowly varying monotonic function of wavelength. Note that both the refractive index n_p and the beam waist w_0 show a slight wavelength dependence.

5.2.2 Quantum Approach

We now want to substitute the polarisability of a two-level quantum emitter into the formula (Equation 5.6) for the gradient force. The polarisability is given by [139]

$$\alpha = \frac{d^2}{\epsilon_0 \hbar} \left(\frac{\omega_0 - \omega}{(\omega_0 - \omega)^2 + \frac{1}{2} \left(\frac{dE_0}{\hbar} \right)^2 + \frac{\Gamma^2}{4}} + \frac{\frac{i\Gamma}{2}}{(\omega_0 - \omega)^2 + \frac{1}{2} \left(\frac{dE_0}{\hbar} \right)^2 + \frac{\Gamma^2}{4}} \right) \quad (5.10)$$

Here, d is the dipole matrix element of the atom, ω_0 is its resonant frequency, ω is the frequency of the excitation wavelength and Γ is the atomic linewidth. Clearly, the polarisability exhibits a resonant-type behaviour and in addition contains intensity-dependent terms reflecting the possibility of saturating the atomic transition. Using the real part of α and assuming again a Gaussian beam shape, the potential U_q becomes [139]

$$U_q = \frac{\hbar(\omega - \omega_0)}{2} \ln \left(1 + \frac{1}{2} \frac{d^2}{\hbar} \frac{4P}{\pi W_0^2 n_m \epsilon_0 c} \frac{1}{(\omega - \omega_0)^2 + \frac{\Gamma^2}{4}} \right) \quad (5.11)$$

Hence the dipole potential for the quantum emitter exhibits a completely different behaviour compared to that obtained in the classical approach (Equation 5.9). When the trapping laser is red-detuned with respect to the dipole transition ($\omega < \omega_0$), the near-resonant optical trapping effect induces an attractive force, whereas when the system is blue-detuned ($\omega > \omega_0$) it induces a repulsive force. Hence, the quantum approach reveals a dispersive potential that is a result of the dipole transition. For visualization, both the classical and collective quantum potentials for an ensemble of SiV centres in nanodiamond are plotted over a wavelength range around the SiV resonance at 739 nm in Figure 5.1. The figure has been produced by numerical simulations assuming a 100 nm nanodiamond containing 500 colour centres, with an inhomogeneous distribution of ZPLs centred around 739 nm, with a 25-mW laser trapping the nanodiamond via a 1.2-NA microscope objective. Note that attractive/repulsive forces correspond to a negative/positive potential depth, respectively.

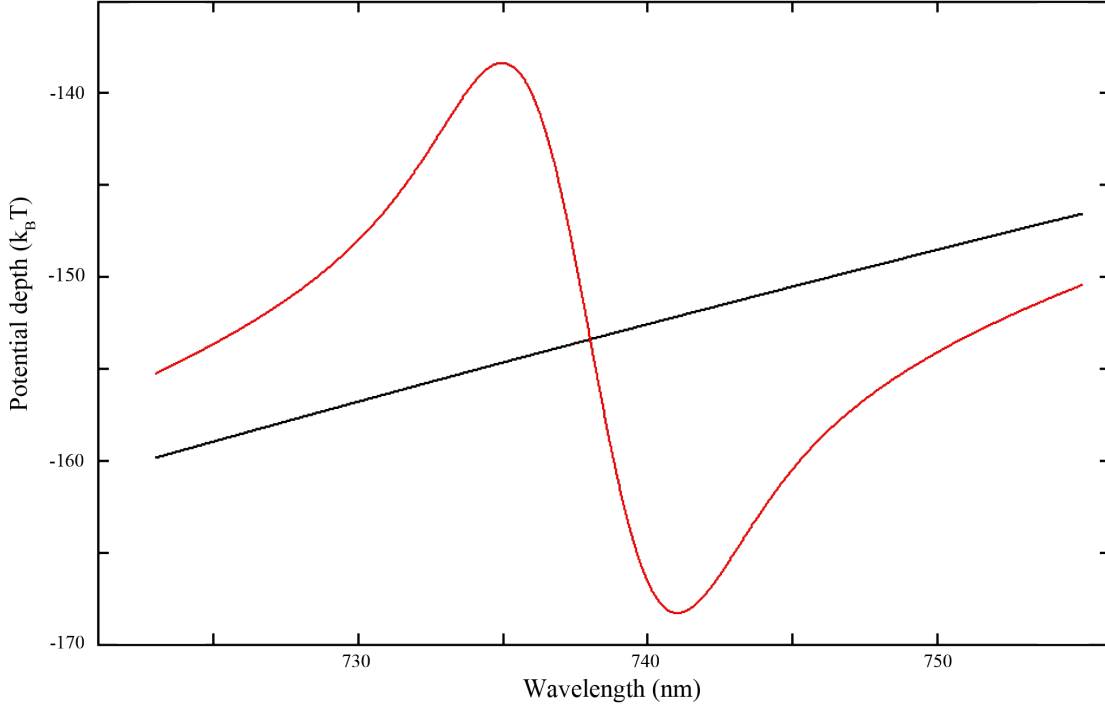


Figure 5.1: **Optical trapping potential near the SiV dipole transition.** The red curve, U_q , shows resonant behaviour around the dipole transition, unlike what we would expect from the classical potential, U_{cl} , represented by the black curve. The curves were calculated using the following parameters: diamond size 100 nm, number of SiV centres 500, ZPL at 739 nm, radiative linewidth: 93 MHz [26], inhomogeneous ZPL distribution 2 nm, laser power 25 mW, and an objective with $\text{NA} = 1.2$.

