Engineering colour centres in tailored diamond

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Abstract

When the word diamond comes up, the majority of people thinks about engagement rings or gemstones. In fact, it is additionally, one of the most promising host materials for the implementation of advanced technology, exploiting the nature of quantum physics. Such quantum technologies have disruptive potential, ones the quantum effects can be applied in macroscopic, commercial products.

The nitrogen-vacancy (NV) centre in diamond is a promising candidate to perform such tasks in the fields of quantum computation, quantum cryptography or metrology. Especially in the field of quantum sensing, the NV sensor impresses with nano-scale spatial resolution paired with high sensitivity. The electronic spin of the atomic-sized point defect can be initialised, manipulated and read-out at ambient conditions and coherence lifetimes are comparably long.

Diamond magnetometers based on negatively charged NV centres have shown to be very attractive, and the sensitivity goes down to the single-atom level. In order to exploit such a high sensitivity level for sensing prospects, in this thesis, the NV centres are fabricated well confined in a certain distance to the diamond surface, since the detectable field usually decays with the third power of the distance between sensor and target. The surface depicts a fracture of the spin wise protecting diamond lattice and charge fluctuations affect the stability of NV centres, which are overcome by diamond surface termination.

In order to improve the sensitivity further, the sensor density, measurement contrast and interaction time are increased. The nitrogen doping technique, which is applied during a plasma-enhanced chemical vapour deposition (PECVD) diamond growth process is used to fabricate NV centre ensembles aligned along one diamond crystal axis, thereby improving the measurement contrast by a factor up to four. The interaction time limiting spin bath is analysed using the sensor capabilities of the NVs, which leads to enhanced growth strategies and the fabrication of sensitivity optimised NV centre ensembles for magnetometry applications.
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1 Introduction

Synthetic diamond is on the rise. Production techniques have improved over the last decades leading to enhanced diamond quality and the availability of gemstones with sizes up to several carats [1]. The average price of a 1.5-carat synthetic diamond decreased by 23.5% within one year (03/2017 to 03/2018) [2], and the trend continues. Laboratory grown diamonds reached a market share, regarding rough diamonds, of about 2% of the overall diamond jewellery market in 2018, and are expected to expand to 10% in 2030 [3].

Besides the jewellery industry, there is a growing interest in the enormous potential of these human-made diamonds. The ability to tune its composition and eventually the physical properties are desirable features which arouse interest within the science community.

Historically, the first physical property which attracted great interest was the exceptional hardness, making diamond a perfect candidate for high precision cutting and polishing tools [4,5]. Polycrystalline diamond powder at the tip of a nowadays dental bur can even prevent fast abrasion [6]. Until today most industry applications of lab-grown diamonds are connected to its hardness.

The second property which has caused a stir was electrical conductivity. Diamond can be used as semiconductor when doped with impurity atoms like boron or phosphorous [7]. Semiconductor process devices as Schottky diodes or field-effect transistors are supposed to stand extremely high voltages and currents if manufactured from diamond [8–10]. Even though these technologies cannot be fully exploited and devices are not commercially available, their development helped tremendously to increase the quality and purity of synthetic diamond [11].

The newest field of interest which synthetic diamond has engrossed is quantum technology. Due to the wide band gap which enables optical access in the visible range and the capability of coherent control of dopant related colour centres within the diamond lattice, many possible applications in quantum science and technology are
within reach.
The nitrogen-vacancy (NV) centre [12] is probably the most prominent candidate among solid-state spin systems with potential applications in the fields of quantum information [13], quantum simulation [14], quantum metrology [15] and quantum sensing [16]. Nowadays the scientific significance lies in the applicability as quantum sensors which have the potential to outperform their classical counterparts in certain tasks. The atomic size of the sensor in combination with the inertness and non-toxicity of diamond makes it possible to investigate properties on the nanometre scale. ac or dc magnetic fields can be measured with a high spectral bandwidth ex- and in-vivo [17–19], thereby reaching a sensitivity which allows the detection of magnetic fields caused by single spins in molecules or nuclei, enabling nuclear magnetic resonance (NMR) spectroscopy on the nanoscale [20–22]. As diamond is bio-compatible, it is possible to place NV-containing nanodiamonds inside a living cell and measure the chemistry and dynamics of the cell core [23–25]. It is also possible to perform single [26,27] and ensemble magnetometry [28–32], where the smallest detectable field is as small as a few tens of femtotesla [33,34]. Even applications in geology [35] or as vector magnetometers [33,36] have been introduced so far.
No matter what application is desired, the reproducible and controlled fabrication of point defects in diamond is key. Minimising the randomness of the production process, in addition to gaining new insights into the creation process during synthesising diamond is the main challenge this work addresses.
**Thesis outline** The thesis is divided into four main parts, a theoretical description of diamond growth with particular focus on the nitrogen-vacancy centre, a methodical description of techniques used in this work, experimental results with aspects on the controlled creation of single and ensembles of NV centres and appendices.

The thesis starts with an overview of synthetic diamond, before its production by plasma-enhanced chemical vapour deposition and the creation of diamond impurities is discussed (chapter 2). Chapter 3 sets focus on one particular diamond impurity, namely the nitrogen-vacancy centre whose properties are discussed in detail.

The methodology part is subdivided into two main chapters 4 and 5, where the first includes techniques necessary for the creation of diamond and diamond impurities and the chemical control of the latter’s charge states. The second part, concluding the methodology part, deals with the post diamond growth analysis, with special focus on diamond surface and layer composition, and single defect centre analysis on the nano-scale.

The experimental part is arranged as a bottom-up approach, where at first the engineering of single shallow NV centres is discussed before the following sections deal with the creation of ensembles. The orientational and isotopic control of the NV centre ensembles including the surrounding spin bath concludes this part.

Chapter 6 deals with the production of single shallow NV centres a few nanometres below the diamond surface, with particular focus on the manufacturing, including the charge state stabilization and subsequent analysis with depth calculation and coherence study. In chapters 7 and 8 the use of ensemble NV centres for magnetometry applications is discussed and the created preferentially aligned ensemble sensors are analysed regarding their increased magnetic field sensitivity compared to conventional ensembles.

In order to call this procedure NV engineering, it is necessary to gain full control of the colour centre creation and the surrounding spin bath generation process. Since natural abundances of $^{15}\text{N}$ and $^{13}\text{C}$ is only 0.4% and 1.1% respectively, isotope control can be used to prove that NV centres, as well as impurities in the diamond lattice, can be tailored to need. Preferentially aligned NV ensembles in an isotopically engineered synthetic diamond are the topic of the final chapter 9.
Part I

Fundamentals
2 Fundamentals of diamond and diamond growth

2.1 Diamond: Material for quantum technologies

Diamond is among the most expensive gemstones in the world, and the brilliant-cut sparkling due to light refraction fascinates humans ever since as it resembles a soupçon of luxury. Not only its beauty attracts attention all over the world, but also the outstanding physical properties make diamond an interesting material for several industrial applications. Due to its high thermal conductivity, its extreme hardness, chemical stability and optical transparency diamond is an ideal platform for heat spreaders, precision polishing and cutting tools or high power electronics. Natural diamond forms over billions of years, hundreds of kilometres deep in the Earth’s mantle, at extreme conditions, since temperatures up to 1600°C and pressures up to eight GPa are needed to create the strong covalent bonds between single carbon atoms [37]. As a result, the appearance of diamond on the Earth’s surface is very rare, and for application in industrial products, the benefit of synthetic, engineered diamonds is priceless.

The goal of this work is to create diamond with superior properties artificially, which requires an understanding of the structural composition of diamond. Its crystalline structure is illustrated in figure 2.1. Diamond consists of sp³ hybridised carbon atoms, where all four valence electrons establish covalent bonds to the valence electrons of the neighbouring atoms (illustrated as grey connections in figure 2.1). The bonding angle is 109.5° and the distance between two carbon atoms is 1.54 Å which results in a unit cell consisting of a face-centred cubic (fcc) lattice with a two-atomic basis. One basis (green in figure 2.1) is shifted by 1/4 of the length of the primitive cell (lattice constant 3.57 Å). Diamond is a semiconductor and has a relatively
high bandgap of 5.5 eV (in comparison to other materials suitable for electronic devices: SiC 3.3 eV, GaN 3.4 eV) and together with the thermal conductivity of 2200 W/mK \cite{38} and a high electron carrier mobility of 4500 cm$^2$/Vs \cite{39} it is a potential candidate for use in high power electronics. The high bandgap makes diamond transparent for optical wavelength in the visible range. A refractive index of 2.42 \cite{40} causes the incomparable sparkling of brilliant-cut diamonds, an intrinsic feature of all diamond types. Nevertheless, there are some diamonds which are more valuable than others. Therefore the gem industry classifies the different types of diamonds depending on the colour classification (see table 2.1, from Gemological Institute of America (GIA)), where D is the most expensive grade. Note that classification is performed visually by an operator which compares a new diamond with a master colour set of pre-classified brilliant-cut diamonds to find out the colour with the highest resemblance. Different coloured diamond plates are shown in figure 2.2 ranging from colourless to yellow. Besides the physical content which dictates the colour of natural diamonds, there are three more classification criteria, namely the shape, the weight and the amount and structure of inclusions. Together these are known as the 4Cs quality criteria for diamond classification created by GIA,
Colour, Clarity, Cut and Carat weight. These 4Cs identify the value of an existing brilliant-cut diamond and therefore its selling price.

Table 2.1: Jewellery industry diamond classification according to GIA standards [41].

<table>
<thead>
<tr>
<th>Diamond Colour</th>
<th>Actual Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-E</td>
<td>colourless</td>
</tr>
<tr>
<td>G-J</td>
<td>near colourless</td>
</tr>
<tr>
<td>K-M</td>
<td>faint yellow</td>
</tr>
<tr>
<td>N-R</td>
<td>very light yellow</td>
</tr>
<tr>
<td>S-Z</td>
<td>light yellow</td>
</tr>
</tbody>
</table>

The colour of a diamond depends on the presence of impurities which are incorporated during the creation process. For natural diamonds, these are mainly nitrogen (N) and boron (B) which have a comparable size to the carbon atom and therefore can replace the carbon site in the lattice easily. A different classification method, which is more common among scientists, depends on the [N] and [B] content in the diamonds [42]. Here, diamonds are classified depending on a high nitrogen (Type I, [N]>1 ppm) or low nitrogen (Type II, [N]<1 ppm) amount. This classification is illustrated in figure 2.3 (values from [43,44]). A further subdivision is made for the Type I diamonds regarding the presence (Ia) or absence (Ib) of nitrogen aggregates. These aggregates are nitrogen related defect centres with a variable amount of nitrogen atoms (n) and empty, unoccupied lattice sites (m), known as vacancies. These defect centres form stable conglomerates, are an inherent part of every diamond and are labelled historically. So the striking yellow colour of Ib type diamonds stems from the C-centre, in the field of electron-paramagnetic resonance (EPR) better known as P1 centre, which consists of a single substitutional nitrogen atom replacing the lattice site of a carbon atom. The presence of A-centres (a pair of two substitutional nitrogen atoms) and B-centres (four substitutional nitrogen atoms that surround one unoccupied lattice site) is used to further sub-classify diamonds into the groups IaA and IaB respectively.

Subdivision of Type II diamond, on the other hand, is quite simple, since the only delimiting parameter is the boron content ([B]) which, if detectable, groups diamond into Type IIb or Type IIa, if not. The latter is the purest of all presented diamond
types and therefore the logical choice for scientific investigations where the diamond is explored on a single centre level. Most natural diamonds are of Type Ia. In or-

![Diamond Classification Diagram](image)

**Figure 2.3:** Scientific diamond classification [42,43]: Depending on the amount of nitrogen within a diamond, it is classified as Type I or Type II. Further discrimination regarding the form in which nitrogen is present leads to classification into Types IaA (pairs of single nitrogen are found, known as A centres), IaB (four nitrogen atoms surround one vacancy, B centre) and Ib (single nitrogen known as P1 or C centre). In contrast, the presence of boron differentiates Types IIa (very low boron content) and IIb (detectable amount of boron).

der to distinguish the different diamond types, the atomic decomposition has to be analysed, which can be performed by secondary ion mass spectrometry (SIMS) or Fourier-transform infrared spectroscopy (FTIR), for example. The latter has the advantage that it is non-destructive since the working principle is based on absorption spectroscopy with infrared irradiation, where each nitrogen related impurity shows a characteristic spectrum. As diamond itself also produces a recognisable spectrum this technique is commonly used for diamond analysis in gemology [45].

There are proposals that the above-described classification method (see figure 2.3) can also be used to classify the colour of gem diamonds according to their nitrogen concentration, which can be measured for the case of neutral substitutional nitrogen (P1) or nitrogen conglomerates (three substitutional nitrogen atoms surrounding one vacancy (P2 or N3 centre) via EPR techniques, for example, [46].
2.1 Diamond: Material for quantum technologies

Furthermore, in combination with ultraviolet-visible spectroscopy (UV-Vis) and photoluminescence (PL) spectroscopy, FTIR can be used to distinguish not only the different diamond types but also if a diamond is grown naturally or synthetically [47]. Since the field of synthetic diamond manufacturing is growing, this feature is of major importance for the jewellery industry, as the value of natural diamond can only be kept high if there is a strict differentiation to synthetic ones.

An augmented need of synthetic diamond for industrial applications made it necessary to scale-up production facilities while the main advantage of synthetic diamond lies in the fact that it can be tailored depending on the application. Strategies to synthesise diamond can be found by looking at the phase diagram of carbon to see where the diamond allotrope is stable (see figure 2.4).

The first approach to create artificial diamond is to imitate the natural conditions under which diamond forms, namely at a high pressure and a high temperature (HPHT) [48, 49]. A diamond seed is placed in an anvil cell at pressures on the order of 5 GPa and temperatures up to 2000 °C to create diamond from a carbon source [50]. With this technique, it is possible to produce large crystals with a low dislocation density [51, 52]. Often a catalyst, like nickel or iron, is used to speed up the growth process [53] and diamonds from HPHT often contain much nitrogen (P1, H3, or aggregated nitrogen, see section 2.4 for details) [43] which is incorporated during the growth. Nitrogen incorporation can be reduced by adding a getter material like titanium or aluminium, which promotes the formation of nitrides but even with this artificial filter, the integration into the diamond lattice cannot be prevented entirely [54].

On the other hand impurities like boron, silicon, germanium or nickel can be chosen as contamination elements and placed in the diamond in very high amounts [55, 56]. For many industrial applications, especially in the tool industry, where diamond is used due to its physical properties as stiffness, hardness or conductivity, this issue is of minor importance. HPHT diamond can be produced very cheaply and therefore most diamonds used in applications nowadays are made in HPHT presses. Gem-quality for the jewellery industry, where the colouring of diamond and especially the production of colourless diamond is the distinct goal, is challenging to achieve with the HPHT technique. Better suited for impurity control is the Chemical Vapour Deposition (CVD) technique. Over the last few years, synthetic diamond produced by this method expanded both in size and in crystal quality and purity. Several
Figure 2.4: Phase diagram of carbon, showing the regions where diamond and graphite are stable. Pressure and temperature domains used for diamond synthesis are marked in blue (natural diamond genesis), green (synthetic diamond by HPHT method) and red (synthetic diamond by CVD growth). Image and values based on [37].

carats of diamond can be produced, and the quality resembles the state-of-the-art natural gem diamonds [1], which could be quite disruptive for the established jewellery market [57], as the market share of synthetic diamond is expected to increase in comparison to natural diamond [58]. Global diamond players as De Beers (Luxembourg) or Chow Tai Fook (Hong Kong) are aware of this development and spend effort to keep their dominant market position in diamond business. Some of the commercially available CVD grown diamonds used in this work are produced by Element Six, a fundamental research unit part of the De Beers group.

The high purity and quality control accompanying the CVD method has the origin in the utilisation of very high purity gases, serving as the fundamental building block for the CVD growth. During the process, hydrogen is used as a carrier gas and radicals selectively etch carbon bonds different from sp$^3$. In other words, the formation of graphite (sp$^2$ bond carbon) is suppressed. Thus CVD growth, operating at comparably low pressures (contrary to HPHT and natural genesis, see figure 2.4) can be used for diamond synthesis. The main advantage of this technique compared to other diamond synthesis and manufacturing methods is, that it allows precise growth parameter control and impurity incorporation, as the growth happens layer by layer. This approach is not only more favourable for the production of jewellery
2.2 Diamond synthesis

Synthetic diamond is on the rise since more and more people pick the human-made version as their gemstone of choice for bracelets or engagement rings and make a conscious decision against natural diamonds, which sometimes are mined under disputable ethical conditions (‘blood diamonds’, child labour, etc.). The initial impulse to produce synthetic diamond can be attributed to the field of electronics, where low dislocation densities are required for the manufacturing of power devices and diamond detectors with outstanding performance [60]. First attempts to fabricate diamond by Plasma Enhanced Chemical Vapour Deposition (PECVD) method go back to the 1960s and it was developed further ever since [1,37,57,61–63]. In comparison to the HPHT method, where diamond is produced in its thermodynamically stable phase, the growth of PECVD diamond is mainly dominated by the kinetics of atomic carbon and hydrogen species.

In order to synthesise diamond, a hydrogen atmosphere is fed with a small fraction of carbon, in our case in the form of methane gas. Typical gas flow ratios are in the range of 0.02-5\% methane with respect to hydrogen. Sometimes, also oxygen is added for further improvement of crystal quality and surface morphology [64]. The gas mixture is activated by applying a resonant microwave (MW) field, which is typically confined by a cavity resonator [65]. At temperatures exceeding 700°C the kinetics of methyl and hydrogen species is such that diamond growth is promoted,
whereas the diamond growth rate follows the curve shown in figure 2.6. The hydrogen plays a crucial role since it is involved in the radical creation of the source hydrocarbon as well as the prevention of deposition of non-diamond like material by etching graphite-like structures on the growth surface. In this metastable region, the produced diamond can be very well engineered on a relatively large area exceeding several centimetres [66]. The number of impurities in the generated diamond crystal, assuming a well evacuated and isolated growth chamber, basically stems from the source gases (hydrogen and methane).

Another key feature of PECVD is that it requires a substrate which provides the lattice structure to be pursued by the deposition process. In general, substrates can be assorted into two different groups, namely diamond and non-diamond substrates. Non-diamond substrates are usually made of molybdenum or silicon [67] and diamond growth in the form of nucleation is promoted by preparing the substrate’s surface with diamond nanoparticle coating or with diamond powder abrading. Another technique to stimulate growth is to bombard and implant the silicon- or molybdenum substrate with carbon-containing ions from the plasma before the growth is carried out. Since a bias field induces this bombardment, this technique is referred to as bias-enhanced nucleation (BEN) [68]. As diamond nucleation occurs simultaneously and is augmented on these pre-selected sites, neighbouring nucleation sites merge and lead to small grains with sizes ranging from micrometres to nanometres. Crystallinity and morphology can be tuned via changing the growth parameters and the outcoming material is polycrystalline diamond from micro- (MCD) to nano- (NCD) [69] to ultra-nano-crystalline diamond (UNCD) [70].

Heteroepitaxial diamond growth can be used to produce polycrystalline diamond films for infrared and microwave windows, heat spreaders or wear resistance coatings [44], for example. However, the existence of grain boundaries and the associated background fluorescence circumvent the usage for optically addressable quantum sensors. Nevertheless, there are research groups producing mono- or single crystalline diamond (SCD) on non-diamond substrates, like a stack of silicon, yttrium-stabilised zirconium and iridium [66]. The importance of this heteroepitaxial diamond growth comes into play when scaling up the possible applications of diamond in quantum technology, especially photonics [71] and sensing [29]. Similar to computer chips where the transistor density grows exponentially and therefore increases the computing power of PCs (Moore’s law [72]), an increased number of sensors,
2.3 Theory of diamond growth

either by increasing the sensor density or the overall sensor size, results in a higher sensitivity. Due to the existence of large silicon substrates, it is possible to produce large diamond plates up to a diameter close to 10 cm [66,73].

Heteroepitaxial diamond growth on materials other than diamond will always suffer from a reduced crystallinity since the lattice mismatch between the materials will produce stress in the grown layers. Homo epitaxial diamond growth, on the other hand, where the PECVD is performed on an existing diamond crystal, does not suffer from this problem. The variety of industrially produced diamond plates nowadays is enormous, and diamond substrates used in this study are described in section 4.1. Note that the phrase *grown diamond* in this dissertation always refers to homoepitaxially grown diamond, since the quality and purity has priority.

There are a number of companies providing commercially available MW plasma systems (Seki Diamond systems, Plassys, etc.) with different accoutrement, covering the whole operational area from high output-driven gemstone production to sophisticated, single-atom controlled quantum material development. The systems mainly differ by choice of a cooled or heated sample holder stage and a high or low power microwave head and the corresponding resonator. The home-built system used during this work is described in detail in section 4.2.

The main advantage of PECVD compared to HPHT technique is the capability to engineer synthetic diamond layer by layer, and the incorporation of atoms is an imprint of the source gases. In fact, very sharp interfaces are possible with PECVD since the source gas exchange can be performed promptly [59,74].

Even though there are many theories and models which try to picture the complexity of PECVD diamond growth [75–82], there is still no model which perfectly predicts the outcome and composition of PECVD grown diamond. In the next section, the standard model for diamond growth and the incorporation of impurities is discussed.

2.3 Theory of diamond growth

There is a long debate regarding the actual process behind PECVD diamond growth which is not fully understood up to date. In the following, two different approaches to model the kinetics during the diamond layer deposition process are presented. The
first approach assumes that diamond growth happens along step edges, also called terraces, whereas the second approach takes local surface chemistry into account.

### 2.3.1 Step flow growth

![Figure 2.5: Schematic representation of step flow growth. The model is based on the assumption that diamond growth occurs on terraces, created by a slight off-angle to the normal (100) vector. An arriving carbon atom (adatom) which is bound to the solid diamond surface, diffuses along the terrace until it is incorporated on the terrace edge. This incorporation depends on terrace width \( L \), diffusivity \( D \) and carbon deposition rate \( \rho_c \).](image)

Step flow growth (SFG) is the standard model for high-quality PECVD diamond growth and is schematically illustrated in figure 2.5. The model assumes that the top surface of the diamond crystal consists of single terraces with width \( L \) due to the diamonds off-cut angle \( \beta \) as a result of the diamond polishing process. This is only true if the off-angle is relatively small (\( \beta < 5^\circ \)). At the arrival of a carbon atom (illustrated in green in figure 2.5) on one of the terraces, it diffuses to the edge where it is integrated into the existing diamond lattice and therefore expands the terrace step. The step-growth velocity \( v_{\text{step}} \) can be written as

\[
v_{\text{step}} = \rho_c L , \tag{2.1}
\]

where \( \rho_c \) is the carbon deposition rate (in monolayers per second) [83]. The velocity of the carbon atoms, on the other hand, can be derived from \( v_{\text{carbon}} = \frac{L}{t_C} \), with \( t_C \) being the time which carbon atoms need to diffuse to the edge of the step.
2.3 Theory of diamond growth

By introducing a diffusion coefficient $D$, the diffusion length can be written as $L \approx \sqrt{Dt_C}$. Including this in the equation of the carbon velocity reveals,

$$v_{\text{carbon}} = \frac{L}{L^2 D} = \frac{D}{L}.$$  \hspace{1cm} (2.2)

A carbon adatom can only be incorporated at the step edge if its velocity is higher than the step velocity,

$$v_{\text{step}} < v_{\text{carbon}} \Rightarrow \frac{\rho C L^2}{D} < 1 \hspace{1cm} (2.3)$$

The PECVD diamond growth can, therefore, be tuned by changing $\rho_C$, $L$ and $D$ in the following way (also compare [84]):

1. The carbon deposition rate $\rho_C$ depends mainly on the number of carbon species available for deposition which is given by the concentration $c_m$ of methane gas in respect to hydrogen in the chamber. In the growth chamber this can be adjusted by controlling the CH$_4$ flow via mass flow controllers. Decreasing the carbon concentration $c_m$ directly decreases the overall diamond growth rate $\nu_{\text{gr}}$ (compare section 5.2).

2. The terrace width $L$ is only dependent on the diamond’s miscut angle. A larger miscut angle results in a smaller terrace width and therefore a higher growth rate $\nu_{\text{gr}}$ (see also section 7.4).

3. The diffusivity can be increased by increasing the temperature $T$ as it can be stated

$$D = D_0 \cdot \exp \left( -\frac{E_a}{\kappa_B T} \right), \hspace{1cm} (2.4)$$

where $E_a$ is the activation energy for diffusion and $\kappa_B$ the Boltzmann’s constant. A higher growth temperature should also increase the diamond growth rate $\nu_{\text{gr}}$ to a certain extend and lead to a better crystal quality.

If the step velocity is higher than the carbon velocity, $\frac{\rho C L^2}{D} > 1$, the carbon atoms do not reach the step edge, and this leads to additional nucleation on the terraces and therefore to three-dimensional growth. Note that the SFG does not take into account the hydrogen atmosphere during the growth which actively can etch adatoms which are not sp$^3$-bond to the diamond substrate. Reports are showing that
methane concentrations as low as 0.025% can smoothen the original diamond surface which is probably due to the hydrogen etching effect \[85,86\]. This effect is also highly dependent on temperature as single hydrogen ions have different energy and therefore, etching potential. A stronger etching effect can be achieved by increasing the temperature. The resulting growth rate depends on a balance between etching and growth of diamond and should behave as illustrated in figure 2.6. The tricky part as a diamond grower is to find the optimal temperature \(T_0\), where etching and growth are in balance, as this is the ideal growth condition to reach the best diamond quality presumably. For details about the temperature measurements and the PECVD set-up, see section 4.2.

\[\text{Figure 2.6: Dialectic of growth and etching. The growth rate } \nu_{gr} \text{ is highly dependent on the growth temperature. The optimal temperature } T_0 \text{ is supposed to result in the best possible diamond quality. A higher temperature leads to an elevated etching mechanism, which favours secondary nucleation rather than areal growth, whereas a lower temperature decreases this etching but leads to unwanted carbon groups on the surface and promotes defect creation.}\]

\[\begin{align*}
\text{2.3.2 Diamond surface chemistry} \\
\text{Even though there are some hints that the step flow growth model is close to the actual description of the PECVD process, there are some parts which are not covered, for example, the hydrogen environment necessary for the suppression of sp}^2 \text{ carbon during the growth. Several approaches try to model the kinetics in the PECVD growth chambers, which differ by their complexity, and some are subject of complicated and time-consuming density functional theory calculations} \ [80]. \text{ A simplified}
\end{align*}\]
model, evolved by looking at the chemical reactions happening at the actual diamond solid-gas interface, was developed in the early 1990’s [87–89]. This diamond surface chemistry simulation gives rise to another possible explanation for the reaction dynamics taking place during PECVD diamond growth. The central assumption (or conclusion) is that mainly single H radicals and CH$_3$ species participate in the chemical reactions on the diamond surface and therefore are responsible for the growth mechanism [90]. The process to incorporate a single additional carbon atom from the gas phase into the existing diamond lattice is schematically represented in figure 2.7. The surface chemistry model is based on the assumption of a hydrogen-terminated diamond surface, which depicts the starting point for the PECVD growth process (figure 2.7(a)). Single hydrogen atoms are coloured in purple in figure 2.7, whereas carbon atoms of the existing diamond lattice, are marked in blue. In a first step, a hydrogen radical creates a free lattice site, labelled in red, by releasing a hydrogen atom to the gas phase (H-abstraction, figure 2.7(b)). A methyl group containing a carbon adatom (green) can be bonded via the radical site to the host lattice (figure 2.7(c)). Additional H radicals can abstract hydrogen atoms by releasing H$_2$ into the gas phase and leave behind two neighbouring radical sites (figure 2.7(d)).
final step, the additional carbon atom is ultimately incorporated into the existing diamond lattice (figure 2.7(e)). Note that this happens on all surface sites at the same time, and the actual diamond growth is an equilibrium process among all these individual steps. Especially the two hydrogen atoms bonded to the carbon adatom is a result of the lack of the neighbouring processes, which would compensate this by creating a whole new diamond layer.

The complexity of all these effects makes it very difficult to predict diamond growth, and it is still not clear if the step flow growth or the diamond surface chemistry model is more reliable. There are some research articles showing simulations of up to 1500 atoms under distinct growth conditions [80], but this is still far away from realistic conditions in the PECVD growth where up to $10^{23}$ atoms/cm$^3$ are involved. Even though the simulations do not yield a more detailed insight, the process parameters of PECVD growth can be tuned in a way that the powerful technology can be beneficial in the production of defect-free diamond, the incorporation of foreign atoms and especially the creation of colour centres.

2.4 Diamond impurities and colour centres

Perfect diamond, consisting only of carbon atoms, is an insulator and transparent, as depicted in table 2.1. Since natural diamond is created in the Earth’s mantle, there are a variety of elements which also find their way into the crystal lattice. These imperfections are reflected in lattice anomalies, lattice distortions and impurity atoms which can be substitutional or interstitial. As a result, the combination of all these imperfections varies the diamond’s properties like conductivity, hardness, stiffness or colour. Therefore, their detection and quantification is of major importance, and different techniques can be used including photoluminescence (PL) spectroscopy, electron paramagnetic resonance (EPR), infrared (IR) and ultraviolet (UV) absorption [91,92].

In nature, many differently coloured diamonds (known as ‘fancy coloured diamonds’) can be found. Some of them are rather famous since they grace the ornaments of kings and queens all over the world (‘the Cullinan Diamond’ (British Crown jewels), ‘Koh-i-Noor’ (Crown of Queen Elizabeth), ‘Regent Diamond’ (Louis XV/XVI and Napoleon Bonaparte) or ‘Golden Jubilee Diamond’ (largest faceted diamond
2.4 Diamond impurities and colour centres

Figure 2.8: Photography of differently coloured diamond used for scientific purposes. One diamond is brilliant-cut and shows the remarkable sparkling stemming from this extraordinary polishing technique. The others have a more practical shape and are more common in laboratories. Their colours range from white (Type II) with a low impurity rate, over yellow (Type I) with a high nitrogen content to black which has the highest amount of impurities. NV rich diamonds appear red under optical illumination. With PECVD growth, HPHT method, diamond polishing and laser cutting techniques, it is possible to generate artificial diamond in nearly every conceivable geometry.

Particularly rare coloured diamonds are traded at extreme prices as happened during the last years where a 19-carat pink diamond (‘Pink Legacy’) was auctioned for 2.6 million dollars per carat [93]. Nowadays, coloured diamonds can be produced synthetically, and some of them are shown in figure 2.8. This colouring is due to the presence of foreign atoms in the diamond lattice. Many of these impurities are stable and add additional energy levels within the diamond’s bandgap. If the transitions lie in the optical range of visible light, the diamond’s colour is changed due to photon absorption and emission (therefore the name colour centre).

As discussed above, boron is one of the most common impurities, which leads to a modified electronic band structure and as a result highly boron-doped diamond is a p-type semiconductor [94] and appears in a blueish colour [95]. There are more than 500 different colour centres known [96], ranging from the lack of single or multiple carbon atoms (vacancies, di-vacancies or multi vacancies [97]) to more complex structures like a combination of a vacancy and an impurity atom. Impurities include but are not limited to boron, nitrogen, hydrogen, phosphorous, silicon, germanium, tin, lead and nickel. Some of them form stable conglomerates and a selection of the
most interesting ones, in terms of quantum sensing and other quantum technology applications, are summarised in table 2.2.

One should note that not all colour centres are potential candidates for possible applications in quantum technology since the available optical and spin properties do not satisfy the requirements for such a task. Among these requirements are the presence of discrete and resolvable energy levels, the possibility to initialise and read-out the quantum system and to coherently control it [16]. The most studied colour centre which fulfilled the mentioned criteria and triggered an avalanche of quantum diamond research is the nitrogen-vacancy centre. Whereas an uncharged

Table 2.2: Impurities in diamond - Overview of different diamond colour centres.

<table>
<thead>
<tr>
<th>Centre</th>
<th>Composition</th>
<th>ZPL</th>
<th>Detection</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>GR1</td>
<td>single neutral vacancy</td>
<td>741 nm</td>
<td>PL</td>
<td>[98]</td>
</tr>
<tr>
<td>NV⁰</td>
<td>one nitrogen atom and one vacancy</td>
<td>575 nm</td>
<td>PL</td>
<td>[28, 98]</td>
</tr>
<tr>
<td>NV⁻</td>
<td>one nitrogen atom and one vacancy</td>
<td>637 nm</td>
<td>PL/EPR</td>
<td>[98–100]</td>
</tr>
<tr>
<td>P1</td>
<td>neutral substitutional nitrogen</td>
<td>-</td>
<td>EPR</td>
<td>[42]</td>
</tr>
<tr>
<td>N3</td>
<td>three nitrogen atoms surround one vacancy</td>
<td>415 nm</td>
<td>PL/EPR</td>
<td>[98, 101]</td>
</tr>
<tr>
<td>H1</td>
<td>one hydrogen atom and one vacancy</td>
<td>-</td>
<td>EPR</td>
<td>[102, 103]</td>
</tr>
<tr>
<td>H3/NVN⁰</td>
<td>two nitrogen atoms sandwich one vacancy</td>
<td>503 nm</td>
<td>PL</td>
<td>[104–106]</td>
</tr>
<tr>
<td>H2/NVN⁻</td>
<td>two nitrogen atoms sandwich one vacancy</td>
<td>987 nm</td>
<td>PL/EPR</td>
<td>[102, 106]</td>
</tr>
<tr>
<td>H4</td>
<td>four nitrogen atoms surround one vacancy</td>
<td>496 nm</td>
<td>PL</td>
<td>[98, 104]</td>
</tr>
<tr>
<td>SiV⁰</td>
<td>two vacant lattice sites sandwich one silicon atom</td>
<td>948 nm</td>
<td>PL</td>
<td>[107]</td>
</tr>
<tr>
<td>SiV⁻</td>
<td>two vacant lattice sites sandwich one silicon atom</td>
<td>737 nm</td>
<td>PL</td>
<td>[107, 108]</td>
</tr>
<tr>
<td>GeV</td>
<td>two vacant lattice sites sandwich one germanium atom</td>
<td>602 nm</td>
<td>PL</td>
<td>[109–111]</td>
</tr>
<tr>
<td>SnV</td>
<td>one tin atom interstitial?</td>
<td>619 nm</td>
<td>PL</td>
<td>[112, 113]</td>
</tr>
<tr>
<td>ST1</td>
<td>unknown</td>
<td>555 nm</td>
<td>PL</td>
<td>[114, 115]</td>
</tr>
</tbody>
</table>
substitutional nitrogen atom replacing a carbon atom in a lattice site makes the diamond appear yellow (this defect is the already mentioned P1 centre), a high NV concentration gives diamond a reddish colour. The explanation for this effect together with other fundamental properties of the nitrogen-vacancy centre, which is the core piece of this work, are described in more detail in the next chapter 3.

Other colour centres with possible applications in the field of quantum technology are for example the negatively charged silicon-vacancy centre (SiV\(^{-}\)), which might be useful for quantum photonics applications. It shows a high Debye-Waller factor and 70\% of the photons are emitted in the zero phonon transition, which is why it serves as a source of indistinguishable photons necessary to realise quantum repeaters using long-distance entanglement. It is intensively studied to explore the possibility to incorporate SiV centres into plasmonic structures, optical cavities and waveguides manufactured from diamond [108,116–121].

Other prominent candidates whose investigation is still proceeding are ST1 [114,115], germanium-vacancy (GeV) [109–111] and tin-vacancy (SnV) centres [112,113]. Note that these kinds of group IV colour centres are mainly produced by HPHT method or ion implantation since it is rather difficult to dissolve elements like silicon, germanium or tin in the gas phase.

Nevertheless, production of colour centres by PECVD method can be applied to create a variety of these centres in high purity and high-quality diamond. In this work, the main efforts are made to produce the NV centre in various concentrations and environments, which is discussed in more detail in the next section.
3 The nitrogen-vacancy (NV) centre

The nitrogen-vacancy centre is the pioneer in diamond colour centre research not only in the number of publications per year but also in the implementation and realisation of applicable quantum technologies. There are various examples what NV centre driven engineering has achieved in terms of device fabrication and market launch of prototypes exploiting quantum effects in synthetic diamond. Commercially available products can be purchased in the field of quantum sensing. NV centres integrated into diamond tips are used for scanning probe microscopy with nanometre resolution for magnetic and electric fields (Qnami, www.qnami.ch). Sales of quantum sensor tips and complete solutions as quantum scanning microscopes are promoted by Qzabre (www.qzabre.com). The company NVision is using hyperpolarisation protocols for NV centres in diamond to develop medical imaging techniques, like magnetic resonance imaging (MRI), which are non-invasive and could lead to a superior cancer diagnostics with an upgraded contrast agent (www.nvision-imaging.com). Even Lockheed Martin, one of the leading companies in the fields of aerospace, defence, security, and advanced technologies in the United States, applies NV centre based magnetometry on measuring magnetic field anomalies which then can be overlaid with known magnetic maps of the earth to determine one’s position. This technique is expected to locate the position even without the usage of satellites and is known as quantum navigation system [122]. A further advantage of such a system is that it cannot be hacked or manipulated as the global positioning system (GPS), for example. So, there are plenty of efforts to push NV centre based quantum technologies to a breakthrough into the real macroscopic world. Besides these widely developed products, there is plenty of research output regarding the NV centre. According to Google scholar (searching for 'nitrogen vacancy centre'), there were more than six hundred publications about NV centre related
topics in 2019, so nearly two per day. The question which comes to mind is: Why
does the NV centre attract so much attention from the scientific community?
The NV centre is a point defect colour centre within the diamond lattice which
acts as a trap and makes the defect immobile. It shows atom-like behaviour, but
in comparison to other single atom experiments, no special cooling or trapping is
required, and all experiments can be performed under ambient conditions. Together
with the non-toxicity of diamond and the spin selective triplet ground state, the
NV centre can be used for pressure \([123,124]\), force \([125]\), temperature \([126–129]\),
magnetic \([18,29,130]\) and electric field \([131–133]\) sensing in various disciplines as
medicine, geology, physics and biology. To understand these possible applications
of NV centres and to answer the question raised before, the fundamental basics of
nitrogen-vacancy centres in diamond are introduced and discussed in the following.
The NV defect consists of a P1 centre (substitutional nitrogen) and an adjacent

![Figure 3.1: Four possible NV orientations in a single crystal diamond. Due to the fixed fcc lattice, the NV defect axis has to be within one of the four possible orientations, \([111]\), \([\bar{1}1\bar{1}]\), \([1\bar{1}1]\), or \([\bar{1}1\bar{1}]\).](image)

vacancy, as illustrated in figure 3.1. This defect is stable within the diamond lattice
and shows \(C_{3v}\) symmetry, implying a 120° rotational symmetry along the NV axis
(imaginary bond connecting the nitrogen atom and the vacancy). The direction
of the NV axis can vary between four different crystallographic directions, namely
\([111]\), \([\bar{1}1\bar{1}]\), \([1\bar{1}1]\), \([\bar{1}1\bar{1}]\) axes. It has been shown that defect centre engineering
enables preferential alignment along two \([134]\) or even just one \([135–140]\) diamond
crystal axis by using specially prepared diamond substrates (\(\langle113\rangle\) and \((111)\ ori-
tented surfaces) and a suited PECVD growth process. The alignment is important for
NV centre sensing applications since it enables scaling up from a single to multiple sensors, and is discussed in more detail in section 3.3.1.