Further to this, Figure 5.2 exhibits a plot of the ratio of the total forces on a trapped particle to that of the classical trapping force alone. Simulations are plotted for both 1000 and 10000 SiV centres in a trapped nanodiamond. These concentrations are estimates extracted for the size of the fabricated nanodiamonds (~ 160 nm) and based on the scaling of typical concentrations found in the literature [27]. Where the curve exceeds the shaded region, the near-resonant optical trapping force dominates over the classical force alone.

5.3 Experiment

Over the past months the diamond nanoscience group has been investigating the near-resonant optical trapping effect on nanodiamond containing NV centres (manuscript in preparation). The attractive optical properties of the SiV, in particular the great strength of the dipole transition and the achievable concentrations of SiV centres in nanodiamond, motivates the experiments described in this chapter. We expect the near-resonant optical trapping effect to be much stronger for nanodiamonds containing SiV than in the case of NV centers.

It is rather difficult to measure the potential depth of an optical tweezer in liquid directly.

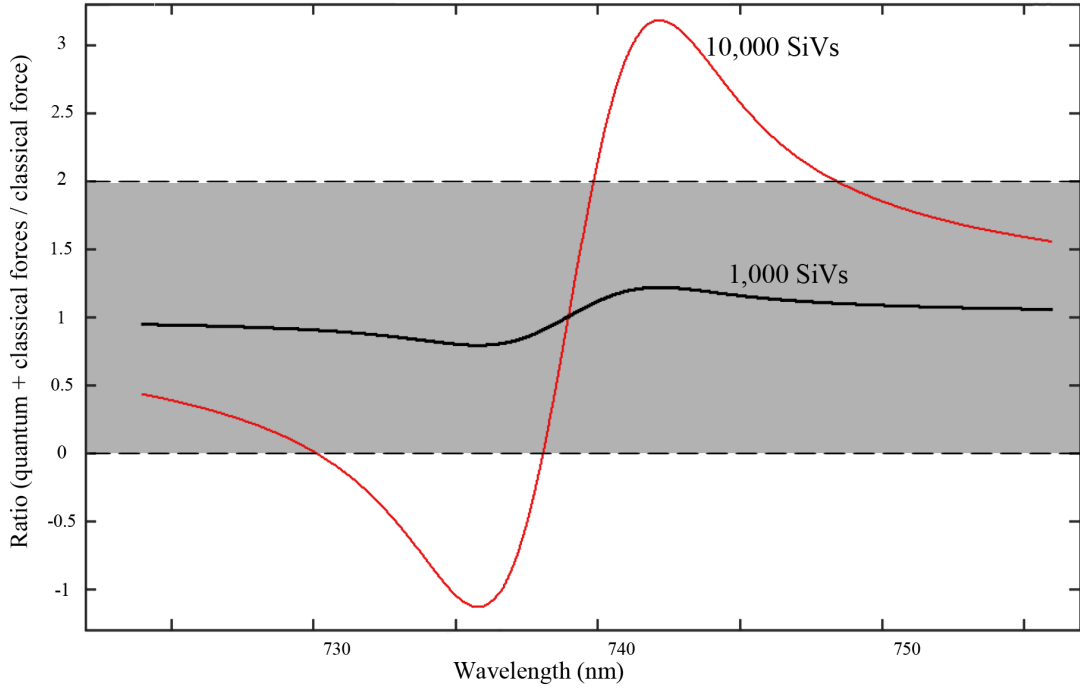


Figure 5.2: **Ratio of the total trapping force (classical plus quantum) to the classical force alone.** For nanodiamonds with a diameter of ~ 100 nm, we expect a concentration of SiV centres between 1000 and 10000 per nanodiamond; the corresponding plots are shown. Where the curve exceeds the shaded region, we expect the near-resonant optical trapping effect to be larger than the classical force on the nanocrystal alone.

However, we do have access to the trap stiffness, κ , which is the second derivative of the potential in the trap center (at $r = 0$)

$$\kappa = \left. \frac{\partial^2 U}{\partial r^2} \right|_{r=0} \quad (5.12)$$

A strongly confined particle in the center of the trap experiences, to the first order, a harmonic trapping potential with stiffness κ (and a corresponding linear force). Assuming harmonic confinement, one can easily link the position fluctuations of a trapped particle to the trap stiffness. For a Gaussian beam, trap depth and trap stiffness are directly proportional. Hence, the trap stiffness is expected to show a similar scaling to the trap depth of Equation 5.11.