3.1 Optical properties

![Figure 3.2: Emission spectra of individual NV centres. (a) Photo luminescence of an NV$^0$ defect (orange), with five available electrons (inset) and the ZPL at 575 nm. (b) Fluorescence spectrum of a NV$^-$ dominated centre with the ZPL at 637 nm (red) and a total number of six electrons. Both centres show a broad emission spectrum due to a phonon-side-band and the fading of colours indicates the emission of non-coherent photons. Due to phonon induced decays, the fluorescence profiles can overlap.](image)

The NV centre has five electrons (three stemming from the dangling bonds of the carbon atoms and two from the nitrogen atom) which form the neutrally charged configuration NV$^0$. The presence of an additional donor electron from the diamond lattice can charge the defect and the overall electron number becomes six. The NV$^-$ centre is magneto-optically active, as its ground state possesses an electronic spin of $S = 1$ and can be used for applications like magnetic or electric field sensing, quantum-enhanced sensing and quantum computing. Independent of the charge state, the NV centre shows a ground and excited state. Both can be excited by green laser light ($\lambda_{\text{ex}} = 532$ nm) but they show different emission spectra, as can be seen in figure 3.2. NV$^0$ has a zero-phonon-line (ZPL) at $\lambda_{\text{NV}^0} = 575$ nm (see figure 3.2(a)) whereas the one of NV$^-$ lies at $\lambda_{\text{NV}^-} = 637$ nm (figure 3.2(b)). Both show a broad phonon sideband (PSB) emission, but the charge states can be differentiated by looking at the ZPL. The luminescence of NV centres is photostable, if blinking occurs it can be related to an unstable charge state since the fluorescence...
level of NV$^0$ is lower than the one for NV$^-$ [141].

In order to understand the fluorescence behaviour of NV$^-$ centres in more detail, its energy structure, given by a three-level system, is shown in figure 3.3 [142]. A spin-triplet ground state with $^3A_2$ symmetry and a spin-triplet excited state with $^3E$ symmetry as well as an intermediate state consisting of $^1A_1$ and $^1E$ states are the result of a group theoretical description [28, 100]. A zero-field splitting (ZFS) of the ground state of $D_{gs} = 2.87$ GHz between the $m_s = 0$ and $m_s = \pm 1$ states is the result of spin-spin interactions of the two unpaired electrons. The transitions between the spin projections along the NV axis, $m_s = 0$ and $m_s = \pm 1$, therefore, can be driven by microwaves. The excited state shows a ZFS of 1.42 GHz at ambient conditions [143, 144].

The most intriguing feature of NV centres is probably that single spin initialisation and read-out are possible at room temperature. Green laser light ($\lambda_{ex} = 532$ nm) is used to excite the NV centre off-resonantly into the phonon sideband, where a fast relaxation to the lowest vibrational band occurs on the picosecond time-scale [146].

The first possible decay path is via emitting a red-shifted photon at a wavelength of $\lambda_{NV^-} = 637$ nm, see figure 3.3(a). This transition is spin conserving and does not

![Figure 3.3: Energy scheme of the nitrogen-vacancy centre in diamond. Off resonant irradiation with green laser light leads to excitation of the electronic spin. (a) Direct decay via spin conserving photon emission results in the ZPL and the phonon-side band of the fluorescence spectrum illustrated in figure 3.2. Values for lifetimes from reference [145] (b) Decay via intermediate singlet states promotes the population of $m_s = 0$ state, and this enables optical initialisation of the electronic spin.](image-url)
change the spin quantum number of the NV. Furthermore, it is the main transition of the system and results in the ZPL, though only 4% of emitted photons contribute to it [116,147]. Most of the fluorescence is emitted in the range of 640 – 800 nm (PSB), compare figure 3.2(b).

The second decay happens via metastable singlet states, which is radiative in the infrared (ZPL $\lambda = 1042$ nm, [15,148,149]) and is not recorded by our detectors. This decay path is more likely for the $m_s = \pm 1$ states than for the $m_s = 0$ spin state [150,151]. At the same time, it is more probable for the NV centre to end up in the $m_s = 0$ ground state when decayed via the singlet states (intersystem crossing, ISC). This transition is not spin conserving ($m_s = \pm 1$ can be changed to $m_s = 0$ and vice versa) and enables spin initialisation into the $m_s = 0$ state by optical pumping with green laser excitation.

Furthermore, the NV centre emits around 30% fewer photons when it is excited from the $m_s = \pm 1$ state, which is because the lifetime of the singlet states is about 200 – 300 ns [15,148], whereas the excited state lifetimes are about 7.8 ns and 12 ns for the $m_s = \pm 1$ and $m_s = 0$ states respectively [145]. So population can be trapped in the singlet states and therefore the $m_s = 0$ appears brighter than the other states and makes it possible to determine the spin state of the NV centre by merely tracking the fluorescence signal (readout). This is only true within the first few hundred nanoseconds of the readout as laser irradiation (optical pumping) results in polarisation into the bright state [152,153].

3.2 Single photon source

Another advantage is that the NV centre can be used as a single quantum emitter, required for potential quantum cryptography applications and especially for quantum key distribution and secure communication [154,155]. The presence of a single photon emitter can be proven by measuring the second order autocorrelation function [156,157], which can be described by

$$g^{(2)}(\tau) = \frac{\langle I(t) \cdot I(t + \tau) \rangle}{\langle I(t) \rangle \cdot \langle I(t + \tau) \rangle},$$  
(3.1)
where the intensity of the light at time $t$ and $(t + \tau)$ are labelled as $I(t)$ and $I(t + \tau)$ respectively [158]. In the case of an NV centre, the measurement can be performed by using a Hanbury Brown and Twiss set-up [159], where the emitted photons are split into two branches by passing a 50:50 beam splitter and afterwards are measured by two different single photon detectors. If the light is emitted by a single photon source, a detection event of both detectors at the same time is impossible since the defect centre requires excitation to be able to emit a photon. This excitation-emission cycle has a lifetime during which no detection events occur and for short times $\tau \approx 0$, the autocorrelation function for a single emitter results in a dip $g^{(2)}(0) = 0$ [12,160]. The depth of this dip is directly correlated to the number of photon emitters ($N_{em}$) present in the observed system, as it scales with

$$g^{(2)}(0) = 1 - \frac{1}{N_{em}}. \quad (3.2)$$

For a single emitter ($N_{em} = 1$) the signal should drop to zero, assuming there is no background light from the lab or detector noise present [161]. In a real experiment, it is concluded that a single emitter is present if the dip drops below $g^{(2)} = 1/2$ as this is the limit for two emitters in the system ($N_{em} = 2$). In order to measure a
3.3 Spin properties

As mentioned above, the NV centre’s negative charge state possesses an electron spin of \( S = 1 \) and a triplet ground state. The crystal field splits the \( m_s = 0 \) and \( m_s = \pm 1 \) states, but this is not the only effect which changes the energy splitting. The Zeeman splitting as a result of the applied magnetic field or the hyperfine coupling to nearby nuclear spins (as the nitrogen nucleus) change the splitting further, and therefore the ground state spin Hamiltonian of the NV can be expressed as a combination of three parts

\[
H_{NV}/\hbar = H_{ZFS} + H_Z + H_{HF} \quad (3.3)
\]

\[
= D_g s^2_z + E (S_x^2 - S_y^2) + \tilde{\gamma}_{NV} B_z S_z + A_{\parallel} S_z I_z + A_{\perp} (S_x I_x + S_y I_y) + P I_z^2. \quad (3.4)
\]

The individual characters and constants of this Hamiltonian are explained in table 3.1. Note that a quadrupole splitting \( P \) exists only in the case of the nitrogen isotope \(^{14}\text{N} \) since its nuclear spin is \( I = 1 \). Values for the hyperfine parameters are taken from [162]. Furthermore, the energy levels can be shifted by any other nuclear
or electronic spin interaction in the vicinity of the NV centre, mainly represented by $^{13}\text{C}$ and P1 centres, which will be discussed later in this work. It is interesting to note that the value of the ground state splitting $D$ varies with temperature and pressure, which makes NV centres in diamond an excellent temperature and pressure sensor [15, 123, 124, 126–129].

Especially the strain field $E$ can vary locally on the nanometre scale and is therefore different for every single NV centre and can vary tremendously between diamond substrates. The applied external magnetic field $B_z$, on the other hand, can be determined by measuring the energy splitting between the degenerated sub levels $m_s = 0$ and $m_s = \pm 1$ which will be discussed in the next section 3.3.1.

### 3.3.1 Optically detected magnetic resonance

As outlined above, the outstanding feature of the NV centre is the spin-dependent fluorescence signal which enables optical detection of its spin state. Identification of the transition frequency between the $m_s$ sub levels can be performed by the so-called optically detected magnetic resonance (ODMR) technique. The working principle is as follows: The NV centre is continuously illuminated with green laser light. Simultaneously a microwave (MW) field of varying frequency is applied. As long as the MW frequency is off-resonant, meaning that it does not match the transition between the $m_s = 0$ and $m_s = \pm 1$ states, the fluorescence level stays high, as the

### Table 3.1: Overview of the characters and constants shown in the NV Hamiltonian (equation 3.4). Values are taken from [28, 162].

<table>
<thead>
<tr>
<th>Character</th>
<th>Representation</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_x, S_y, S_z$</td>
<td>electron spin operators</td>
<td>-</td>
</tr>
<tr>
<td>$I_x, I_y, I_z$</td>
<td>nuclear spin operators</td>
<td>-</td>
</tr>
<tr>
<td>$D_{gs}$</td>
<td>ground state zero-field-splitting</td>
<td>2.87 GHz</td>
</tr>
<tr>
<td>$E$</td>
<td>strain-field-splitting</td>
<td>MHz range</td>
</tr>
<tr>
<td>$\tilde{\gamma}_{\text{NV}}$</td>
<td>NV’s gyromagnetic ratio</td>
<td>2.8 MHz</td>
</tr>
<tr>
<td>$B_z$</td>
<td>external magnetic field along NV axis</td>
<td>mT range</td>
</tr>
<tr>
<td>$A_{\parallel}$</td>
<td>parallel hyperfine parameter</td>
<td>$14^{14}\text{NV}$</td>
</tr>
<tr>
<td>$A_{\perp}$</td>
<td>perpendicular hyperfine parameter</td>
<td>$14^{15}\text{NV}$</td>
</tr>
<tr>
<td>$P$</td>
<td>quadrupole splitting</td>
<td>-</td>
</tr>
</tbody>
</table>
3.3 Spin properties

Figure 3.5: Optically detected magnetic resonance signal of different NVs. (a) Measurement of a single NV showing the zero-field splittings of the ground and excited states without an external magnetic field. (b) The strength of the external magnetic field can be determined by the variation of the NVs ground state splitting caused by the Zeeman effect. Purple points show this splitting under various magnetic fields, whereas the black lines represent the theoretical line of the transition under an increased magnetic field. (c) Ensembles of NV centres show four different orientations in ordinary crystals which results in a total of eight transitions, and these can be reduced to one by crystal engineering and an aligned external magnetic field along with the $\langle 111 \rangle$ crystal orientation. In the latter case, only two transitions stemming from preferentially aligned NV ensembles are recorded (d).

system is pumped to the bright state (compare also figure 3.3). But when the MW frequency matches the $m_s = 0 \leftrightarrow m_s = \pm 1$ transition, the fluorescence level drops, as the spin state is excited into the $m_s = \pm 1$ states resulting in up to 30% less emitted photons. By ODMR measurements, it is possible to resolve the ZFS of the ground state (and also the excited state), as shown in figure 3.5(a).

Furthermore, if an external magnetic field is present, the $m_s = \pm 1$ states split up due to the Zeeman interaction with a frequency splitting of $\gamma_{NV} B_z$ in respect to the unaltered $m_s = 0$ level. Therefore, two transition frequencies appear in the ODMR spectrum 3.5(b), which scale with the strength of the magnetic field (represented as
The nitrogen-vacancy (NV) centre

black lines). As the projection of the $\vec{B}$ field vector on the NV-axis is responsible for the frequency shift, the angle between them is of importance. When using an ensemble of NV centres, ODMR measurements can be used to determine the relative orientation within the crystal lattice [152]. An ordinary diamond crystal contains NVs of four different orientation groups (compare figure 3.1) which show eight ODMR transitions in the case of a randomly aligned magnetic field (see figure 3.5(c)). By aligning the magnetic field perpendicular or parallel to one of the NV axis, it is possible to suppress or enhance the contrast of single transitions [137]. ODMR measurements can, therefore, be used to determine the NV orientation within the diamond, but precise control of the external magnetic field is needed. If the magnetic field, for example, is aligned along the $\langle111\rangle$ crystallographic axis, the angle to NVs of groups II-IV is the same ($109.5^\circ$), the transition frequencies overlap and only four instead of the eight transitions appear in the ODMR spectrum [163]. Now, if only group I NVs are present in the sample, the ODMR spectrum looks like the one shown in figure 3.5(d). This feature of ODMR measurements is used later in the section of preferentially aligned NV centres 8.1.

The fundamental limit of the ODMR dips linewidths is the $T_2^*$ time, but usually, the lines are broadened by microwave and laser [164, 165]. If their power is small enough, the lines are narrower, and it is possible to resolve the hyperfine splitting caused by the nitrogen nucleus. The method which fulfils this criterion is the pulsed ODMR technique, where a microwave pulse of fixed duration is used to drive the transition between the magnetic sublevels [166]. The length of the pulse is chosen to correspond to a $\pi$-pulse, as described in section 3.3.3. The sequence indicating the pulsed laser and microwave fields is illustrated in figure 3.6(a). The advantage of this scheme in respect to the continuous ODMR technique described above is that the initialisation process as a result of the optical pumping and the spin flipping process due to microwave absorption are not competing. Therefore, low field amplitudes can be used which suppress the broadening of the spectral lines. This effect is clearly visible in figure 3.6(b) where various field amplitudes are used to drive the $m_s = 0 \leftrightarrow m_s = \pm 1$ transition. Only the lowest field amplitude of 2.5 mV makes it possible to resolve the hyperfine splitting. Figure 3.6(c) shows pulsed ODMR measurements, where the splittings of 3.1 MHz and 2.2 MHz can be assigned to the NV isotopes $^{15}$NV and $^{14}$NV respectively.
3.3 Spin properties

Figure 3.6: A laser pulse initialises the NV centre in the $m_s = 0$ state. A microwave field of varying frequency but fixed time changes the spin state to $m_s = \pm 1$. In the case of a resonant MW field, a drop of the fluorescence level can be observed. (a) Pulsed ODMR spectra for different applied microwave power. Only small field amplitudes yield the resolution to resolve the hyperfine splitting caused by the nitrogen nucleus. (b) Pulsed ODMR measurements are showing the hyperfine splitting caused by nitrogen isotopes $^{14}$N and $^{15}$N according to the reported splittings from table 3.1.

3.3.2 Bloch sphere

As shown in the previous section, the external magnetic field can be used to split up the magnetic sublevels $m_s = +1$ and $m_s = -1$ and make them non-degenerate. If the splitting is large (magnetic field of several Gauss), an effective two-level system can be selected between the $m_s = 0$ and the $m_s = \pm 1$ states since one of the transitions is highly detuned from the MW field. For simplicity the system based on the states $m_s = 0$ and $m_s = -1$ is considered. A nice way to illustrate and interpret such a system is the geometrical representation in a Bloch sphere, see figure 3.7, named after Felix Bloch [167]. The north and south pole of the sphere are chosen to correspond to the basis vectors $|0\rangle$ and $|-1\rangle$. Any pure state of the system can be written as a superposition of these two states.

$$|\Psi\rangle = \cos \left( \frac{\theta}{2} \right) |0\rangle + e^{i\phi} \cdot \sin \left( \frac{\theta}{2} \right) |-1\rangle,$$  \hspace{1cm} (3.5)
where the angles $\theta$ and $\varphi$ are represented in figure 3.7. The population of the two basis states is described by the projection of the state vector $|\Psi\rangle$ onto the $z$ axis. This means an equally populated state, mathematically described as $|\Psi_{\text{super}}\rangle = \frac{1}{\sqrt{2}}(|0\rangle + e^{i\varphi}|-1\rangle)$, can be interpreted as a state on the equator of the sphere. The angle $\varphi$ in this case represents the phase. For example, a phase of $\varphi = \pi/2$ represents the $y$-axis of the Bloch sphere, whereas the $x$-axis corresponds to the phase $\varphi = 0$.

### 3.3.3 Rabi oscillations

Rabi oscillations describe the interaction between an external periodic field and a quantum mechanical two-level system. In our case, the external field is the magnetic component $\vec{B}_1$ of a microwave field, and the two-level system as described above is the reduced NV electronic ground state. By resonant excitation it is possible to drive the $|-1\rangle \leftrightarrow |0\rangle$ transition. The resonance condition for this is the microwave frequency $\omega$ has to be chosen to match the transition frequency $\omega_0$. A constantly applied microwave field with matched frequency $\omega = \omega_0$ results in a periodic oscillation of the population between the bright and the dark state, which can be read-out optically and results in an oscillation of the emitted fluorescence signal. The pulse
3.3 Spin properties

Figure 3.8: (a) Upper panel: Pulse sequence to detect Rabi oscillations. The initial laser pulse polarises the NV electronic spin in \( m_s = 0 \), before a microwave of variable duration \( \tau \) is applied to manipulate the spin state coherently, which is then read out with a second laser pulse. Lower panel: Illustration of coherent Rabi driving on the Bloch sphere. The initialised Bloch vector is rotated around the y-axis before the system is readout and re-polarised with the second laser pulse. (b) The resulting signal oscillates depending on the microwave field strength between normalised values of 1 and 0.7. Several remarkable times \( \tau \) are highlighted, indicating the interaction or driving time to create a superposition state (\( \pi/2 \)-pulse length of 7.5 ns), flip the spin population (\( \pi \)-pulse) or to recover the spin polarisation (2\( \pi \)-pulse).

scheme to perform such a Rabi experiment, including the corresponding illustration of the Bloch vector is shown in figure 3.8(a). The first laser pulse initialises the system into the \( |0\rangle \) state (Bloch vector pointing to the north pole) before the microwave is applied for a variable time \( \tau \) (which causes a rotation of the Bloch vector around the y-axis). The second laser pulse is used for read-out and re-initialisation. The visualisation of Rabi oscillations is achieved by plotting the resulting fluorescence signal for different microwave application times \( \tau \), which is shown in figure 3.8(b). Remarkable application times, further called microwave pulse durations, are specially labelled. These temporally fixed microwave pulses can be used to manipulate an initialised NV system to transfer the population completely to the \( |-1\rangle \) state (\( \pi \)-pulse), to create equal superposition states (\( \pi/2 \)-pulse or \( 3\pi/2 \)-pulse) or to perform a complete Rabi cycle (2\( \pi \)-pulse). The frequency of the oscillation depends on the strength of the driving field and can be expressed as \( \Omega \propto B_1 \), and in the case of a detuned microwave field as \( \Omega_{\text{eff}} = \sqrt{\Omega^2 + \Delta^2} \) where \( \Delta = \omega - \omega_0 \) is the detuning of the applied microwave field in respect to the transition frequency.
3 The nitrogen-vacancy (NV) centre

(a)

(b)

Figure 3.9: The Ramsey sequence to measure free induction decay (FID). (a) The pulse sequence and corresponding Bloch sphere representation to measure FID consists of an initialisation and a readout laser pulse, two $\pi/2$-pulses to create the superposition state which is sensitive to magnetic fields and to flip the population back to the z-axis. In between the two microwave pulses a phase is acquired which results from field fluctuations, the external $B_0$ field and parallel hyperfine couplings of the NV's environment. This time is referred to as free evolution or interaction time $\tau$. (b) A FID decay measured with an NV ensemble (green points). The dephasing time $T_2^*$ marks the signal decay to $1/e$ of the starting amplitude and can be estimated to 3.4 $\mu$s by fitting with a sine decay envelope function (purple).