The experiment was conducted as follows: nanodiamond particles containing many SiV centres were trapped in solution and the trap stiffness was characterized as a function of wavelength in the vicinity of the SiV centre resonance. The diamond nanoparticles (with a size of ~ 160 nm) were held at the focus of classical optical tweezers in liquid and a second near-resonant laser beam slightly detuned from the SiV dipole transition was added. The

light backscattered from the trapped particle was recorded and the spatial fluctuations of this light were used to extract the trap stiffness.

5.3.1 Setup

A schematic of the lab-built setup is presented in Figure 5.5. The setup ultimately consists of two laser beams superimposed and focused in the middle of a static microfluidic chamber which contains the solution of nanodiamonds hosting SiV centres. One of the beams has a wavelength far from the dipole transition of the SiV — with its purpose to both classically trap a nanodiamond particle and also to provide a means of detection. The second beam is tunable near the wavelength of the SiV dipole transition, and is used to probe the trap stiffness for different wavelengths.

Stability is paramount. Great care was taken during the design and building of the setup to remove any vibrations as these would interfere with the measurements. In fact, as we measure the motion of the particle in the trap, any vibrations would significantly impact the collected data. The measures taken to reduce vibrations are introduced below where relevant.

The two lasers used in the setup were a picosecond Titanium:Sapphire laser (Coherent MIRA) operating in continuous wave (CW) mode at 780 nm and a cw Titanium:Sapphire laser (M Squared) operating over the range 745–738 nm. The MIRA was utilised for conventional optical tweezing of the particle with its wavelength remaining constant at 780 nm. The M Squared laser was tuned over the range 745–738 nm to investigate the effect of the resonant trapping on the red-detuned side, as the ZPL of the SiV centre is at 739 nm. The typical measurement sequence is shown in Figure 5.4, with the M Squared laser being controlled by shutters.

Both lasers were coupled into the same single mode fibre after overlapping them with a dichroic mirror (Semrock FF757-Di01-25x36). This ensures that after the fibre both beams are in the same spatial mode and hence also produce the same Gaussian beam profile in the trap. Great care was taken to maintain this beam profile throughout the setup. A photodiode was placed in the line of the beam light reflected from the dichroic such that changes in light intensity through the dichroic could be recorded for use in data processing. In the future, we plan to add active power control for both lasers using acousto-optic modulators and electronic feedback loops.

Once the beam exits the fibre and passes through a polariser, it is reflected vertically through a 45:55 pellicle beamsplitter (Thorlabs CM1-BP145B2) towards an elevated breadboard. All surfaces of the elevated breadboard holding the mounting components are insulated with ~ 2 –mm thick silicon mats to damp any vibrations. A 1.2-NA water-immersion microscope objective (Olympus UPLSAPO 60XW) is employed to focus the beam onto the sample which is held by a x-y-z piezoelectric stage (Physik Instrumente P-563.3CD). The stage is linked to a PC and its position controlled by joystick via a LabVIEW interface.

A chamber containing the nanodiamond solution is constructed using two coverslips and placing 10- μ m thick tape in between the coverslips, with the center removed to form the chamber (Figure 5.3). **Sample A** (see Chapter 4) is sonicated for 60 minutes, then a small volume of the nanodiamond solution placed into the chamber using a syringe; the coverslips

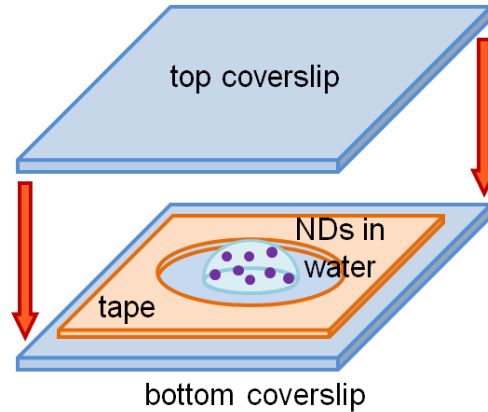


Figure 5.3: **Microfluidic lab-built trapping chamber.** A water droplet containing the SiV nanodiamonds is ‘sandwiched’ between two coverslips. The thickness of the chamber is defined by the thickness of the tape ($10\ \mu\text{m}$).

of the chamber are cleaned with acetone prior to use. The chamber is then sealed and secured to the piezoelectric stage. The sample was illuminated from above with a white lamp (Thorlabs OSL2) to image the particle.

Imaging light and backscattered laser light (a result of Rayleigh scattering) pass back through the objective to the pellicle beamsplitter where they are reflected to the imaging and detection paths. A 660-nm dichroic mirror reflects light shorter than 660 nm and transmits light longer than 660 nm. The reflected light forms the imaging path, which passes through an additional 700-nm long pass filter to stop the laser light from reaching the high-sensitivity CMOS camera (Thorlabs DCC3240N). This imaging system is implemented such that we are able to actively search for and trap particles over the $300\text{--}\mu\text{m}^2$ travel range given by the piezoelectric stage.