3.3.4 Ramsey sequence

As mentioned in the introduction of this chapter, the NV is a promising candidate to realise a quantum sensor. The underlying physics for this expectation is the dipolar interaction with additional magnetic fields, when the NV system is in the superposition state $|\Psi_{\text{super}}\rangle$. Magnetic fields along the quantisation axis of the NV's electron spin, so fields parallel to the external $B_0$ field in addition to the controlled $B_1$ driving (which is perpendicular to $B_0$) lead to an additional phase, which in the case of randomly fluctuating fields leads to dephasing. The pulse sequence to measure this dephasing time $T_2^*$ is the so-called Ramsey sequence, also known as free induction decay (FID). It is illustrated in figure 3.9(a) including the corresponding evolution of the Bloch vector due to the spin state manipulation. The NV is initialised in the $m_s = 0$ state by a laser pulse. A $\pi/2$ pulse flips the NV spin into an equally populated superposition state, where it evolves freely for a specific time $\tau$. Note that the additional phase from external magnetic fields causes a rotation of the Bloch vector in the x-y-plane. Magnetic field fluctuations change the final position of each measurement on the Bloch sphere and this leads to the dephasing of the averaged signal. The last $\pi/2$-pulse maps the acquired into a population difference which can then be read-out by the second laser pulse. A typical FID decay is shown in figure
3.3 Spin properties

3.9(b). The signal (green points) contains information of any magnetic field present during the sensing or interaction time $\tau$. Especially, the hyperfine splitting of the NV’s nitrogen nuclear spin, which results in a beating on top of the signal can be measured with this technique if the MW frequency is resonant with one transition frequency (selective pulse).

Investigation of the envelope of these oscillations (purple line in figure 3.9(b)) reveals the $T_2^*$ time of the observed NV centre. The absolute value of the dephasing time depends mainly on the degree of fluctuations during the interaction time, and therefore on the spin environment around the NV centre.

3.3.5 Hahn echo

An expansion of the Ramsey sequence, which is used to detect very slow oscillating or constant fields in dc sensing, is depicted by the so-called Hahn echo sequence where an additional $\pi$-pulse is introduced in the middle of the free evolution time $\tau$.

The relevance of this pulse is that it acts as a refocusing mechanism since it inverts the accumulation of the phase during the second part of the sequence. Therefore, dephasing effects are suppressed for static or slowly fluctuating fields, leading to a prolonged coherence time $T_2$. In general, it can be stated $T_2 > T_2^*$.

The Hahn echo sequence and the corresponding effects of each operation on the Bloch sphere are represented in figure 3.10(a). A typical Hahn echo decay for increasing free-evolution times $\tau$ is plotted in figure 3.10(b). The fluorescence signal is fitted with a stretched exponential function of the form $\exp\left[-(\tau/T_2)^p\right]$, where $p$ is a parameter which depends on the spin bath and the type of noise created by it. The value of $p$ therefore contains information about the spin bath, but unfortunately, the knowledge of this fit value does not give direct information about the bath dynamics. Nevertheless, the coherence time $T_2$ can be used to estimate the spin concentration in the neighbouring environment of the NV as well as the presence or absence of nuclear spins as for example, $^{13}$C. Figure 3.10(c) shows different Hahn echo measurements among different samples with different spin bath concentrations. The value of $T_2$ increases from 1 $\mu$s to 625 $\mu$s for less dense $^{13}$C spin baths which are schematically illustrated in figure 3.10(d).
3. The nitrogen-vacancy (NV) centre

Figure 3.10: The Hahn echo sequence to measure the coherence time $T_2$. (a) Pulse sequence for Hahn echo possesses in comparison to Ramsey sequence (figure 3.9(a)) an additional refocussing $\pi$-pulse in the middle of the sequence which cancels magnetic signals varying slower than the interaction time. As a result the coherence time is prolonged in comparison to the dephasing time. (b) A coherence time of $T_2 = 23.72 \mu s$ can be extracted from the measurement (green) with a stretched exponential fit (purple). (c)+(d) Depending on the spin bath present in the vicinity of the NV centre, different $T_2$ values are possible. A rule of thumb in this regime is: The less dense the spin noise bath, the longer the coherence time. The central arrow with two spheres represents the NV electron spin and the number of the coloured arrows correspond to $^{13}\text{C}$ nuclear spins in differently isotopically engineered diamonds.

3.3.6 Overview of coherence times

The coherence and dephasing times presented above are good indicators for the spin bath composition in the diamond lattice as a faster decay corresponds to a less controlled, more dense spin bath. Unfortunately, it is not possible to conclude the nature of the spin bath by just looking at the absolute number. Knowledge about the spin bath from another measurement though, makes it possible to correlate certain impurities as P1 or $^{13}\text{C}$ with $T_2$ and $T_2^*$ (details are discussed in chapters 5 and 9). Within a controlled production process, these measurements can be used to classify the quality of a potential NV centre based sensor. Furthermore, if the
3.3 Spin properties

Table 3.2: Typical coherence times of NV centres depending on the production type of natural and synthetic diamond. Synthetic techniques are subdivided into the groups HPHT, regular CVD and NV driven CVD, where the distinct goal is to create NV centres for quantum applications.

<table>
<thead>
<tr>
<th></th>
<th>HPHT</th>
<th>PECVD</th>
<th>NV driven PECVD</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_2^*$</td>
<td>$\sim 0.1 , \mu s$ [29]</td>
<td>$\sim 2.0 , \mu s$ [176]</td>
<td>$\sim 100 , \mu s$ [177]</td>
</tr>
<tr>
<td>$T_2$</td>
<td>$\sim 1.0 , \mu s$ [178]</td>
<td>$\sim 300 , \mu s$ [179]</td>
<td>$\sim 2000 , \mu s$ [174]</td>
</tr>
</tbody>
</table>

Decoherence sources are known, it is possible to decouple the NV electronic spin by using different dynamical decoupling protocols as CPMG [168, 169], XY8 [170] or AXY [171] to prolong the coherence time further (more on this topic is discussed in section 9.3).

From a material science point of view, enhancements of coherence times can be realised by improved growth techniques which prevent the creation of paramagnetic defects [39], by isotopic engineering to suppress the interaction with nuclear spins [172] and by high-temperature annealing techniques to remove several defects [97]. By depleting the nuclear spin bath, coherence times on the order of $T_2^* \approx 470 \, \mu s$ [173] and $T_2 \approx 2 \, ms$ [174] have been reported. Theoretically, the $T_2$ coherence time can be extended to the $T_1$ spin lattice relaxation time which can reach up to 6-7 ms at room temperature [174, 175]. Experimentally, however, this has not been achieved yet, probably due to the presence of paramagnetic defects and impurities which are produced during the NV creation process. Especially during ion implantation (see section 4.3.1), vacancy related defects and clusters are produced which do not heal out during high-temperature annealing and thus disturb the spin environment of NV centres. Therefore, NV centres produced by PECVD technique usually reach longer coherence times.

Natural and HPHT diamonds intrinsically contain more impurities than PECVD grown diamonds and therefore, the average dephasing time could additionally be used to distinguish the different types of diamond. Typical coherence times are summarised in table 3.2. Note that the trend goes away from reaching the ultimate coherence time limits (reported record values: $T_2 \approx 2.4 \, ms$ and $T_2^* \approx 1.5 \, ms$ [180]), as most applications require shallow NV centres a few nanometres below the diamond surface and the latter strongly affect coherence properties of colour centres since dangling bonds and other surface defects create non-controllable noise. Therefore,
a trade-off has to be made between shallowness, with the accompanying increase in interaction strength with the probe, and the unavoidable decrease in coherence time of the NV. Furthermore, there exist techniques like correlation spectroscopy [181] or quantum heterodyne detection (Qdyne) [182], where the sensing capability is limited by $T_1$ times or the stability of an external clock, respectively.
Part II

Methods
4 Fabrication of synthetic diamond and colour centres

This chapter focusses on the methods used to produce PECVD grown, isotopically controlled diamond material containing labelled NV centres and the surveillance instruments involved to monitor the deposition process in-vivo. Therefore, a quick overview of different diamond substrates is given, before the employed PECVD system is presented with a specific focus on workflow, vacuum system, temperature control and gas analysis via a mass spectrometer. The controlled creation of colour centres by PECVD and ion implantation technique as well as possibilities to terminate the diamond surface are discussed in the latter part of this chapter.

4.1 Diamond substrates

![Figure 4.1: Overview of different diamond substrates used in this work. Type Ib substrates from Sumitomo, with a high nitrogen concentration and transparent Type Ila diamond substrates provided by Element 6, New Diamond Technology and Applied Diamond Inc.](image-url)
As discussed in section 2.2, homoepitaxial PECVD diamond growth processes require a substrate which provides the diamond lattice kept during the growth. Synthetic diamond is available from several suppliers, and it is convenient to use an existing diamond lattice as a starting point for high-quality crystalline diamond PECVD overgrowth and the controlled fabrication of defect centres. Nevertheless, there are other approaches, using different substrate materials like silicon (Si) [183] or Si, YsZ (yttria-stabilised zirconia), Ir (iridium) stacks [184], aiming to overcome the lattice constant mismatch between different semiconductors. The diamond films produced in this work are exclusively grown on diamond substrates provided by the following companies: Sumitomo Electric Industries (Sumi), Element Six (E6), New Diamond Technology (NDT) and Applied Diamond Inc. (API). Photography showing a selection of them can be found in figure 4.1. Sumitomo crystals contain much nitrogen and belong to Type Ib (typical size $\sim 3.0 \times 3.0 \times 0.5 \text{mm}^3$), whereas the other suppliers delivered IIa type material (typical size $2.0 \times 2.0 \times 0.5 \text{mm}^3$). An overview of the physical properties of different substrates can be seen in table 4.1. Specifications given in this table 4.1 are from supplier’s datasheets. All diamonds were scratched with a mark on the backside to distinguish the processed from the unprocessed side and used as received, by following the operation chart shown in figure 4.7. In a first step, the diamond substrates are cleaned in the university's clean-room, before they are mounted in the reaction chamber. The latter and the whole growth procedure is described in the next section.

<table>
<thead>
<tr>
<th>Supplier</th>
<th>Roughness ($R_a$)</th>
<th>$[N]_{(100)}$</th>
<th>$[N]_{(111)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sumitomo</td>
<td>N.N.</td>
<td>100 ppm</td>
<td>not used</td>
</tr>
<tr>
<td>Element 6</td>
<td>5 nm</td>
<td>5 ppb</td>
<td>N.N.</td>
</tr>
<tr>
<td>New Diamond Technology</td>
<td>5 nm</td>
<td>10 ppb</td>
<td>10 ppb</td>
</tr>
<tr>
<td>Applied Diamond Inc.</td>
<td>2 nm</td>
<td>not used</td>
<td>1 ppm</td>
</tr>
</tbody>
</table>
4.2 Plasma-enhanced chemical vapour deposition (PECVD) system

Figure 4.2: Schematic drawing of the PECVD reactor set-up. The vacuum chamber with the substrate holder and the internal cavity builds the main part of the system. Vacuum pumps, microwave generator, gas inlets, ventilation nitrogen and gate valve complete the necessary parts for diamond growth. For analysis, a pyrometer and mass spectrometer are also attached to the chamber.

The diamond PECVD system, illustrated in figure 4.2, consists of a vacuum chamber, volume approximately two hundred litres, which can be pumped by a pre-pump (Edwards ixL 120) and a turbopump (Pfeiffer Vacuum TPU 330S) to a minimum
pressure of \( p = 1.0 \times 10^{-7} \) mbar. The chamber and the pumping stand are separated by a gate valve (manufacturer VAT), which can be bypassed during a growth process. A microwave cavity is placed inside the vacuum chamber, with the top part consisting of a fixed quartz window and the bottom part of a molybdenum plate (sample plate) on a movable table, setting the cavity height. The table position can be controlled from the bottom with a sub-millimetre screw. The table itself is equipped with a graphite heater whose temperature can be controlled with an external power supply. A thermocouple in contact with the sample plate underneath the heater and an infrared pyrometer (Optra CT Laser) measure the substrate temperature independently. The microwave generator (Muegge MW-GPEOM77B) works at a frequency of 2.46 GHz and the output power can be adjusted up to 6 kW. A microwave guiding structure (AsteX standard type) couples the microwave field via a cone through the quartz window [65]. Gas inlets are installed at the top of the resonator, and an overview of the available gases is given in figure 4.3. A mass spectrometer (Pfeiffer Vacuum QMS 100) monitors the gas composition during the growth. Especially individual gases can be analysed regarding their purity since, for example, isotopically pure methane gases contain impurities in the form of carbon oxides or nitrogen. The whole chamber can be vented for mounting and unmounting with an extra nitrogen gas supply.

The composition of the created diamond is highly dependent on the purity and ratio of the gases used during the PECVD process. The diamond growth rate, the crystallinity and quality of resulting diamonds can be modified by changing the methane concentration during a PECVD process. Performing this is achieved by varying the flow rate of particular gases, which is achieved by the usage of mass-flow-controllers (MFC, MKS Instruments GmbH type MF1). Such an MFC is used for each individual gas (M1-M8) followed by a security valve (V1-V8) to prevent leakage from any unwanted gas. The available gases corresponding to the gas lines 1-8 are hydrogen, natural abundance methane (98.9% \(^{12}\text{CH}_4\), 1.1% \(^{13}\text{CH}_4\)), natural abundance nitrogen (99.6% \(^{14}\text{N}_2\), 0.4% \(^{15}\text{N}_2\)), isotopically enriched nitrogen (98% \(^{15}\text{N}_2\)), 99.9% \(^{12}\text{C}\) enriched methane, 99.99% \(^{12}\text{C}\) enriched methane, 99.999% \(^{12}\text{C}\) enriched methane and 99.9% \(^{13}\text{C}\) enriched methane. The gas mixture is adjusted with the MFCs, enabling any combination of the described gases which is then injected into the reaction chamber. Note that principally every desirable \(^{13}\text{C}\) concentration within the grown diamond is possible.
4.2 Plasma-enhanced chemical vapour deposition (PECVD) system

Figure 4.3: Gas mix plate with all the available gases. Each gas line is specially cleaned before it is mounted on the set-up and contains in addition to the MFC (M) a gate valve (V) to prevent unwanted leakage from gas lines not selected to participate in the growth. Currently, eight hydraulic valves are installed on the gas lines equipped with 1: hydrogen, 2: methane, 3: nitrogen, 4: nitrogen $^{15}$N, 5,6,7: $^{12}$C isotopically enriched methane (3.0), (4.0), (5.0), 8: $^{13}$C isotopically enriched methane (3.0).

4.2.1 Vacuum pumping station

The vacuum system attached to the growth chamber is of prime importance as the crystal quality and composition depend on the gas concentration in the reaction chamber, which is of course mainly dominated by hydrogen and methane. Any residual gases or elements will eventually also be present in the final diamond crystal and can lead to unwanted effects, such as lattice distortion, strain or even a shift of the charge carrier equilibrium.

The elimination of uncontrolled doping is a major goal in the process of PECVD diamond growth. In order to quantify the number of undesired impurity atoms, the so-called leakage rate $Q_L$ is consulted. This rate is measured in mbar l s$^{-1}$ and can be interpreted as a constant flow of a gas mixture of unknown origin or composition.
4 Fabrication of synthetic diamond and colour centres

![Graph showing leakage rate vs evacuation time](image)

**Figure 4.4:** Determination of the leakage rate repeatedly measured for 180 minutes for each point at different pumping times. Blue coloured points correspond to experiments at room temperature and red coloured ones to an elevated temperature of 750 °C. The squares ($Q^0_L$) indicate the status quo before the build-up of the new modified vacuum system (round markers, $Q^1_L$) (details in the main text).

Evacuation time, before the pumps were stopped of
(a) 21 hours, $Q^{a,0}_L=4.99\times10^{-5}$ sccm and $Q^{a,1}_L=1.65\times10^{-5}$ sccm.
(b) 48 hours, $Q^{b,0}_L=9.90\times10^{-5}$ sccm and $Q^{b,1}_L=3.51\times10^{-5}$ sccm.
(c) 3 hours $Q^{c,0}_L=3.84\times10^{-2}$ sccm and $Q^{c,1}_L=1.93\times10^{-2}$ sccm.
(d) 18 hours $Q^{d,0}_L=2.24\times10^{-2}$ sccm and $Q^{d,1}_L=7.45\times10^{-3}$ sccm.

Note that all vacuum systems suffer from this problem where the most likely origins are the opening and closing mechanisms of the chamber. As a matter of fact, the components used for doors and other loading fixtures are *per se* not perfectly isolated. The leakage rate is also used to define different classes of vacuum systems [185], ultra-high vacuum (UHV) systems for example have a $Q_L < 10^{-6}$ mbar l/s. If all pumps are shut down it would then take $10^6$ seconds or 11.5 days until 1 sccm of leakage gas entered the system. The lower the leak rate, the better the vacuum system. An experiment to measure the leakage rate is to pump the system to vacuum and to isolate the chamber from the pumping system. Due to leakage, the pressure will increase with time, from which the leakage rate $Q_L$ can be calculated.

In our experiments the pressure is recorded repeatedly for a total measurement time of 3 hours, for different starting conditions and the resulting leakage rates in
sccm = \frac{mbar\times l}{60s} are shown in figure 4.4. Measurements a and b are performed under ambient conditions, whereas measurement sets c and d are recorded at a preheated chamber at a temperature of \( T = 750 \, ^\circ C \). The pale-coloured squares in figure 4.4 indicate the recording before the modification and improvement of the vacuum pumping system. These improvements include the usage of a dry pump, the direct connection of the turbopump to the chamber and the adding of a gate valve (VAT valve in figure 4.2) which separates the chamber from the pumping system. It can be concluded that the leakage rate depends strongly on the chamber temperature and slightly on the evacuation time suggesting a big influence from the chamber walls and the graphite heater, which gas out during the measurement. The leakage rate for the heated case is three orders of magnitude higher than for the room temperature experiment whereas a longer evacuation time leads to an improvement factor of 1.55 on average for the room temperature experiment and 2.13 for the high-temperature experiment. Furthermore, it seems that the improvement by the introduction of the gate valve scales with the same factor of about 2.6 on average. In conclusion, it has been shown that the introduction of a gate valve diminishes the leakage rate and therefore improves the growth conditions in respect of purity and quality.

4.2.2 Temperature control: Pyrometer

As described in the previous sections, the temperature control during the PECVD diamond growth process is of major importance for the quality and composition of created diamond layers. In order to monitor the temperature development during such a process, an infrared pyrometer is used. It has to fulfil a number of requirements which are given by the design of the PECVD chamber itself and discussed briefly in the following (compare also figure 4.2).

In order to cover a temperature range from 385 - 1600 \(^\circ C\), an Optris CT Laser CF4 (OPTCTL2MHC-F4) measuring head is used. The wavelength of 1.5\( \mu m \) is set in a way, that the glass window does not absorb. Its focusing optics allows the laser beam to pass through one of the holes of the internal cavity and still having a focus size of 1.5mm\(^2\) on the diamond sample itself, the actual point of interest, placed approximately 45cm away from the pyrometer. The signal is processed in a provided electronic controller box and can be monitored with additional software. A typical temperature profile of a PECVD growth process is shown in figure 4.5.
Figure 4.5: Temperature development in the growth chamber, measured with an infrared pyrometer during different phases of the PECVD process (Phase I = Gas in, Phase II = MW start, Phase III = Methane in step and Phase IV = after stopping the MW plasma).

The first Phase I corresponds to the preheating step illustrated in the operation chart in figure 4.7, where the endpoint marks the temperature of the hydrogen-filled camber. Phase II shows the temperature increase due to the ignition of the MW plasma. A saturation effect can be observed after approximately 5 minutes. Phase III represents the actual growth process. After preparing the hydrogen termination in Phase II, methane is added to the growth, and the step flow growth is launched. The growth time can be selected freely, and the growth is ended by switching off the MW plasma (start of Phase IV). The graphite heater is switched off immediately, and the chamber rapidly cools down to room temperature, which cannot be completely monitored due to the specifications of the pyrometer measurement head (lower detection limit is 385 °C).