The detection path includes a 750-nm long pass filter to ensure that only laser light from the MIRA (at 780 nm) is detected. The beam is split using a silver D mirror and the two paths are then focused on the two parts of a balance detector (Thorlabs PDB450A). The balance detector feeds a signal that is comprised of the difference between the two balanced photodiodes to the oscilloscope. The difference signal directly gives a measure for the displacement of the trapped particle and hence directly measures the excursion of the particle in the trap.

The oscilloscope (Teledyne LeCroy WaveSurfer 24MXs-B) records data with a $5\text{--}\mu\text{s}$ resolution over a 160-second time period, during which the trapping conditions are varied. The MIRA beam, which provides the classical optical tweezing, stays on during the whole acquisition and is used to measure the motion of the particle and therefore the trap stiffness. The M Squared is periodically blocked. Hence, only when this beam is incident upon the trapped particle its motion becomes a combination of classical trapping and the near-resonant optical trapping effect. The intervals in between serve as reference values while also providing time for the wavelength of the M Squared laser to be tuned (see Figure 5.4 for the measurement procedure).

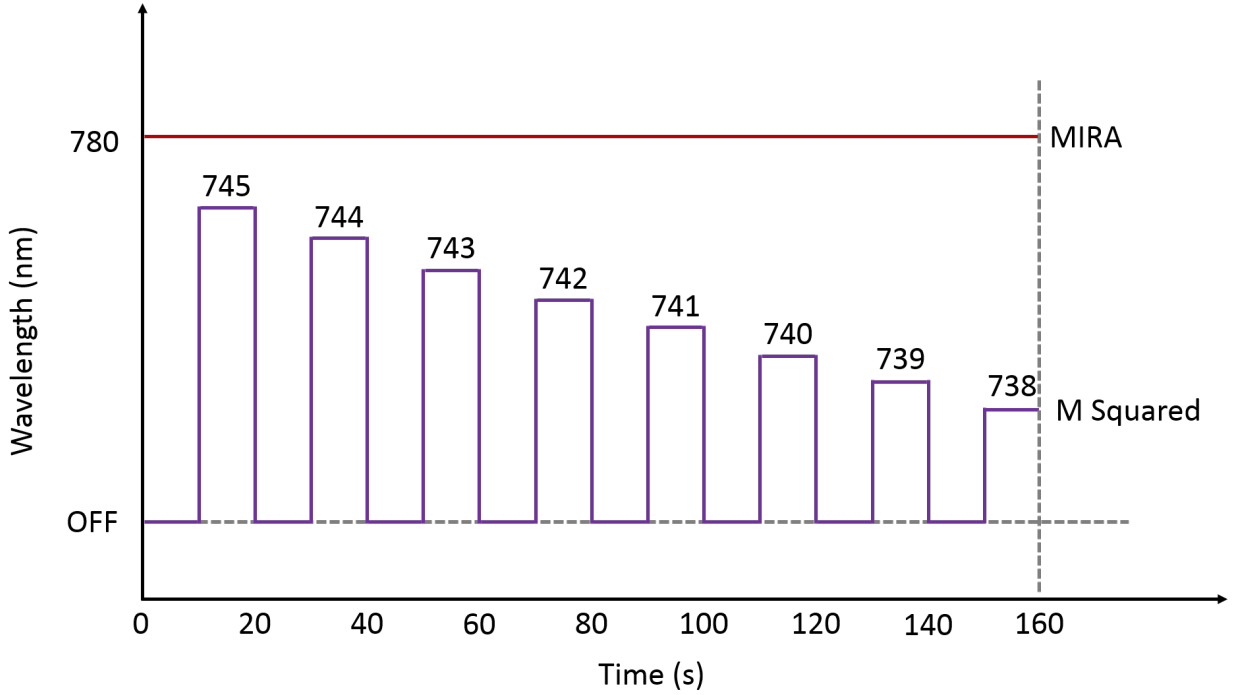


Figure 5.4: **Measurement procedure.** The MIRA laser remains on at a wavelength of 780 nm over the entire duration of a measurement. The M Squared laser is periodically interrupted and tuned in 1-nm steps from 745 nm to 738 nm over the course of the measurement.

5.3.2 Results

Due to the liquid environment the particle is subject to Brownian motion and behaves as an over damped harmonic oscillator while in the trap. A typical time-trace of the balance detector difference signal is shown in Figure 5.6a. In order to gain information about the particle we take a Fourier transform of the time trace to acquire a power spectrum density (Figure 5.6b), from which we can determine the corner frequency, f_c , by fitting a Lorentzian of the form [141]:

$$|\tilde{x}(f)|^2 = \frac{k_B T}{\pi^2 \beta \left[\left(\frac{\kappa}{2\pi\beta} \right)^2 + f^2 \right]} \quad (5.13)$$

where T is temperature, β is the diffusion coefficient and κ is the trap stiffness. The corner frequency, f_c , is then defined as [141]:

$$f_c = \frac{\kappa}{2\pi\beta} \quad (5.14)$$

Hence, through determining the corner frequency, f_c , we can determine the trap stiffness, κ , which is the second derivative of the trap depth, characterised by the dispersive behaviour we aim to measure.