4.2.3 Gas composition analysis: Mass spectrometer

Besides the growth temperature, the gas composition inside the growth chamber is of tremendous importance for the success of high-quality diamond growth. As discussed in the beginning of this section 4.2, the composition of the different gases is created by MFCs on the gas mix plate (see figure 4.3). Monitoring the actual
gas composition is by far more important though, since residuals from the chamber walls or impurities in the source gases contribute as well to the outcome of the PECVD process. For this purpose, a mass spectrometer (Pfeiffer Quadrupole QMS 100) is attached to the growth chamber with a detection range from 1-100 amu. A typical mass spectrum of the carrier gases can be seen in figure 4.6(a). A palladium filter purifies the hydrogen gas, and as can be seen from the measurement, only peaks at the hydrogen mass numbers one and two are visible. In comparison, the $^{12}$C enriched methane gas also contains hydrogen and nitrogen (peaks around 28), besides the characteristic methane peaks (ranging from mass number 12-16). This is in good agreement with the manufacturers gas analysis which confirms the presence of nitrogen of the order of 70 ppm.

For NV engineering purposes it is crucial to isotopically distinguish $^{12}$C from $^{13}$C carbon species to be able to tune the amount of nuclear spin carrying $^{13}$C atoms in the resulting diamond lattice. Depending on the application, a spin-free $^{12}$C lattice or the interaction with $^{13}$C nuclei is wanted. By looking at the mass spectrum, this task can be fulfilled, as can be seen in figure 4.6(b). Three different methane gases with controlled $^{13}$C content are analysed ranging from 0.01%, over 1.1% to 99.9%. The grey box marks the position of the $^{12}$C and $^{13}$CH$_4$ related peaks in the spectrum.
Note that the absolute heights of the peaks cannot be compared to each other as the calibration of each measurement is different. Nevertheless, this technique gives an insight into the dynamics of the PECVD growth as it resembles an accurate, real-time control technique ensuring stable and reproducible growth conditions.

### 4.2.4 Operation chart

![Operation chart of the PECVD diamond growth process, including sample preparation in form of cleaning, mounting, processing and unmounting of the diamond substrate.](image)

As diamond is hydrophobic, the first step is the removal of contaminating particles by rubbing the diamond’s surface with a cotton bud consecutively in acetone and isopropanol. To further remove organic residuals, the diamond is treated in a strong oxidising agent, namely piranha acid (peroxymonosulfuric acid, a mixture of hydrogen peroxide $\text{H}_2\text{O}_2$, 20 ml and sulphuric acid $\text{H}_2\text{SO}_4$, 40 ml), for 15 minutes. Next treatments are chromo sulfuric acid (40 ml $\text{H}_2\text{SO}_4$ and 40 ml $\text{CrO}_3$ for 30 minutes at 100°C) and aqua regia (nitric HNO$_3$, 10 ml and hydrochloric acid HCl, 30 ml for 120 minutes at 100°C) to remove graphite, gold and platinum from the surface. Silver and copper are removed by a mix of ammonia (NH$_4$OH, 20 ml) with hydrogen peroxide (20 ml, 15 minutes at 120°C) whereas silicon can be removed by KOH (potassium hydroxide, 100°C for 15 minutes). Another piranha step is included to ensure the diamond is not contaminated with any organic substances before a final examination is performed under an optical microscope. Only if there are no marks, residuals and left-overs on the diamond surface, it is mounted in the PECVD reaction chamber.
4.2 Plasma-enhanced chemical vapour deposition (PECVD) system

In order to prepare the chamber for mounting of the samples, the graphite heater is switched on in order to preheat the chamber walls which prevents the deposition of water from outside, once the chamber door is opened. After the heater is cooled down to ambient temperature, potential penetrated oxygen has no corrosive effects. In the next step, the chamber is vented with nitrogen. The diamond substrate is then mounted on the molybdenum substrate holder, and the chamber is evacuated to a base pressure of $10^{-7}$ mbar, which takes roughly eight hours, as the volume of the chamber is approximately 200 litres. The actual growth step starts again with slowly preheating the chamber to $750\,^\circ\text{C}$ with simultaneous pumping to keep the vacuum in the $10^{-7}$ mbar regime. When the target temperature is reached, the chamber is flushed with hydrogen until the process pressure is hit, which typically lies in the range of 20-60 mbar. The microwave generator is switched on, and under the right conditions (pressure, temperature, resonator height, microwave frequency and power) a plasma is ignited above the diamond substrate. This hydrogen plasma is for self-sustaining stabilisation by allowing steady-state conditions such as reverse and forward power matching, pressure and temperature. It also creates a hydrogen-terminated diamond surface which depicts the starting point for the growth process (in detail explained in section 2.3.1). The actual growth process is started by adding a carbon source to the chamber, methane in our case. The temperature profile of such a growth process can be seen in figure 4.5. As described above, it is possible to include impurities into the diamond lattice, such as nitrogen, which can be achieved by adding nitrogen gas during the growth. The nitrogen is built into the grown layers and can form nitrogen-vacancy centres on demand.

The growth process is stopped by switching off the microwave generator, and the deposition stops immediately. The system is cooled down, pumped to high vacuum ($10^{-7}$ mbar) and the chamber walls are preheated again by using the residual heat of the chamber. This cooling down process is also measured with the pyrometer and shown in figure 4.5. Nitrogen is used as vent gas again and the sample can be unmounted and further processed (see sections 4.3.1 and 4.4) or investigated with the confocal microscopy set-up (see section 5.3).
4.3 Controlled creation of nitrogen-vacancy centres

The manufacturing of synthetic diamond is an important task for many industry branches, but for scientific purposes, the main interest lies in the tailored to need engineering of colour centres and their spin bath environments. To compete and imitate the natural random creation process during the diamond genesis, two state-of-the-art techniques evolved, which are up for the task of controlled colour centre creation. Both of them are described in this section, including a brief discussion regarding their potential usage in certain fields of application. Note that the main focus of this section lies on the creation of NV centres, but the techniques can be expanded to other colour centres from table 2.2.

4.3.1 Ion implantation and annealing

![Diagram of ion implantation and annealing](image)

**Figure 4.8:** Schematic image of ion implantation. (a) Desired target atoms are ionized and accelerated onto the high quality, low impurity containing IIa type diamond substrate. (b) After a subsequent high-temperature annealing step colour centres are formed locally and confined depending on the implantation pattern and energy.

The first and probably more widely used technique is nitrogen ion implantation, where nitrogen atoms from a gas or solid source are ionized and accelerated onto an existing diamond surface, schematically illustrated in figure 4.8(a). By this bombardment, nitrogen ions enter the diamond and stop due to collision events with carbon lattice atoms which on the other hand create vacancies. The stopping range (depth) of the ions depends strongly on the acceleration energy, which can be easily tuned to create NV centres in a desired depth below the diamond surface. An ion energy of 2.5 keV gives an average depth of 6 nm for example. A post-implantation annealing procedure, during which the vacancies become mobile...
and can be trapped by nitrogen atoms, is necessary for the formation of nitrogen-vacancy centres which can be generated inside the diamond with nanometre precision (figure 4.8(b)). The annealing temperature should be above 650 °C [186,187] but the effect of higher annealing temperatures on the formation yield and NV properties is still under investigation [140,188,189]. Nevertheless, the implantation of nitrogen conglomerates such as molecules (N₂) and adenine (C₅N₄H₉) to create pairs and triples of NV centres has been shown [190,191]. Implantation through masks or lithographically engineered holes [192,193] reduces the vertical separation of the nitrogen atoms and supports the creation of strongly coupled NV pairs. Additionally, the co-implantation of carbon, oxygen, fluorine or phosphorous has been performed to study the effect on creation yield and coherence properties of NV centres [190,194]. However, the penetration of nitrogen ions destroys the diamond lattice leading to the creation of defects which do not heal out entirely during the annealing process. As a result, this reconstructed diamond lattice acts as a source of decoherence for the created NV centres. Furthermore, the damage is not uniform, as the implantation beam is broad and billions of ions are implanted at the same time, which leads to a different spin bath environment for each created colour centre. Especially shallow implanted NVs suffer from short and not uniformly distributed coherence times T² [195], a reduced creation yield [196] and a decreased charge state stability [179]. Typical creation yields are on the order of several per cents, where higher implantation energies also increase the yield [166,196]. Increasing this yield was subject of many studies during the last decade, where methods as high-temperature annealing [195], surface termination [197] or lattice charging [198] were used. The usage of high energy implantation in the MeV regime leads to an elevated creation yield of 50% [199]. Recently it was reported that the co-implantation of sulphur atoms leads to creation yields up to 75% [200].

4.3.2 Nitrogen δ-doping during PECVD

The second technique, namely the nitrogen delta doping during a PECVD diamond growth process, has several advantages over ion implantation technique which are highlighted in the following. The crystal quality in the vicinity of the as-grown NV centres is higher than for implanted ones as no or only little damage from the growth is introduced. In situ annealing during growth at approx 1000 °C leads to direct
annihilation of vacancies when they are produced, and this prevents the formation of di-vacancies or vacancy clusters which are thermally very stable [97]. As a result, the produced colour centres are electrically stable and have longer coherence times, limited by the natural abundance (1.1 %) $^{13}$C nuclear spins (nuclear spin $I = 1/2$). It was shown that NVs within a 100 nm thick, PECVD grown layer could reach $T_2$ times up to a millisecond [177]. By using a $^{13}$C depleted diamond even longer coherence times can be measured [174]. However, the later mentioned NVs are buried deep in the diamond crystal (few micrometres), so they are useless for sensing spins on the diamond surface as the magnetic dipole-dipole interaction rapidly decays with distance and is insignificant after few tens of nanometres. In order to solve this problem, the delta-doping method can be used where nitrogen gas is let into the growth chamber at the last stage of the PECVD growth. This technique enables NV creation as close as a few nanometres to the diamond surface [74, 201], which show, in comparison to implanted ones, improved properties regarding charge state and long $T_2$, limited mainly by the surface spin bath [202].

4.3.3 Ion implantation or PECVD growth?

The two techniques for NV centre creation described in sections 4.3.1 and 4.3.2 should not be considered as competing. Indeed there are good arguments for either of the presented techniques, but basically, the decision which one is more favourable depends on the application and the particular requirements. In principle the following rules of thumb can be adhered to: The implantation technique is more favourable if lateral control of created colour centres is necessary, for example, by creating pairs or arrays with a fixed distance. Also, shallow ones for sensing applications seem to work better with implantation. The maximum NV centre density in ensembles is higher (3 ppm [203] compared to 1 ppm in CVD grown diamonds [31]), as the ion dose can be increased until the graphitization threshold is reached (vacancy concentrations on the order of $10^{23}$ cm$^{-3}$ [204]). Due to a highly damaged crystal lattice, diamond is transformed under thermal treatment to graphite. Furthermore, the ion implantation technique is not limited to usage of nitrogen ions, so basically any atom can be implanted into a diamond as long as it is abundant in gas or solid phase. Over the past few years, numerous colour centres have been created by this technique, amongst them SiV, GeV, SnV and PbV.
Delta doping during the PECVD process is more favourable if a thin colour centre layer is needed in more or less arbitrary distance to the surface. Also, the coherence properties are improved since the diamond lattice was not exposed to bombardment, and the intact version depicts a lesser source of noise. And finally, the probably most significant advantage of PECVD technique is the possibility the create preferentially aligned colour centres along one crystal direction, as shown for NV centres [135,136,138–140,205].

More and more work exploit advantages of both techniques and make use of the synergy effect between the production methods which mainly resolves the trade-off situation between a high spatial accuracy of shallow implantation with shorter spin lifetimes and deep in the diamond buried NVs with worse positioning accuracy but better spin properties. Recently, there were introduced a couple of other techniques which enable confined NV creation, among them the laser writing of NVs, where a nitrogen-doped diamond layer is the target of an intense laser beam which is used to create vacancies [206,207] locally. An additional annealing step leads to NV creation. Another technique is by helium ion implantation which has the same working principle of locally creating vacancies for nitrogen activation inside doped diamond layers [208].

Another known point is that commercially available polished diamond substrates possess subsurface polishing damage [209,210] which limits coherence properties of implanted shallow NVs. A buffer layer created by PECVD can help to overcome this problem. Also, PECVD overgrowth of shallow implanted NV centres, and especially created NV pairs, combines the high lateral positioning with the possibility of diminished surface noise due to a burying effect from PECVD [211,212].

Another way to control the diamond surface and therefore influence the created shallow NV centres is by surface termination, which is presented in the next section.

4.4 Surface termination

The nitrogen-vacancy centre in diamond is present in different electronic configurations as described in section 3.1. The negatively charged configuration is the desired one since it is usable for quantum applications, especially for the detection and sensing of magnetic fields. Depending on the presence or absence of electrons from
the host lattice it can be found in NV$^-$ or NV$^0$ charge state. Also, the presence and successful stabilisation of the NV$^+$ state has been shown [213]. In experiments where the NV centre is illuminated with green laser light, a constant back and forth conversion between the negative and neutral charge states has been observed, where the NV$^0$ is present approximately 30% of the time [141,214]. By optical pumping and the usage of differently coloured lasers, the charge state of the NV can be switched in favour of the negative one. Spectral stability enhancements up to a factor of four have been reported [215].

From a material scientists point of view, the nearby solution to stabilise the charge state is by increasing the number of electrons present in the diamond host lattice rather than to post stabilise the charge state artificially, even though the latter can be used for active switching on both directions during the experiments. Placing donors and acceptors in addition to the desired NV centres inside the diamond has been shown to affect the charge state as well, where the presence of boron (electron acceptor) promotes the presence of NV$^0$ and the doping with phosphorous (electron donor) the presence of NV$^-$ [94].

If NV centres are close to the diamond surface, also referred to as shallow NV centres, the coherence properties are very poor, and charge state fluctuations increase, probably due to the spin wise uncontrolled diamond surface. The study of this surface-induced noise [216] is of major importance for the fabrication of shallow NVs. At the diamond surface, the lattice symmetry is broken, and the presence of dangling bonds and other charge traps detract the electron borrowed from a donor in the diamond lattice [217]. As a result, the probability of finding the NV centre in the unfavourable neutral charge state is increased. On top of that, the surface comes up with several different undefined electromagnetic noise sources which directly affect the coherence properties of the surviving negatively charged NV$^-$ centres.

In order to exploit the benefits of shallowly produced NV centres, it is necessary to stabilize the charge state fluctuations, as illustrated in figure 3.2. A method to do so is the diamond surface termination, where it is attempted to finalize the last layer of carbon atoms and the involved dangling bonds with a defined atom. These ideally possess a high electronegativity by which an electron absorbent surface is changed to a repulsive one [197,218–221].

Note that this surface modification to enhance the charge state stability is just not limited to NV centres in bulk diamond, but applies to the whole variety of colour
centres. For example, the spectral diffusion of silicon-vacancy centres in nanodiamonds was successfully decreased by using proper surface termination [222].

There are several proposals on how such a treatment should be performed, and mainly they can be categorized into two main groups. The first group contains wet chemical treatments where diamonds are exposed to highly reactive liquids as acids or bases, whereas the second covers dry chemical treatments which alter the surface composition using gas plasma discharges. We mainly focus on two different plasma termination processes, where the first atomic layers of the diamond are etched very gently to exchange the termination.

4.4.1 Reactive ion etching (Mu-etch)

![Diagram of reactive ion etching](image)

**Figure 4.9:** Principle of reactive ion etching. An RF plasma is generated between two electrodes which create an electric field to accelerate the ions onto the target sample (inset). Additional chemically active species effectuate an anisotropic etching of the diamond surface, leading to a terminated or structured surface, depending on the process parameters.

Reactive ion etching (RIE) is a state-of-the-art low-pressure technique to etch various semiconductor materials including silicon, germanium, gallium arsenide and diamond. The dry etching procedure thereby combines two different etching mech-
Fabrication of synthetic diamond and colour centres

Mechanisms, namely physical ion bombardment and chemical etching by reactions of the ion species with the surface atoms. Reactive ions are created by igniting a radio frequency driven plasma of the process gas atoms which are introduced into a vacuum chamber. The created ions are further accelerated by an electric field generated by two electrodes, as illustrated in figure 4.9. Due to this ion bombardment, the etching is directed and therefore considered as anisotropic. The additional chemically active species on the surface lead to higher etching rates. RIE can be used to structure the diamond surface to create pillars, narrow channels or structured diamond tips which can then be used for scanning probe magnetometry, for example, [223]. Exemplary shown are triangular-shaped diamond pillars in the scanning electron microscopy (SEM) images in figure 4.10. Such structures could potentially be used to suppress phonon modes in silicon-vacancy centres in diamond and therefore prolong their excited state lifetime. A low power RIE process with a short exposure time can be used to terminate the diamond surface. In this work, two different RIE terminations are explored, namely an oxygen termination using O$_2$ source gas and fluorine termination using CF$_4$ gas. The quality of the surface terminations is measured via X-rays on the one hand (see section 5.1) and by investigating the stabilising effect on NV centres on the other hand (section 6.2).

Figure 4.10: SEM images of triangular shaped pillars, etched with the RIE technique (O$_2$ gas) into the PECVD overgrown surface of ⟨100⟩ oriented diamond. (a) Top view. (b) Side view with an angle of 55°.
4.4.2 Inductively coupled plasma (ICP PlasmaLab System 100)

Another technique which is used to create a stable surface termination is the inductively coupled plasma (ICP) process. In contrast to the RIE process where the plasma is generated between two accelerating electrodes, the plasma, in this case, is created inductively. Therefore, there is no bias voltage and no induced ion bombardment, which can harm the first few nanometres of the diamond surface. Intact diamond surfaces are crucial for the usage of shallow NV centres, only a few nanometres below the diamond surface which suffer from surface damage as discussed before. However, their shallowness is a problem, since they can easily be removed at high RIE powers or longer exposure times. Fluorine terminations using SF$_6$ inductively coupled plasma are compared to fluorine, and other terminations produced by RIE and are intensively studied regarding stabilization effect on shallowly produced NV centres by PECVD method in section 6.2.
5 Diamond and colour centre characterisation methods

This chapter focusses on the characterisation of the homegrown PECVD diamond layers with a particular focus on the nitrogen incorporation from the gas phase into the solid diamond. Several techniques and methods are presented to analyse the diamond composition, as well as the diamond surface. In the last part, a system to analyse the diamond on the nanometre-scale is presented, namely, the confocal microscope, which enables monitoring of single defects such as NV centres inside the diamond layers. By detecting the fluorescence signal of NV centres, it is also possible to investigate the magnetic environment in close vicinity of the defect and in the case of shallow ones even regions outside of the diamond.
5.1 X-ray photoelectron spectroscopy (XPS)

The X-ray photoelectron spectroscopy (XPS) is a well-known method to determine the chemical composition of solid-state systems or rather their surface, which is based on the photoelectric effect where electrons are emitted after light illumination onto a target material. Kai M. Siegbahn received the Nobel price in 1981 for the verification of Albert Einstein’s theory that electrons of an atom can be separated from their nucleus by providing enough energy [224]. This work also led to the first high-resolution XPS instruments, which nowadays are commercially available. The experimental set-up for such an XPS instrument is schematically illustrated in figure 5.1. An X-ray beam is focussed on the diamond’s surface, which causes electron emission if the photon energy is higher than the ionisation energy. Emitted electrons are sent to an analyser where electrostatic lenses are used to filter one particular electron energy. Only electrons with this very energy are detected by the detector. The energy can be tuned by the analyser, and so a spectrum can be generated for a wide energy range. The result of this measurement is a plot of the number of detected electrons against their binding energy, as illustrated in figure 5.2. Since the energy of the used X-ray photons $E_{\text{photon}}$, usually in the keV-MeV
5.1 X-ray photoelectron spectroscopy (XPS)

Figure 5.2: Different XPS spectra are showing the presence of different atoms bond to the diamond’s surface. Surface termination with hydrogen, nitrogen, oxygen and fluorine were examined during this work. The peak positions correspond to the C1s, N1s, O1s and F1s electrons and are marked with vertical dotted lines.

range [225], as well as the energy of the emitted electrons $E_{\text{kin}}$ are known, the binding energy $E_{\text{bind}}$ can be calculated by

$$E_{\text{bind}} = E_{\text{photon}} - E_{\text{kin}} + \Xi,$$

where $\Xi$, often called work function, represents a specific correction factor dependent on the spectrometer and the used target material (diamond in our case).

The technique is used during this work mainly to analyse the diamond surface termination and to compare the coverage of different termination techniques. Surface termination was performed dry chemically by the PECVD, RIE and ICP techniques presented in section 4.4 and a summary of different termination processes is given in table 5.1. The XPS measurement verifies each termination atom and the corresponding peaks are marked in figure 5.2 to analyse the quality or degree of each termination procedure. It is reported that the surface terminations are of major importance for the stabilisation of shallow nitrogen-vacancy centres in diamond [197,218–221] and therefore the case of fluorine (F) termination is studied in more detail in this work (see also chapter 6).

With the XPS technique, it is possible to compare different F-terminations as for
Table 5.1: Overview of different surface termination methods and parameters used for the stabilisation of the charge state of shallow NV centres in diamond.

<table>
<thead>
<tr>
<th>Termination</th>
<th>Technique</th>
<th>Machine</th>
<th>Power</th>
<th>Pressure</th>
<th>Flow</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen (H₂)</td>
<td>PECVD</td>
<td>Roth &amp; Rau</td>
<td>0.72</td>
<td>22.5</td>
<td>200</td>
<td>4</td>
</tr>
<tr>
<td>Nitrogen (N₂)</td>
<td>PECVD</td>
<td>Roth &amp; Rau</td>
<td>1.2</td>
<td>25.0</td>
<td>400</td>
<td>5</td>
</tr>
<tr>
<td>Oxygen (O₂)</td>
<td>RIE</td>
<td>µ-Etch</td>
<td>0.1</td>
<td>0.13</td>
<td>100</td>
<td>2</td>
</tr>
<tr>
<td>Fluorine (CF₄)</td>
<td>RIE</td>
<td>µ-Etch</td>
<td>0.1</td>
<td>0.13</td>
<td>100</td>
<td>2</td>
</tr>
<tr>
<td>Fluorine (SF₆)</td>
<td>ICP</td>
<td>ICP 100</td>
<td>0.5</td>
<td>0.03</td>
<td>100</td>
<td>4</td>
</tr>
</tbody>
</table>

example, by using a CF₄ plasma with the RIE and by a SF₆ plasma with the ICP 100. This particular comparison is shown in figure 5.3, where we find clear C1s peaks at 285 eV for both of the procedures indicating an intact diamond surface. The F1s peaks are also visible at 687 eV, but with much higher intensity in the case of SF₆ (blue line), where the presence of oxygen is suppressed as well. This peak appears if PTFE (polytetrafluoroethylene) type polymers which are formed during the termination process. The shift of the C1s peaks (inset in figure 5.3 (a)) could be due to a charging effect suggesting a different chemical environment of the fluorine atoms for the CF₄ and SF₆ process. However, the SF₆ plasma process is superior as the surface coverage as well as the quality of the termination are improved.

In order to study the effect of the exposure time of the SF₆ plasma on the termination quality, figure 5.3(b) shows XPS spectra of differently treated diamond samples. In order to increase the visibility, the spectra are shifted vertically, and it is obvious that the peak positions of the C1s and F1s are the same, suggesting that there are no charge instabilities on the surface. Also, the relative peak heights and therefore, the surface coverage with fluorine stays nearly constant. A more detailed study, together with the effects on shallow NVs using this termination technique, are further discussed and presented in chapter 6. From this measurement, it can be concluded that even a short exposure time of four minutes is sufficient to cover the diamond surface with fluorine atoms, which also has the benefit that potential etching effects are kept to a minimum.
5.2 Secondary ion mass spectrometry (SIMS)

Besides the surface constitution, the actual diamond composition is of major interest, not only for the jewellery industry, as mentioned in section 2.1, but also for scientific applications. Ratios of carbon ($^{12}$C to $^{13}$C) and nitrogen isotopes ($^{14}$N to $^{15}$N) as well as the number of foreign atoms as hydrogen, boron or silicon change the physical properties of diamond and therefore both its financial and scientific value. Secondary ion mass spectrometry (SIMS) measurements are depth sensitive and reflect the actual diamond composition in each layer. The usage of different isotopes in the diamond substrate and the grown layer paves the way for material related results as the diamond growth rate, impurity concentration or doping efficiency and makes SIMS an indispensable technique to characterize PECVD grown diamond layers.

The SIMS method uses primary ions (for example Ga$^+$, Cs$^+$ or Ar$^+$) which are accelerated up to 30 keV on the target sample. By this bombardment secondary negatively charged particles are created which are mass filtered, for example by time-of-flight or quadrupole mass analysers. The detected ion current (using a Faraday cup detector with electron multiplier) represents the quantity of a certain element.

**Figure 5.3:** (a) Comparison of fluorine terminations. The blue and green curves show XPS spectra of samples treated in SF$_6$ and CF$_4$ plasma, respectively. In order to increase visibility, the spectra are shifted vertically. Higher fluorine, as well as the lack of the oxygen peak, mark an improved surface termination by using the SF$_6$ treatment. The inset shows the shift of the central C1s peak for the two processes. (b) XPS spectra for samples treated with different SF$_6$ plasma procedures. Blue, red and black curves correspond to plasma exposure times of four, six and eight minutes. The inset shows a zoom-in of the F1s peak.
Figure 5.4: SIMS measurement of overgrown samples X and Y, where the substrates shown in yellow are Ib type (100) diamonds. The grey part represents a clean diamond layer without any impurity doping and the red part a nitrogen-doped layer. The blue curve shows the nitrogen and the black curve the hydrogen profile. (a) Sample X: The methane concentration for this overgrowth was set to 0.5% and the nitrogen concentration in the doped layer to 0.08% in respect to the hydrogen flow rate. (b) Sample Y: Methane concentration was set to 0.05% and nitrogen to 0.05% of the hydrogen flow. The resulting nitrogen content in the grown layer is lower than in the substrate, and the layer thickness is smaller than in the process shown in (a).

present in the target material, with a detection limit down to ppm or even ppb. This detection limit is actually the biggest challenge as nitrogen in diamond often can be detected with a noise level on the order of $10^{18}$/cm$^3$. But, as shown in table 4.1 the substrates used during this work contain nitrogen on the order of $10^{17}$/cm$^3$. Therefore, the diamond substrate and the nitrogen-free diamond layer cannot be distinguished. Luckily there are research institutions which reach a detection limit of $10^{16}$/cm$^3$ - MST company, Japan and Loughborough Surface Analysis Ltd., United Kingdom. All SIMS measurements shown in this thesis are performed in their laboratories.

The nitrogen profile is the most interesting for us as the overall goal is to control the creation of NV centres on the nanometre scale and this is directly connected to the amount of nitrogen in the PECVD layers. The result of a typical SIMS measurement is shown in figure 5.4(a), where clearly three different areas are labelled. The yellow area represents the signal from the diamond substrate; the grey area corresponds to an intrinsically grown inter-layer, and the red coloured area resembles a nitrogen-doped one. This fits nicely to the growth recipe for this sample which is summarised in table 5.2. The growth rates for the two areas can be directly extracted by correl-
5.2 Secondary ion mass spectrometry (SIMS)

ating the layer thicknesses to the corresponding growth times. As a result, we can
calculate the growth rate $\nu_{gr}$ by

$$\nu_{gr} = \frac{d_{\text{layer}}}{t_{\text{growth}}}.$$ (5.2)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Doping</th>
<th>$\text{H}_2$</th>
<th>$\text{CH}_4$</th>
<th>$^{15}\text{N}_2$</th>
<th>$t_{\text{growth}}$</th>
<th>$d_{\text{layer}}$</th>
<th>$\nu_{gr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>non-dope</td>
<td>200 sccm</td>
<td>1 sccm</td>
<td>—</td>
<td>6 h</td>
<td>1126 nm</td>
<td>188 nm/h</td>
</tr>
<tr>
<td>X</td>
<td>N-dope</td>
<td>600 sccm</td>
<td>3 sccm</td>
<td>0.5 sccm</td>
<td>5 h</td>
<td>1927 nm</td>
<td>386 nm/h</td>
</tr>
<tr>
<td>Y</td>
<td>N-dope</td>
<td>600 sccm</td>
<td>0.3 sccm</td>
<td>0.3 sccm</td>
<td>24 h</td>
<td>680 nm</td>
<td>28 nm/h</td>
</tr>
</tbody>
</table>

It can be seen in table 5.2 that nitrogen can change the growth dynamics tremen-
dulously, as a fraction of 0.08% of nitrogen added to the standard growth gases,
doubles the overall diamond growth rate, which is in good agreement with previous
results [226, 227].

Another important conclusion of this first set of measurements is that the growth
rate, as predicted from the standard growth model (section 2.3.1), is highly depend-
ent on the methane concentration (0.5% for Sample X and 0.05% for Sample Y). Here, a factor of ten less methane in addition to a factor of 1.6 decreased nitrogen
content change the growth rate to 7.2% of the initial value.

Furthermore, SIMS measurements show the conversion from nitrogen in the gas
phase of the PECVD chamber to the nitrogen content in the final diamond sample.
This ratio is called the nitrogen doping efficiency $\zeta$ and its calculation is exemplar-
ily demonstrated for the two processes shown in figure 5.4 and makes use of the
following equation

$$\zeta = \frac{[\text{N}]}{[\text{C}]} \cdot \frac{[\text{N}_{\text{gas}}]}{[\text{C}_{\text{gas}}]}.$$ (5.3)

Here $[\text{N}]$ and $[\text{C}]$ represent the nitrogen and carbon amount in the diamond sample, whereas $[\text{N}_{\text{gas}}]$ and $[\text{C}_{\text{gas}}]$ describe the nitrogen and methane gas flows. For the first
Sample X, the equation fills:

$$\zeta_X = \frac{8.98 \times 10^{19}}{(2 \times 0.5)/3} = 0.153 \%,$$ (5.4)
whereas the doping efficiency for the second sample reveals $\zeta_Y = (1.11 \times 10^{18}/1.76 \times 10^{23})/2 = 6.3$ ppm. It seems that the doping efficiency directly correlates with the methane concentration, and it is reported that the N/C ratio is an important number for this [228,229]. The doping efficiency of delta-doped samples is rather low since the nitrogen amount inside the diamond is low. Also, it is questionable if this number is a good figure of merit regarding potential NV driven applications. Therefore, another way of improving the doping efficiency in favour of NV is only to consider the nitrogen content inside the diamond. The ratio of created NV centres right from the PECVD growth in relation to the nitrogen present in the form of P1 centres is a better benchmark for scientific applications of synthetic diamond. More details about this method and a distinct discussion are given in chapter 9.

Another intriguing effect is that the growth rate depends on the used diamond substrate. Besides the surface quality, measurable by the surface roughness $R_a$, the number of dislocations, and mainly the crystal orientation influence the growth speed and quality of produced diamond under the same plasma conditions. A variation of plasma power and the effect on the growth rate development is shown in figure 5.5. As expected from the standard growth model, an increase in plasma power leads to more agile carbon species on the diamond surface and therefore an increased growth rate. This increase is indicated by the linear fit to the black points in figure 5.5, where the slope gives the theoretical increase of the growth rate as 0.179 nm/h per Watt of input power. The experiments suggest that the growth rate seems to be the most critical parameter in order to describe diamond growth. All changes regarding the plasma conditions can be carried forward to a change in the diamond growth rate. Thus, it is not surprising that a change of the growth rate implies a different average nitrogen content in the particular samples as presented in figure 5.6. Specifically, a higher growth rate leads to higher nitrogen content in the diamond sample, where the highest value of approximately 470 ppm was achieved at a growth rate of 380 nm/h.

One should note that the given nitrogen content (isotope $^{14}$N) is averaged over the whole diamond layer produced on top of the diamond substrate. In this particular study, only $\langle 111 \rangle$ oriented IIa type diamond substrates from Element Six were used (for details see table 4.1). The study also compares the nitrogen content between usage of two different isotopically purified methane gases, namely 99.99 % purified $^{12}$CH$_4$ and methane with a natural abundance of 1.1 % nuclear spin carrying isotope $^{13}$C. It can be stated that in the case of natural abundance methane, a higher growth
5.2 Secondary ion mass spectrometry (SIMS)

![Graph showing growth rate vs. microwave power](image)

**Figure 5.5:** Influence of the microwave power on the growth rate of \langle 111 \rangle oriented substrates overgrown without any additional nitrogen doping. A higher microwave power leads to an elevated growth rate (black points), confirmed by a fit through the three points (red line). The increase is calculated to be $179 \text{ nm/h/kW}$. In order to stabilize the plasma conditions at very high power, the chamber pressure was increased to 52.5 mbar (black rectangle). The methane concentration $c_M$ was varied for one sample, and the growth rate drops to one-fifth of the original value (blue).

...rate is necessary to achieve the same nitrogen incorporation as for the isotopically modified one. One possible explanation could be that the latter contains nitrogen in the range of 70 ppm which is a result of the production process from Cambridge Isotopes Laboratories (CIL). The 99.99% $^{12}\text{CH}_4$ can be additionally purified by a zirconium heated getter filter, which is supposed to clean the source gas to a nitrogen content of below 2 ppb. Especially in the case of $^{15}\text{N}$ nitrogen doping in chapter 9 this is of particular importance.
5.3 Confocal imaging and NV electron spin manipulation

The previously mentioned techniques are mainly used to analyse the diamond’s surface and composition by averaging the corresponding signals over certain areas. The NV centre though is of atomic size, and in order to study it exclusively, an optical system with high spatial resolution is required. A confocal microscope fulfils this criterion and is described in the following as it is used for all NV related experiments in this work. A schematic representation of the core parts of the home-built optical confocal microscope set-up is shown in figure 5.7. The monochromatic light source of the microscope is a 517nm pulsed laser diode which, as the name implies, can be operated in a pulsed mode (with a rise time of 1.5ns) to create the necessary pulse shapes for NV experiments as discussed before (see section 3.3). The light leaving the optical fibre attached to the laser diode is collimated by an internal lens and is directed onto a 514/10nm bandpass filter for clean-up, meaning that spec-
5.3 Confocal imaging and NV electron spin manipulation

Figure 5.7: Schematic image of the confocal microscope set-up used for NV experiments. A green pulsed laser diode is focused via the movable objective lens onto the NV centre containing a diamond. The emitted red-shifted fluorescence light is focused via movable lens, pinhole and lens on the avalanche photodiode (APD). Scanning the objective lens and recording the photon signal by APD enables compilation of a confocal image of 200x200 \( \mu m^2 \) size.

Central components other than the desired ones are suppressed. A telescope, consisting of two lenses with overlapping focal planes, is used to expand the beam. Tuning the polarisation of the laser can increase the absorption of the NV centres (if NV axis is perpendicular to laser polarisation axis) and a \( \lambda/2 \)-plate is installed for this purpose.

A mirror guides the laser to the beam sampler, which transmits the red-shifted NV fluorescence and reflects the green laser excitation light onto the objective lens. The objective lens is movable in a way that it is mounted on a piezo stage with a scanning range of 200 \( \mu m \times 200 \mu m \times 100 \mu m \), which enables the creation of confocal images by focussing the laser on different positions on the diamond. The NV containing diamond is placed on a printed circuit board which allows microwave control (detailed illustration in figure 5.8). A permanent magnet to apply a bias field is mounted on a 3D positioning stage which allows alignment of the field in respect to the NV axis (parallel would be the desired configuration).

The red-shifted fluorescence light emitted by the NV centre is collected by the same objective lens and passes the dichroic mirror. A movable lens, mounted on a 3D manual micrometre screw stage, is used to focus the light on a pinhole with a diameter of 25 \( \mu m \), which filters light other than from the confocal plane. An additional lens creates a 1:1 image of the pinhole onto the avalanche photodiode (APD) by using the \( g = b = 2f \) condition, where \( g \) is the object, \( b \) the image and \( f \) the focal distance. A 645 nm long-pass filter is used to block possible fractions from the excitation laser and the diamond Raman lines (1\textsuperscript{st} order 555 nm and 2\textsuperscript{nd} order 599 nm) to
Diamond and colour centre characterisation methods

ensure that the single-photon counting device detects an NV optimised fluorescence image with single defect centre sensitivity.

As will be seen later in chapter 7, the size of the illuminated confocal volume is of significant importance in the determination of the size of NV ensembles. This illumination volume depends on the properties of the objective, like the numerical aperture (NA) and the diffraction index \( n \) of the immersion medium. The lateral \( \Delta x, y \) and axial \( \Delta z \) resolution of an ideal confocal microscope are given by [230]:

\[
\Delta x, y = \frac{0.44 \times \lambda}{NA}, \quad (5.5)
\]

and

\[
\Delta z = \frac{1.5 \times n \times \lambda}{NA^2}. \quad (5.6)
\]

Typical values for the numerical aperture (\( NA = 1.42 \)) and the diffraction index of the immersion medium which is mainly oil (\( n_{oil} = 1.517 \)) reveal the lateral and axial resolution to \( \Delta x, y \approx 160 \) nm and \( \Delta z \approx 580 \) nm respectively.

By moving the objective in small steps, it is possible to scan the sample and identify regions of interest on which further experiments can be performed. Such a confocal NV map is illustrated in figure 5.8 where NV centres are produced in a nicely arranged array by implantation through lithographically engineered nanoholes. Note that in this case, more than one NV centre is sitting in one array site.

**Microwave manipulation of the NV centre electronic spin**

As discussed in section 3.3, the electronic spin of the NV centre can be coherently manipulated if adequate microwave fields are applied. The set-up to perform such a task is illustrated in figure 5.8. Basically, the figure is a magnification of the right part of figure 5.7. The amount of the collected fluorescence light depends on the electronic spin state of the investigated NV centre.

A continuous-wave (cw) microwave is generated by a Rohde & Schwarz SMIQ source which is mainly used for ODMR measurements. The microwave pulses used for manipulation of the spin states are generated by an arbitrary waveform generator (AWG), amplified by a MW amplifier and transferred to the NV centre by an antenna. The later consists of a copper wire with a diameter of 20 µm which is tensed over the diamond substrate in the vicinity of the NV centre to be examined and
5.3 Confocal imaging and NV electron spin manipulation

Figure 5.8: Confocal set-up with the diamond sample (yellow coloured), containing the NV centres with their accessible electronic spins (blue circles with arrows), the microwave wire (copper), the excitation laser (green) which is focused onto the diamond by the objective lens and the NV centre, spin state-related, fluorescence light which is collected by the same objective (red). Additionally, a confocal image is shown, where NV centres are produced by nanohole implantation technique together with a pulsed ODMR and a Hahn echo experiment.

is connected to the circuit board strip lines by soldering. The entire experiment including the MW pulse creation is controlled by the Qudi software, which is a general, multi-operating software suite written in Python [231].

A scanning confocal image can be recorded by collecting the red-shifted fluorescence photons, as discussed before. Such an image is shown in figure 5.8. In order to achieve the nicely arranged array, nitrogen ions were implanted through nanometre-sized holes produced on top of the diamond by an electron beam assisted lithography process. Details about the fabrication process can be found in [193]. The advantage of such an array structure is that individual NV sites, relative to the marker (G16 in this case) can reproducibly be selected and further experiments as pulsed ODMR or Hahn echo can be performed (shown in the insets of figure 5.8) repeatedly. Also,
PECVD overgrowth can potentially be performed to bury the NVs deeper in the diamond and thereby reducing the disturbing influences from the surface, and the effect could be studied at the same NV centre which has not been performed so far. Read-out enhancement by producing solid immersion lenses on top of the NV centres can be another benefit from this overgrowth [232].
Part III

Experiments
6 Shallow single NV centres

NV centres are an up-and-coming platform for quantum sensing. Especially shallow NVs, placed within the first ten nanometres below the diamond surface, are traded high as a potential quantum sensor with sub-nanometre resolution and high sensitivity. The distance to the surface plays an important role, since the interaction between the NV centres electronic spin and potential electron or nuclear spins outside of the diamond decays with the third power of the distance, due to dipolar coupling. Numerous studies employ the features of shallow NVs which open a new way in sensor technology with wide applications in nuclear magnetic resonance (NMR), molecular biology or as a quantum simulator [14]. NVs in close proximity to the diamond surface are used to detect single external nuclear [21] and electron [233] spins.