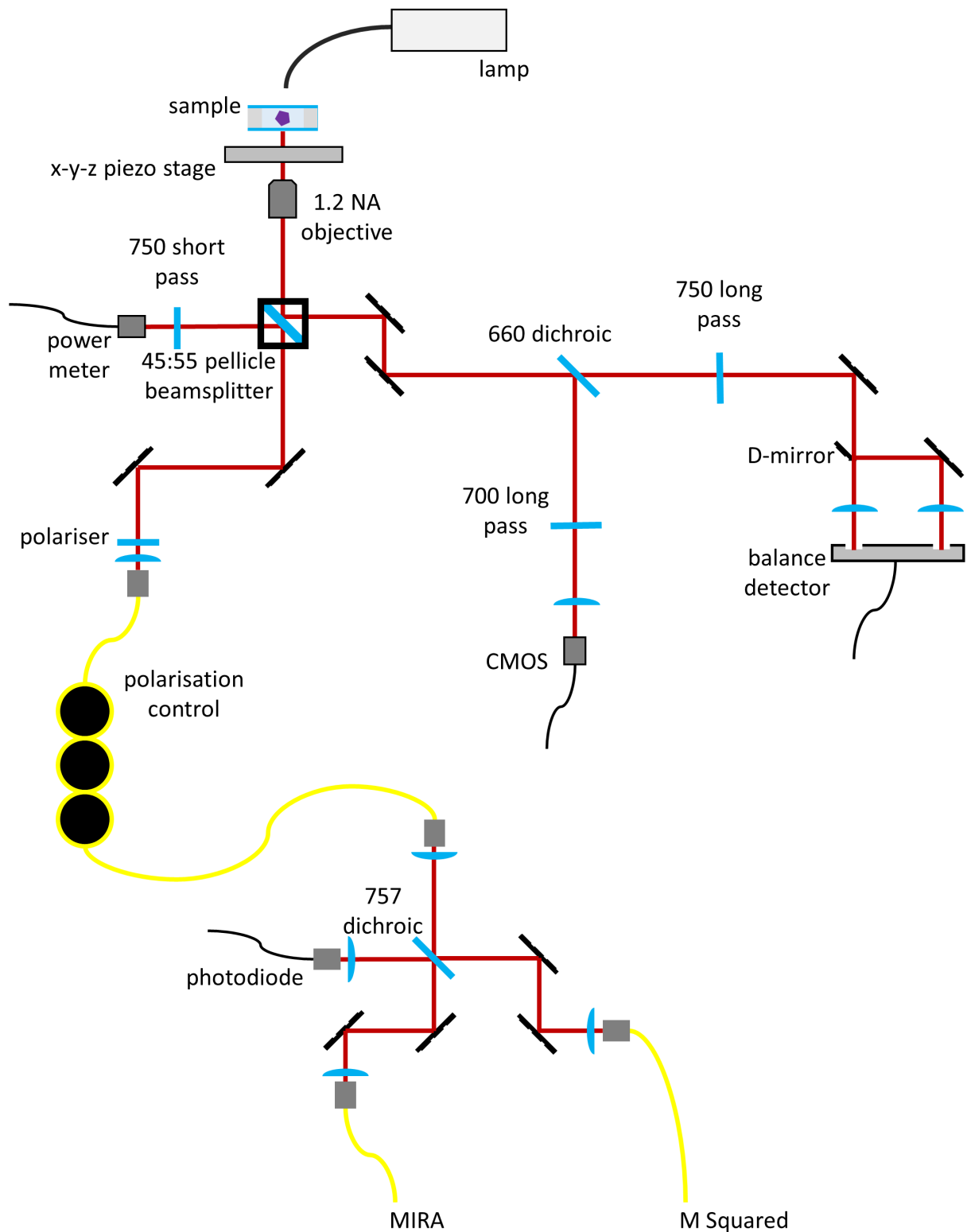
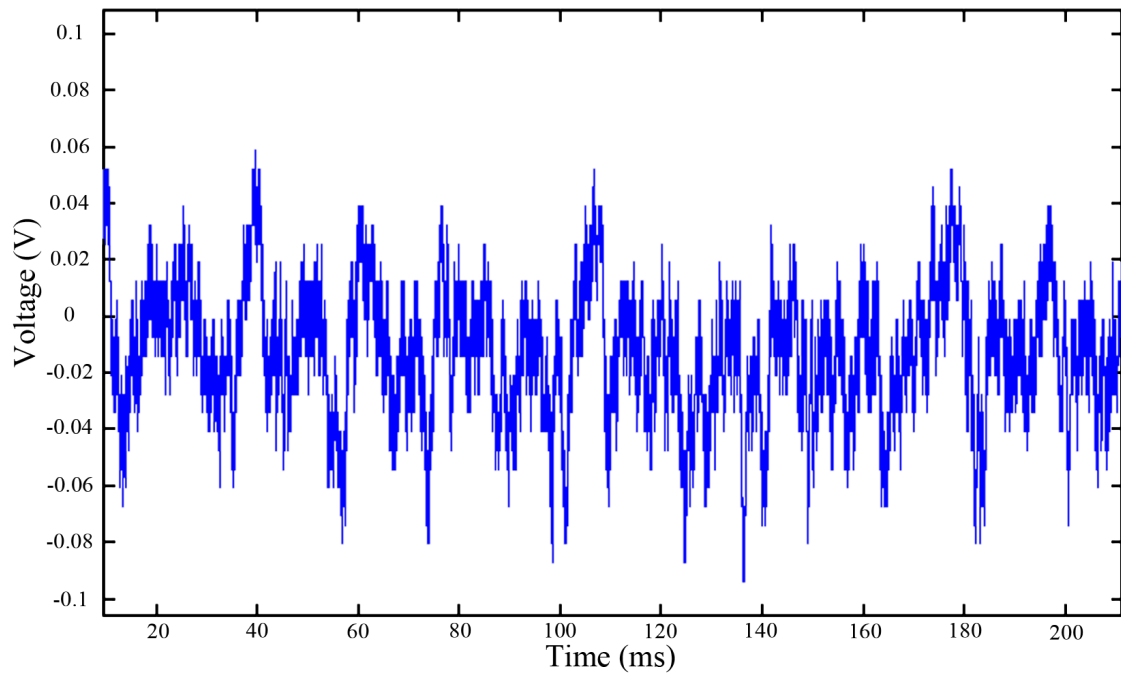