In commercially available diamond substrates, the presence of these near-surface NVs is sporadic, which automatically creates the need for artificial engineering solutions. It is possible to precisely generate NV centres close to the diamond surface by PECVD nitrogen delta doping or low energy ion implantation (see section 4.3.1). Most efforts have been spent on the latter technique, which is widely spread, since nitrogen collisions are minimal due to the low penetration depth, therefore enabling a high lateral and transversal positioning accuracy. Nevertheless, NV centres created by this technique often suffer from a short spin coherence time due to created damage within the diamond lattice. Another approach is to perform nitrogen delta doping during a PECVD diamond growth process (see section 4.3.2). Even though the lateral positioning control is rather low, the depth can be controlled very precisely and since this method is in situ, so does not create damage, long coherence times have been observed for NV centres sitting in the top 100 nm of the diamond [74,177].

The vicinity of the surface, which can host defects which lead to magnetic noise during the sensing of desired targets, represents the biggest challenge for shallow NV centres. The control over the diamond surface with a special focus on the chemical
composition is of major importance for the successful exploration of shallow NVs. The following chapter will show results on the production of shallow NV centres by nitrogen delta doping during the CVD growth process, which are stabilised by a fluorine diamond surface termination. In the first part, the creation of shallow NVs is described, and their stability, as well as their coherence properties, are discussed. The second part deals with the stabilisation of the NV’s charge state by using an SF$_6$ plasma treatment.

### 6.1 Creation of shallow NV centres by nitrogen delta doping

In this section, the production of shallow NV centres using nitrogen delta doping during a microwave-assisted, plasma-enhanced chemical vapour deposition process is described. The starting point for this process is a commercial diamond substrate, in this case, an Ib type $\langle 100 \rangle$ single crystal from Sumitomo Electric Industries. In order to ensure not to contaminate the reaction chamber, the substrate is exposed to several acid treatments to remove possible contaminations like gold, copper or silicon. The complete cleaning process consisting among others of aqua regia, ammonia-hydrogen peroxide and potassium hydroxide, as well as the overall workflow for the CVD system, is described in figure 4.7 in section 4.2. The clean diamond substrate sample is then mounted in the vacuum chamber and exposed to a hydrogen plasma for 5 minutes. This has two purposes, first the plasma itself is stabilised, which allows steady-state conditions such as reverse and forward power matching, as well as reaching equilibrium pressure and temperature in the chamber. Second, the diamond surface is hydrogen-terminated which depicts the starting point for the overgrowth process (also compare section 2.3). In a first step, an intrinsic Type IIa diamond layer of about 5 µm thickness is grown using a growth temperature $T = 750 \, ^\circ \text{C}$, microwave power and frequency of $P = 1.2 \, \text{kW}$ and $f = 2.46 \, \text{GHz}$, a mixture of hydrogen (flow of 200 sccm) and methane (flow of 1 sccm) at a pressure of $p = 20 \, \text{mbar}$. This parameter set leads to a growth rate of approximately 200 nm/h, which was calibrated by weight difference of the samples before and after the growth. The confocal microscopy images show no NV centres, suggesting a low concentration of nitrogen, probably in the ppb range (see figure 6.1(b)). In the next
6.1 Creation of shallow NV centres by nitrogen delta doping

Step nitrogen gas (flow of 5 sccm) is added to the growth for 5 minutes which results in a nitrogen delta-doped diamond layer and the formation of buried NV centres, as the sample is directly overgrown with another IIa type layer of several microns. Another nitrogen delta doping is performed with the same conditions just before the plasma is switched off. An overview of the sample is shown in figure 6.1(a).

The buried NV centres are found in a concentration of 1 per 5 µm² and the corresponding coherence time $T_2$ is on the order of several hundred microseconds which means $^{13}$C nuclear spins are the main source of decoherence [172] (see figure 6.2). The NVs close to the diamond surface, on the other hand, suffer from the uncontrolled structure of the surface, as the lack of the structured lattice gives rise to charge traps and other unknown spin species (e.g. dangling bonds). For example, a hydrogen-terminated diamond surface which is present directly after the CVD growth changes the charge state of shallow NVs from NV$^-$ to NV$^0$ [218]. For this reason, the diamond is boiled in a three acid mixture (sulphuric, nitric and perchloric acid, ratio 1:1:1) for 2 hours to create an oxygen terminated surface which promotes the negative charge state due to Fermi level shifting. Nevertheless, no NVs are found close enough to the surface to detect an NMR signal of hydrogen contained in the immersion oil on top of the diamond.

Recently there has been published an article by Santawesin et al. 234, suggesting that surface termination by three acid cleaning and by annealing the diamond at
Figure 6.2: Overview of Hahn echo measurements. Long coherence times are observed for NV centres buried a few micrometres below the diamond surface, suggesting a $^{13}\text{C}$ limited spin bath. After stabilising the NV’s charge state by surface termination, shallow NV centres are observed with average coherence times of 4-5 $\mu$s. The longest one found in this sample was about 15 $\mu$s and is labelled as medium in the legend of the figure.

temperatures around 500 °C under oxygen atmosphere, results in different surface configurations. These configurations host different defects and have different effects on shallow NVs. They suggest that oxygen annealing is more favourable since measured spin coherence ($T_2$) and spin relaxation ($T_1$) times are longer. A similar effect is reported in Ref. 217. Since the surface configuration has a tremendous effect on shallow NV centres, different stabilisation processes based on fluorine termination are discussed and performed in the next section.

6.2 Stabilisation of shallow NVs by fluorine surface termination

The unstable charge state of NV centres in close proximity to the diamond surface causes a decreased sensitivity of NV based sensing devices, as this leads to blinking (NV fluorescence drops and reappears on the time-scale of seconds due to lower fluorescence level of the NV$^0$) and spectral instability (confirmed by the appearance of the NV$^0$ zero-phonon-line). The main reason for this instability is most likely the
6.2 Stabilisation of shallow NVs by fluorine surface termination

diamond surface itself as the border layer does not consist of clear carbon-carbon bonds but uncontrolled electron bonds as dangling bonds and other charge traps. In order to overcome this problem, a homogeneously terminated surface is desirable as this eliminates unpaired bond structures and therefore stabilizes the NV’s charge state. Surface terminations with hydrogen [218], oxygen [197, 219, 233] and fluorine [197, 219] atoms have been studied previously, and it has been shown that O₂ and CF₄ plasma treatments can stabilize shallow implanted NV centres. The latter fluorination technique is known to build a polymer layer on top of the diamond surface on the order of several nanometres [235, 236] and also it does not fully cover the diamond surface with fluorine. A SF₆ plasma treatment, on the other hand, shows better surface coverage, as depicted in figure 6.3(a), while no oxygen groups or polytetrafluoroethylene (PTFE) like layer is produced. Furthermore, this procedure flattens the surface as it is mainly used for diamond etching [237].

![Figure 6.3](a) A summary of the surface coverage of different termination techniques. The blue bar corresponds to fluorine (F1s), the red one to carbon (C1s) and the grey bar to other peaks (O1s, Si2p, etc.) calculated from the XPS spectra shown in figures 5.3(a) and 5.3(b). (b) The blue curve represents an X-Ray photoelectron spectroscopy measurement of a diamond surface treated with SF₆ plasma. The peak at 685 eV (inset) corresponds to F1s. No oxygen peak is observed, in contrary to a CF₄ plasma treatment [197, 219, 235, 236]. The black line is a Gaussian fit to the data. Reprinted from Ref. 221 with the permission of AIP Publishing.

fluorination is carried out according to the following recipe. First, the diamond surface is hydrogenated by the termination procedure described in section 6.1. After transferring the diamond from the CVD reactor to the ICP Oxford Plasma Lab 100 chamber it is treated with SF₆ plasma for 4 minutes at a gas flow of 100 sccm and a power of 500 W. This exposure time, as can be seen in figure 5.3(b), gives the best
surface coverage and appears to be the most harmless treatment in means of diamond etching. In order to prove that fluorine is indeed present on the diamond surface, an X-ray photo-electron-spectroscopy measurement is performed, which can be seen in figure 6.3(b). Remarkable in this measurement is the absence of the oxygen peak at around 532 eV, which is an indicator for a good fluorine surface coverage. Note that the F1s peak is shifted by approximately 3 eV compared to a sample which was treated with CF$_4$ plasma [197]. Nevertheless, by this XPS measurement, it cannot be concluded that fluorine is present in the form of a monolayer, but as the peak intensities of the F1s and C1s peaks are comparable, it can be stated that the first 15-20 atomic layers contain a significant amount of fluorine atoms, most probably in the form of CF chains bonded to the surface as the plasma power was quite low, which hinders fluorine from entering the diamond lattice.

A sample treated with this SF$_6$ plasma shows an increased number of stable NV centres with no blinking or sign of NV$^0$ spectrum. Coherence time measurements show a rather short T$_2$ of about 4 ± 1 µs which could originate from the strong influence of paramagnetic defects as dangling bonds on the surface (compare figure 6.2).

NV centres are susceptible to magnetic fields, and so this outstanding property can be used to determine their distance to the diamond surface by actively sensing a quantity outside of the diamond crystal [21]. A state-of-the-art technique has become the NMR on the nano-scale, where hydrogen atoms contained in the immersion oil are detected, and the signal strength is used to estimate the depth of the NVs [20, 238]. A typical NMR spectrum is shown in figure 6.4(a). The statistical polarisation of the external proton spins of the hydrogen atoms create a magnetic field which is correlated with the area of the peak. The latter can be directly related to the depth of the NV as described in [21,238]. By analysing several signals, where only 10% of the measured NVs did not show an NMR signal, an average depth of about 5 nm can be extracted.

In order to prove that the stabilisation of the NVs truly was created by the surface termination, the sample is treated again in the three acid mix procedure, in order to remove the fluorine atoms from the surface. Figure 6.4(b) shows the XPS measurement after the acid cleaning, and surprisingly there is still fluorine present on the diamond surface, albeit the intensity is significantly reduced. An oxygen peak appears at 532 eV as expected and if the F1s peak is investigated more carefully it
Figure 6.4: (a) NMR spectrum of the immersion oil above the diamond surface showing the proton resonance at 1.727 MHz, while an external magnetic field of $B_0 = 406$ G was applied. The signal strength corresponds to a depth of the NV centre of about 5 nm. Image based on Osterkamp et al.\textsuperscript{221}. (b) X-ray photoelectron spectroscopy of a diamond sample treated with SF$_6$ plasma with a subsequent acid treatment, which results in the observation of an oxygen-related peak at 532 eV. The fluorine peak is still observed but is shifted by 2 eV compared to the original treatment in figure 6.3 (inset). The carbon C1s peak of the diamond exposed to SF$_6$ plasma (red) and after the acid treatment (black) is shown in the bottom inset. Reprinted from Ref. 221 with the permission of AIP Publishing.

can be observed that it is shifted by 2 eV compared to the pure SF$_6$ treatment. Further analysis reveals a shift of the C1s peak of 2.8 eV (bottom inset of figure 6.4(b)), which could be due to the fact that the fluorine atoms now have a different chemical environment probably in the form of a type of polytetrafluoroethylene (PTFE) or a polymer which is built on the diamond surface. Charging of the diamond surface could also lead to a shift of both the F1s and C1s peaks. Nevertheless, the observed NV centres after the second acid treatment are not stable, which is a clear indicator that the applied SF$_6$ treatment indeed stabilises shallow NVs.

6.3 Conclusions

It has been shown that single NV centres can be produced in a distance of 5 nm from the diamond surface by delta doping during a PECVD diamond growth process. Due to a hydrogen-terminated surface as a result of the growth without any further treatment, the NV centres are present in an unstable charge state which limits the nano NMR capabilities. This problem can be overcome by fluorination
of the diamond surface, which does not lead to prolonged spin lifetimes, but to a
stable charge state which enables detection of the proton signal from the immersion
oil. This result suggests that the removal of fluorine atoms by a wet chemical acid
treatment leads to destabilisation of the NVs’ charge state and confirms the inev-
itable impact of fluorine termination on shallow NV centres produced by PECVD
method.
7 Ensemble of NV centres for magnetometry applications

Quantum enhanced sensing is one of the most promising fields with potential real-world applications which can be achieved with NV centres in the near future. This is due to the fact that it is possible to produce the atom-like defect on-demand with nanometre precision and its outstanding properties like long coherence time and high spatial resolution are valid even at room temperature. Even though the overall sensitivity of superconducting quantum interference devices (SQUIDs, 10aT/√Hz [239]) cannot be reached, NV based sensors can exceed these existing systems regarding some applications. The advantage of NV centres is that, due to its atomic size, small magnetic fields on the order of a single nuclear spin can be detected with high precision. This and the fact that the sensor works at ambient conditions and therefore does not require liquid helium cooling paves the way for NV centre based magnetometry. NV sensors are suited to detect small magnetic fields and the sensitivity scales with

\[ \eta \approx \frac{h}{g \times \mu_B} \frac{1}{C \sqrt{\tau}}, \]  

(7.1)

where \( h \) is the Planck constant, \( g \) the electronic Landé factor, \( \mu_B \) the Bohr magneton, \( C \) the measurement contrast and \( \tau \) the coherence time. In the case of ensemble sensing this equation scales with \( \sqrt{N} \), the number of sensor spins and can be rewritten as

\[ \eta \approx \frac{h}{g \times \mu_B} \frac{1}{C \sqrt{N} \times \tau}. \]  

(7.2)

From an engineers point of view, this equation has to be minimised to improve the sensor sensitivity, and this can be achieved by increasing the measurement contrast \( C \), increasing the size of the ensemble \( N \) or by increasing the coherence time \( \tau \). These three points present the strategy to improve NV magnetometers, which will
be pursued in this and the following chapters.

**Strategy to improve NV magnetometers**

1. Reach an elevated coherence time by improving the diamond quality and the form/presence of a spin bath by optimising the growth parameters (section 7.1).

2. Raise the number of NV centres by enhancing the nitrogen incorporation into diamond and optimise the NV creation yield (chapter 7 and 8).

3. Increase the measurement contrast by preferentially align NV centres along one crystal axis (chapter 8).

The first point is addressed by optimising the growth parameters for ⟨100⟩ diamond growth and the incorporation of nitrogen for the formation of NV centres. Optimised conditions are presented in section 7.1 and this point is further discussed in section 7.4.

The second point will be discussed in this chapter 7 where we will act on the assumption that a higher amount of nitrogen within the diamond sample will lead to a higher amount of NV centres. Therefore, the increased nitrogen content is realised during a CVD process, and the results of such an overgrowth are discussed in the following. In order to analyse the doping efficiency in more detail, investigations regarding the correlation between diamond off-cut angle and corresponding diamond growth rate, which is directly linked to the nitrogen incorporation, will be made.

The strategy will be pursued during the next chapters and the second point will be followed, since an extreme off-angle, namely 54.7°, would result in the ⟨111⟩ diamond crystal axis. Such diamond substrates with specially cut and prepared surfaces will be used in chapter 8, where the first attempt is to match the growth rates of the different growth mechanisms, conditional on the different surface orientations of the substrates. A subtle side effect of the usage of a ⟨111⟩ oriented diamond as a substrate for the PECVD overgrowth is that all generated NV centres are preferentially aligned along the ⟨111⟩ crystal direction. Therefore, the optical dipole associated with the NV centres lies parallel to the surface, hence optimal for photon emission. Additionally, the transition frequencies of all NV centres overlap, at an applied magnetic field, leading to an enhanced measurement contrast. Attempts to
7.1 Creation of NV ensembles

further increase the number of created NV centres by high-temperature annealing
will be made.

The last chapter 9 deals with points one and two again, since the same growth con-
ditions lead to different growth rates, \( \nu_{gr}^{111} < \nu_{gr}^{100} \) and therefore the \( \langle 111 \rangle \) growth
has to be optimised. This is achieved by matching the growth rates by parameter
tuning, so that both diamond quality and the impurity incorporation, is improved.
Together with the use of \( ^{15}N \) nitrogen as a doping gas, this enables a new definition
of the conversion efficiency, since the number and quality of created NV centres are
not, as usually performed, correlated with the number of nitrogen atoms present in
the growth chamber, but with the number of created P1 centres within the diamond.
The advantage of such a definition is that P1 centres in a \( ^{12}C \) enriched environment
depict the main source of decoherence and therefore this ratio has much more phys-
ical meaning as the correlation to the nitrogen from the gas phase.

7.1 Creation of NV ensembles

Table 7.1: Recipe for diamond growth on \( \langle 100 \rangle \) substrates for high nitrogen incorporation.
The gas flow rates for hydrogen (H\(_2\)), methane (CH\(_4\)) and nitrogen (\(^{15}N_2\)) are presented, as
well as the pure growth and doping time (\( t_{growth} \)) microwave power (\( P \)), microwave frequency
(\( f \)) and the resulting growth temperature (\( T \)) which is measured with a thermocouple.

<table>
<thead>
<tr>
<th>H(_2)</th>
<th>CH(_4)</th>
<th>(^{15}N_2)</th>
<th>( t_{growth} )</th>
<th>( P )</th>
<th>( f )</th>
<th>( T )</th>
</tr>
</thead>
<tbody>
<tr>
<td>200 sccm</td>
<td>1 sccm</td>
<td>1 sccm</td>
<td>5 h</td>
<td>1200 W</td>
<td>2.46 GHz</td>
<td>755 °C</td>
</tr>
</tbody>
</table>

In a first approach, the number of NV centres is increased by nitrogen doping
during the CVD diamond growth. Therefore, a standard Element Six substrate
with \( \langle 100 \rangle \) surface orientation was overgrown with the conditions shown in table
7.1. From SIMS measurements of a sample produced under similar conditions (see
figure 5.4), we can estimate the thickness of the produced layer to be between
one and two \( \mu \)m, illustrated in figure 7.1(a). The density of NV centres can be
determined by investigating the sample in a confocal microscope set-up. Therefore,
a confocal image of the sample’s cross-section is taken, as shown in figure 7.1 (b).
Proof that we are dealing with NV centres is the characteristic fluorescence spectrum
of the investigated spot which clearly is dominated by NV\(^{-}\) with the ZPL at 637 nm
and the broad phonon sideband, which are shown in figure 7.1(c). In order to
further proof that investigated NVs are really created during the CVD growth, pulsed ODMR measurements reveal the hyperfine coupling of the $^{15}$N nucleus to the NV’s electron spin. The natural abundance of $^{15}$N is only 0.4%, so statistically less than one $^{15}$NV is expected among a measurement of one hundred spots. The repeatedly measured 3.1 MHz splitting clearly indicates a higher presence of $^{15}$NV in our sample. Furthermore, for some sensing applications, NV centres with a spin one half nuclear spin are desired, as only two hyperfine states are present in comparison to the spin one system in the form of $^{14}$NV, where three hyperfine transitions are observed. This fact is discussed in more detail in chapter 9. In order to estimate the number of emitters in the sample, we use a state-of-the-art technique, explained in

![Figure 7.1](image_url)

**Figure 7.1:** Ensemble NV centre creation. (a) Schematic image of the produced diamond sample, where a highly $^{15}$N doped layer was homo-epitaxially grown on an IIa type diamond substrate. (b) High nitrogen concentration leads to high NV concentration in the layer, as shown by the confocal cross-section scan. (c) Measuring the PL spectrum ensures the signal stems from NV centres since clear NV features as the ZPL are recognisable. (d) Intentional NV creation can be proven by an elevated presence of $^{15}$NV and the characteristic 3.1 MHz splitting of the ODMR line, in comparison to natural abundance.
7.2 Benchmark for characterization of NV ensembles

detail in the next section 7.2. For a rough estimate, we simply normalise the count rate signal achieved by the confocal mapping (here 14 Mcts/s) with the expected count rate of a single emitter (here 120 kcts/s). The number of emitters \( N \) therefore can be calculated with

\[
N = \frac{\text{overall count rate}}{\text{count rate of a single emitter}}. \tag{7.3}
\]

For this sample, we derive an emitter concentration of 116 emitters in the confocal volume (volume which is irradiated by the laser due to diffraction limit and depth of focus). We estimate the confocal volume carefully as \( 350 \text{ nm} \times 350 \text{ nm} \times 700 \text{ nm} \), where 350 nm is the diffraction-limited x-y resolution and 700 nm represents the z resolution. Performing the actual calculation according to equation 7.3 leads to the NV density in our layers, which can be written as 10.88 ppb. This value can even be increased by further electron irradiation to create additional vacancies which then can be used to increase the NV creation yield by a subsequent annealing step. It is reported that this enhanced creation method leads to a concentration of 1 ppm of NV [129, 240]. Due to this high density it was used for a temperature sensing experiment [129], where the zero-field splitting \( D_{gs} \) is shifted by -74.2 kHz/K [241]. Since all four possible NV orientations are present, the sample could potentially also be used to perform vector magnetometry as shown in [33].