Figure 5.5: **Experimental setup.** Sketched is the trapping setup as outlined in Section 5.3.1. The two lasers which are located on a separate table are also shown. The light from the lasers is transported to the optical table with the trapping setup using optical fibres. Polarization control is achieved through the use of fibre paddles.

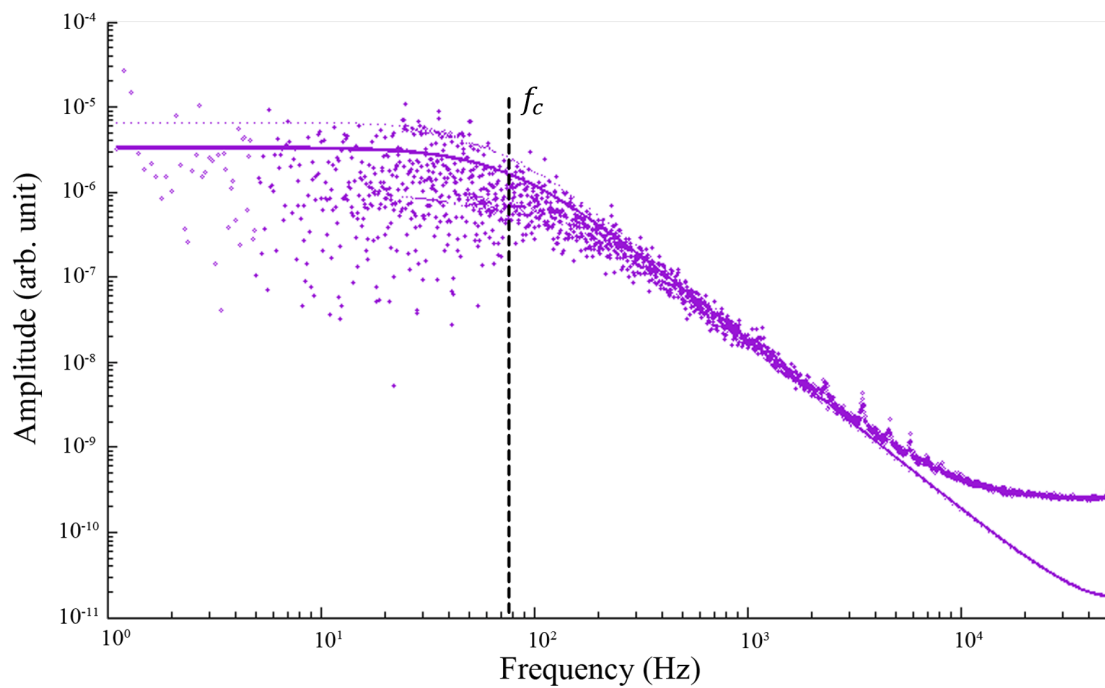
The measured corner frequencies of the combined traps normalized to the corner frequency of the single trap at 780 nm is plotted against excitation laser wavelength in Figure 5.7. The graph includes a fit curve (red line) that has the expected functional form. Here, the fit serves merely as a guide to the eye. However, the trend in the data seems to indicate that the corner frequency increases as we approach the ZPL from above. Note that from the collected data so far we were able to extract only the three data points shown, while the remainder had to be discarded due to experimental irregularities — thus at this stage our results are very preliminary. After submission of this thesis, we will conduct further measurements in order to obtain a more comprehensive set of data.

Analysis of the preliminary data and the corresponding fit indicates a $\sim 25\%$ increase in the corner frequency ratio when decreasing the trapping wavelength from 745 nm to 743 nm. When only classical trapping of the nanocrystal is considered, a change of 10% in the corner frequency over the much larger wavelength range 739–780 nm is expected. This change is primarily due to the change in beam waist (compare Equation 5.9). The 10% assumes the two beams to be superimposed precisely, with no effects of chromatic aberration from the optical elements. Based on this estimate, we expect a $\sim 0.13\%$ when changing over the range 745–743 nm. Chromatic aberration could lead to displacement of the foci of the two trapping beams which in turn could mimic a significant change in trap frequency when changing the wavelength of the tunable laser. However, over a range of 3 nm the 25%-change in corner frequency that we measure can not be attributed to chromatic aberration (as this would account only for changes in the order of $\sim 1\%$).

As the 25% increase in the corner frequency ratio is significantly larger than the 0.13% expected classically and chromatic aberrations should also lead to a much smaller effect, we tentatively associate the observed trend in the data with the expected near-resonant optical trapping effect. However, at this stage the data is still very preliminary and further measurements have to be taken in order to confirm this assumption, though the first results seem to lead in a promising direction. Note that the fit in Figure 5.7 is the calculated trap depth as a function of wavelength in the case presented (see figure caption for details). At this stage the collected data merely indicates that there exists resonant behaviour around the ZPL of the SiV and that the trend of our data indicates that this is an effect of near-resonant optical trapping. It is clear that further data is required to confirm our preliminary findings.



(a)



(b)

Figure 5.6: **Brownian motion of a trapped nanodiamond.** (a) An example of a time trace recorded with a balance detector. (b) A corresponding power spectrum density (PSD), acquired by taking the Fourier transform of the time trace. From a Lorentzian fit to the PSD (solid line) we obtain the corner frequency, f_c .

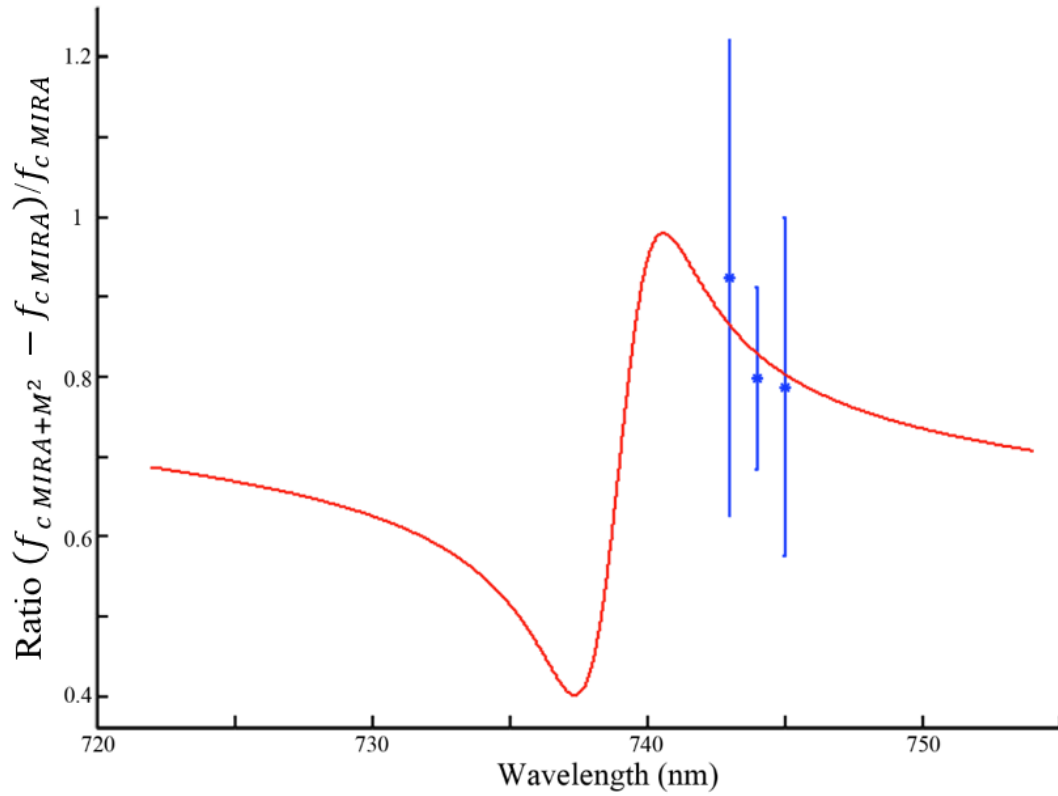


Figure 5.7: **Preliminary data on near-resonant optical trapping.** Three data points with a fit (red line) that is merely a guide to the eye in this case. The fit accounts for 1000 SiV centres within a nanodiamond, with the ZPL at 739 nm and a broadening of 1 nm, but has been vertically adjusted to give a better indication of the trend of the data points. In particular, the extracted broadening of 1 nm seems to small compared to the widths measured in Chapter 4, compare Figure 4.9b. Clearly, more data points are needed to confirm the expected behaviour of the near-resonant optical trapping effect.

6

Outlook

“The mind, once stretched by a new idea, never regains its original dimensions.”
Oliver Wendell Holmes Sr.

In introducing the background and scope of this thesis (Section 1.1), I have discussed how the optical properties of the SiV colour centre in diamond is attracting considerable attention for the future of diamond-based nanotechnologies. In this regard, the outcome of this thesis has been twofold. Firstly, I established a method for the synthesis of nanodiamonds containing SiV centres and secondly, I presented a new technique for the optical trapping of diamond nanoparticles.

Fabrication of Nanodiamond SiV Colour Centres

In this work I have presented a top-down process (Section 3.3) for the fabrication of nanodiamond containing SiV colour centres via Chemical Vapour Deposition (CVD). This method has now become a key technology readily accessible to our Quantum Materials and Applications Group at Macquarie University. This will allow us to work independently, synthesising in situ our own samples without depending on external fabrication facilities. It also acts as a starting point to explore the fabrication of nanodiamonds containing very few colour centres: one specific goal is to fabricate nanodiamonds with single SiV colour centres, as they have been identified as potentially superior quantum systems for quantum information technologies, single photon sources and cavity QED applications [26].

Moreover in Sections 3.1.2 and 4.1.1, I have discussed how certain parameters can be controlled in the CVD diamond synthesis process. For instance how heating and cooling during growth and varying the concentration of CH_4 in H_2 influence the properties of the produced diamond. The work done in this thesis has started the thorough investigation of such variables. By understanding and ultimately controlling their effect we expect to

improve the properties of the nanodiamond material and the hosted colour centres. For instance, we hope to reduce the variability in the centres' ZPL locations from nanodiamond to nanodiamond and the narrowing of their FWHM. This will be particularly important in the context of our work on the trapping of nanodiamonds containing colour centres.

Trapping of Nanodiamonds Containing SiV Centres

In the last part of this thesis, I have reported on a new trapping effect for nanodiamonds containing SiV centres. Preliminary data was collected in a proof-of-principle experiment aimed at demonstrating the viability of a new method to optically trap nanoparticles containing many colour centres — a method that could potentially be pushed to the trapping of nanocrystals that are only $\sim$ tens of nanometers in size (Chapter 5).

The frontiers of nanoscience are evolving towards smaller and smaller regimes. Classical optical tweezers are quickly reaching fundamental limitations, being unable to trap diamond nanoparticles less than 100 nm in size. However, harnessing our newly developed method of near-resonant optical trapping (Chapter 5) may lead to the implementation of near-resonant optical tweezers for manipulating particles with sizes much less than 100 nm.

This has particular implications in life science applications. The combination of a single NV centre within an ultra-small (< 10 nm) nanodiamond containing many SiV centres would enable the simultaneous tracking and 3D manipulation of a nanoscale sensor with single-molecule sensitivity. Fabricating such a nanodiamond sensor poses a great challenge which I have started addressing with my work on diamond growth and fabrication described in this thesis, and which I will continue to explore in the future. Eventually a nanodiamond sensor of the type proposed here could bring upon the possibility of biology in singulo: the study of biological systems in vivo, one molecule at a time. After all, at the most fundamental level our physiology and all biological processes are the result of intricate actions of single proteins such as enzymes, motor proteins, DNA and RNA molecules. To date, imaging techniques are incapable of accessing the subnanometric world of molecular machines and biomolecules within cells. The near-resonant optical tweezing system we have hereby proposed and we are currently developing for manipulating a diamond nanoscale sensor tackles this limitation and has therefore the true potential to become a game-changing nanotechnology.

A

Appendix

This appendix includes the ramp-up procedure used for both **Sample A**, Table A.1, and **Sample B**, Table A.2. Each procedure spans for approximately 20 minutes.

Table A.1: CVD ramp up procedure for **Sample A**.

H ₂ (sccm)	CH ₄ (sccm)	O ₂ (sccm)	Pressure (torr)	Microwave Power (Watts)	Substrate Temp. (°C)	Plasma Temp. (°C)
50	0	0	10	576	42	-
200	0	0	20	588	58	-
250	0	0	25	585	60	-
300	0	0	30	579	61	-
350	0	0	35	717	69	496
400	0	0	40	928	77	580
450	0	0	45	1124	88	660
478	0	0	50	1333	105	738
478	0	0	55	1723	111	800
478	0	0	60	1974	117	844
478	0	0	65	2212	126	902
478	0	0	70	2450	132	969
478	0	0	75	2696	140	999
478	0	0	80	3006	144	1045
478	20.2	2.0	79.7	3024	153	1074

Table A.2: CVD ramp up procedure for **Sample B**.

H ₂ (sccm)	CH ₄ (sccm)	O ₂ (sccm)	Pressure (torr)	Microwave Power (Watts)	Substrate Temp. (°C)	Plasma Temp. (°C)
101	0	0	6.9	595	500	560
151	0	0	16.1	594	500	597
200	0	0	18	603	500	613
302	0	0	29	596	500	624
352	0	0	33	751	500	658
401	0	0	39.2	1016	503	706
454	0	0	45.8	1244	500	745
479	0	0	49.4	1508	501	777
479	0	0	49.2	1757	500	797
479	20.2	2.0	48.9	2007	502	798

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