7.2 Benchmark for characterization of NV ensembles

The above mentioned samples contain NV ensembles with a concentration of approximately 1 ppm. But in a real sensing experiment not all of these contribute to the sensing signal. There are several problems which have to be taken into account, which will be shortly discussed subsequently in this section before a benchmark for material characterization is proposed to better quantify the achievable magnetic field sensitivity.

The first problem when working with ensembles is the distribution. Other than single NVs, an ensemble is not an atomic size defect any more, and its size is limited to the laser irradiation spot (confocal volume) of several hundreds of nanometre.
7 Ensemble of NV centres for magnetometry applications

This causes several issues from the set-up point of view, where for example the external magnetic field has to be uniform throughout the ensemble. When using a copper wire as microwave antenna, the generated $B_1$ field decays with distance and therefore is not uniform. If these criteria are not fulfilled, the transition frequencies of the single emitters of the ensemble will not be identical and not all of them can be addressed with the same microwave pulse.

Another point is the distribution in z direction, called depth. For some sensing applications an external spin system is desired to be detected with the NV ensemble. Therefore, an equal distance between single NVs in the ensemble and the target is required. Ideally this depth is less than 20nm, as the target spin signal is supposed to be a dipolar field which decays strongly with distance. A depth distribution as in the above mentioned sample causes a loss of nearly 97-99% of the NV centres, as they cannot detect a signal of the desired quantity on top of the diamond surface. A thinner NV rich layer is therefore desired for this purpose. This scenario is illustrated in figure 7.2.

As described in the fundamental part 3 NV centres can have four different orientations in the diamond lattice. The external magnetic field, the microwave $B_1$ field and the laser polarization can only be optimised for one orientation. Even worse is the fact that the transition frequencies at strong magnetic fields do not overlap, therefore sensing can only be performed with one of the four groups. If we assume equal presence of all four possible orientations, the number of ‘useful’ NVs decreases.
7.3 Quantifying the size of NV ensembles

by a factor of four. Furthermore, the three 'undesired' NV groups limit the ODMR measurement. Taking the above mentioned example the measured NV density in the sample of 1 ppm decreases in meanings of sensing to approximately 2.5-7.5 ppb which can be used for the experiment. So, instead of using the sensitivity given in equation 7.4, a better benchmark would be to use a volume normalised sensitivity for magnetic field sensing in a pulsed scheme, which can be written as

\[
\eta_V \approx \frac{\hbar}{g \times \mu_B} \times \frac{1}{C_0 \sqrt{n \times p_L \times \tau_L}} \times \frac{1}{\sqrt{\tau}},
\]

(7.4)

where \(C_0\) is the actual measurement contrast for one NV orientation, \(n = N/V\) is the sensor density (with \(N\): number of NVs, \(V\):volume), \(p_L\) the average number of detected photons per pulse and \(\tau_L\) the length of the readout laser pulse.

To push the volume normalized sensitivity to the limit, it is necessary to increase \(\tau\) by minimizing the decoherence effect of the surrounding spin bath, by using \(^{12}\)C isotopically enriched diamond. Preferential alignment of all NVs in the ensemble would also be beneficial to maximize the measurement contrast \(C_0\) and is reported to be achieved partially by using \(\langle 111 \rangle\) oriented diamond [135]. Last but not least the initial point of this chapter remains to be true, as the NV density has to be increased, by either produce an elevated number of NV centres or produce them in a smaller volume. A study showing more insight into all of these points is carried out later in this thesis.

7.3 Quantifying the size of NV ensembles

While working with NV ensembles instead of a single NV reveals several advantages regarding magnetic field alignment, measurement time and overall sensitivity, the quantification of the ensemble is non-trivial. The simple question 'how many individual NV centres are part of the ensemble?' and its non-trivial answer will be discussed in this section. As discussed above in section 7.2, the distribution of NV centres within the confocal volume plays an essential role in sensing applications. Here a method is presented to estimate the number of single NV emitters in a diffraction-limited laser spot (confocal volume) and over larger areas which are
typically on the order of the size of a normal confocal image (20 µm x 20 µm).

In a first step, a fluorescence signal calibration has to be performed, to determine the number of emitted photons from a single NV centre. Therefore, a \( g^{(2)} \) (second-order autocorrelation function) experiment, as described in section 3.2, is performed in order to prove that a single NV is investigated (see figure 7.3(b)). This can be found in the used diamond substrate or in a different low NV density sample. In the meantime, the photon count rate is averaged in time to receive the fluorescence level of a single NV (\( F_{\text{single}} \ [\text{kcts/s}] \)). This can be used to normalise the confocal image which is recorded, in a next step, by the home-built confocal microscope set-up, where NV centres are marked as bright spots (figure 7.3(a)). Here each pixel is normalised with \( F_{\text{single}} \) and the number of pixels which correspond to a diffraction-limited spot are averaged to obtain a count rate per confocal volume. Note, that depending on the resolution chosen for imaging the confocal picture, the number of pixels representing the point spread function can vary. Furthermore, only pixel conglomerates with NV like fluorescence profile, namely Gaussian distribution, are considered for analysis. These conglomerates are for simplicity called spots and are marked in figure 7.3(c).

Finally, the number of NV centres per confocal volume is calculated for each spot of the confocal image and is illustrated in the histogram in figure 7.3(d). In order to obtain an average value over the analysed area, the distribution is fitted with a Gaussian. The procedure can be repeated for several confocal images taken over various positions of the sample for better statistics. Since the standard deviation of the Gaussian fit function (FWHM) is nearly the square root of the mean value, the NV centre ensembles can be considered as Poisson distributed.
7.3 Quantifying the size of NV ensembles

Figure 7.3: Method to determine the number of NV centres in diffraction limited confocal volume. (a) A confocal image is taken with the home-built microscope, where NVs are presented as bright spots. In order to extract the number of NV centres present in the ensemble, a count rate calibration has to be performed. (b) The normalization factor is determined by the count rate of a single NV and its presence is verified by measuring a second order correlation function, where the dip is dropping below 0.5. (c) Pixel conglomerates with Gaussian fluorescence profiles are considered for further analysis and marked as purple spots. (d) The result of the analysis is a histogram showing the number of NV centres per confocal volume averaged over a large area and supported by a Gaussian fit (purple).
7.4 Increasing the nitrogen incorporation

As mentioned briefly in the second point of the introduction to this chapter, the sensitivity improves as the number of NV sensors increases. As this number is directly related to the amount of nitrogen present in the diamond substrate, the incorporation efficiency for varying diamond compositions is investigated.

The constitution and especially the surface crystal orientation of the diamond substrate itself has a tremendous effect on the growth rate and the quality of the resulting diamond. In order to prove this statement, a CVD process on a multi-step orientation substrate is executed. The sample is produced by Syntek Co Ltd, Yokohama-Shi Japan, via diamond fine polishing of a diamond plate with dimensions 2 mm x 2 mm x 0.5 mm (standard IIa type from Element Six). A sketch of the sample can be seen in figure 7.4(a), where five areas A-E are produced with different off-cut angles ranging from -2° to 3.6°. The off-cut angle \( \beta \) is defined as the difference between the normal vector of a \( \langle 100 \rangle \) oriented surface \( \vec{n}_{\langle 100 \rangle} \) and the normal...
7.4 Increasing the nitrogen incorporation

The CVD process has the following parameters: microwave Power $P = 1.2 \, \text{kW}$, microwave frequency $f = 2.46 \, \text{GHz}$, growth temperature $T = 750 \, ^\circ\text{C}$, process pressure $p = 22.5 \, \text{mbar}$. The gas flows during the different stages of the process were $\text{H}_2$: 600 sccm, $\text{^{12}CH}_4$: 0.3 sccm, $\text{N}_2$: 0.3 sccm. After the sample was exposed for 5 minutes to hydrogen plasma, an intrinsic, nitrogen-free buffer layer was created for 120 minutes, before nitrogen gas was added to the growth to produce a heavily nitrogen-doped layer for another 120 minutes.

The advantage of this sample is that the crystal orientation is the only changed parameter. Vacuum, plasma and gas conditions are identical for all five areas. Ensuring these reproducible conditions among several growth processes is still a challenging task which has to be overcome to engineer colour centres reproducibly and on-demand. Furthermore, the sample can be used to investigate different growth dynamics depending on the off-angle and therefore, the resulting diamond layers are analysed with the SIMS technique, where the $^{15}\text{N}$ profiles are taken as a measure (shown in figure 7.4(c)). A detailed analysis reveals the $^{15}\text{N}$ incorporation, as well as the diamond growth rate, for the differently oriented surfaces (figures 7.4(d) and (e)). It can be concluded that extremal off-cut angles promote nitrogen incorporation as well as growth speed, whereas small variations of $\beta$ do not change this behaviour. For completion, the resulting growth rates and average nitrogen contents, as well as the doping efficiency for the areas A-E, are summarised in table 7.2.

<table>
<thead>
<tr>
<th>Region</th>
<th>$\beta$</th>
<th>Growth rate $\nu_{gr}$ (Å/min)</th>
<th>$^{15}\text{N}$ (cm$^{-3}$)</th>
<th>Doping efficiency ($\zeta$ (ppm))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>non-dope</td>
<td>$^{15}\text{N}$ dope</td>
<td>$^{15}\text{N}$ rich layer</td>
</tr>
<tr>
<td>A</td>
<td>$-2^\circ$</td>
<td>2.07</td>
<td>2.97</td>
<td>$1.57 \times 10^{17}$</td>
</tr>
<tr>
<td>B</td>
<td>$-0.3^\circ$</td>
<td>1.02</td>
<td>1.14</td>
<td>$5.84 \times 10^{16}$</td>
</tr>
<tr>
<td>C</td>
<td>$0.3^\circ$</td>
<td>1.11</td>
<td>1.30</td>
<td>$6.12 \times 10^{16}$</td>
</tr>
<tr>
<td>D</td>
<td>$2^\circ$</td>
<td>1.68</td>
<td>1.87</td>
<td>$1.32 \times 10^{17}$</td>
</tr>
<tr>
<td>E</td>
<td>$3.6^\circ$</td>
<td>2.22</td>
<td>3.59</td>
<td>$2.57 \times 10^{17}$</td>
</tr>
</tbody>
</table>

In comparison to table 5.2, where the addition of nitrogen at a N/C ratio of 0.17 was used and the growth rate was doubled for a natural abundance methane growth
on \langle 100 \rangle oriented diamond substrates, here the N/C ratio was two. If we assume
that the growth mechanism does not change by replacing the carbon isotopes from
\textsuperscript{13}C to \textsuperscript{12}C, it can be concluded that the higher nitrogen content in the gas phase has
a smaller effect on the growth rate, since growth rate changes by factors between 1.1
and 1.6 are observed here. From table 7.2 it can be seen that the growth rate for non-
nitrogen doping reaches its maximal values, the higher the off-angle. The same is
valid for the speed-up of the growth rate by adding nitrogen. This increased growth
rate leads to higher incorporation of nitrogen into the diamond lattice, together with
an increased doping efficiency. So depending on the application, an off-cut diamond
substrate can be used to de- or increase the nitrogen content in the sample. As the
goal for most CVD growers is to reduce the nitrogen content in the diamond sample,
a small miscut angle \( \beta \) is favourable to near the goal of a nitrogen-free synthetic
diamond. For NV centre sensing applications it is desirable to increase the amount
of NV sensors in a given sample and therefore, a high nitrogen content can be of
interest as it is directly correlated to the amount of NVs. The choice of high off-cut
angle with respect to the \langle 100 \rangle direction could lead to a higher NV concentration.
An extreme case for an off-angle is \( \beta = 54.74^\circ \) which would correspond to a
\langle 111 \rangle oriented diamond surface. The effect of choosing such an oriented diamond as
a substrate and the involved increased NV creation yield, together with the ability
of preferential alignment are discussed in the next chapter.

7.5 Conclusion

In conclusion, it was shown that the NV centre ensembles within nitrogen delta-
doped diamond layers can be produced by our home-built PECVD system. Quantifi-
cation of the ensemble sizes can be made with the confocal microscope by normal-
isising the observed fluorescence signal with the fluorescence level of a single NV emis-
ter. The nitrogen incorporation correlates with the number of created NV centres
within a distinct diamond layer, and it was shown that the nitrogen doping efficiency
depends highly on the diamond substrate’s off-angle. A high NV concentration while
remaining a thin diamond layer is desired since this improves the volume normal-
isated sensitivity, which is a good benchmark criterion for the comparison of NV rich
diamond samples with potential use as magnetometers.
8 Preferentially aligned NV centre ensembles for magnetometry

In regular NV containing diamond samples, the ratio between all four orientations is equal to 25% (as illustrated in figure 8.1(a)). One of the most challenging features of solid-state based quantum sensors, as the NV ensemble magnetometer, is the reduced measurement contrast $C_0$. In order to overcome this problem, preferentially-aligned nitrogen-vacancy centres are required, which can be produced during a microwave-assisted plasma-enhanced chemical vapour deposition process using a diamond substrate with $\langle 111 \rangle$ orientation (illustrated in figure 8.1(b)). If the substrate’s surface has $\langle 111 \rangle$ orientation, the alignment of NV centres along the $\langle 111 \rangle$ direction is beneficial since the associated optical dipole lies parallel to the surface and therefore has optimal orientation for photon emission. It has been shown, that 99% of the NVs can be aligned along one direction [163] and even shallow ensembles can be created [139].

Figure 8.1: Schematic image of homoepitaxially in-grown NV centres on top of an (a) $\langle 100 \rangle$ oriented and (b) $\langle 111 \rangle$ diamond substrate. The small arrows represent NV centre orientations where in case of a $\langle 111 \rangle$ substrate all point in the same direction ($\langle 111 \rangle$ crystal direction), showing preferential alignment.
8 Preferentially aligned NV centre ensembles for magnetometry

8.1 Creating preferentially aligned NV centres

In order to study the NV creation process, two samples with nearly similar conditions are fabricated. The IIa type diamond substrates for this work are supplied by Applied Diamond Inc., for details, see section 4.1, table 4.1. The NV containing layers are homoepitaxially grown in our home-built PECVD reactor with different microwave power conditions (Sample A with 1.2 kW and Sample B with 0.72 kW). These different microwave plasma densities result in altered growth temperatures, which can be measured via the attached pyrometer (shown in figure 8.2(a)). Growth temperature is the most critical parameter to control the amount of impurities in the resulting diamond layer, especially the nitrogen content can be controlled which directly correlates with the number of created NVs [229,242,243]. It is reported that the ratio between single substitutional nitrogen (P1 centres) and NV centres is on the order of (300:1) [134].

The other applied growth conditions used for the two processes are microwave (MW) frequency $f = 2.46 \text{GHz}$, pressure $p = 22.5 \text{mbar}$, $^{12}\text{CH}_4$ concentration $c = 0.5\%$ concerning hydrogen which was applied with a flow of 200 sccm. The growth time for every growth was set to two hours.

As described in section 4.2, our system is equipped with a mass spectrometer, which allows us to monitor the gas composition during the growth process in real-time. A mass spectrum of the two different growth processes is taken, where characteristic peaks for isotopically purified methane and nitrogen are tracked during the whole growth process of 2 hours. Division of these two lines, reveals the nitrogen to carbon ratio during the process (shown in figure 8.2(b)). This ratio is a good indicator for the nitrogen incorporation during CVD growth [243], mainly if, like in our case, the growth temperature stays constant during the process. During the growth process, this value is decreased from one to 0.78, indicating that the nitrogen content is not homogeneous throughout the layer. This will later be proven by the SIMS measurements, as presented in figure 8.8. Note, that the dip in the temperature profile of Sample A correlates with a change in the N/C ratio plot. Therefore, a possible explanation for this is a gas fluctuation during the growth, which leads to a temporary decrease of the overall growth temperature. After the successful creation of the samples, further analysis using the confocal set-up is performed and demonstrated in the following. First, we analyse only the optical signal from the
8.1 Creating preferentially aligned NV centres

![Figure 8.2: (a) Pyrometer and (b) N/C ratio revealed from mass spectrometer measurements during the growths of Samples A and B. Clearly visible is the characteristic change throughout the growth process, indicating an inhomogeneous nitrogen bath in the layer.](image)

dense NV layers, illustrated in figure 8.3(a), to estimate the NV defect density created during the growth. Therefore, we developed a technique to calibrate to fluorescence signal with the count rate of a single NV, which after careful analysis reveals the average NV density in our sample. This method is described in detail in section 7.3. Applying it to the two different Samples A and B reveals the histogram in figure 8.3(b), where an elevated number of NVs is observed in Sample A, which was produced at higher MW power. The average NV centre density \( n \) (respectively \( n_{\text{ppm}} \)) for the two samples can be calculated by the following formula,

\[
n = \frac{N_{av}}{V_C} = \frac{N_{av}}{a^2 \times d_{\text{layer}}} ,
\]

where \( N_{av} \) is the average number of NV centres revealed from the Gaussian fit, and \( V_C \) is the confocal volume with the lateral laser expansion estimated as \( a \approx 350 \text{ nm} \) and \( d_{\text{layer}} \) is the thickness of the growth layer. The atom density in a diamond can be calculated as \( 186 \text{ atoms/nm}^3 \) and therefore the density can be given as a fraction of all atoms in ppm (or ppb= \( 10^{-3} \text{ ppm} \)) as,

\[
n_{\text{ppm}} = \frac{n}{186} \times 10^6 .
\]

With layer thicknesses for Samples A and B of 420 nm and 240 nm, as measured by SIMS (see section 5.2), this equation gives 6.9 and 2.6 ppb, respectively.

The presence of NV centres in the samples is confirmed by ODMR measurements,
Figure 8.3: Characterization of preferentially-aligned NV centres. (a) Cross-sectional confocal image of Sample A, where the NV containing layer is labelled and appears very bright in comparison to the ⟨111⟩ substrate’s background. (b) Resulting histogram from the analysis method discussed in section 7.3. The high power configuration is more favourable for increased NV creation without any post-treatment. (c) Preferential alignment of the NV centres in Sample A is proven by ODMR spectrum, where the black points are experimentally measured data, the purple curve is a Lorentzian fit to this data, and the green curve represents simulated transitions (under the assumption that NVs are present equally in all four directions) for the aligned external magnetic field perpendicular to the diamond’s surface. Only transitions corresponding to ⟨111⟩ oriented NVs are present at 2776MHz and 2964MHz, whereas the other lines are not observable.

which reveal a perfect preferential alignment of the colour centres along the ⟨111⟩ crystal direction. This fact can be seen in figure 8.3(c), where the black dotted line shows the actual ODMR measurement. This data is recorded in a static magnetic field of approximately 33G where the magnetic field vector is pointing perpendicular to the diamond surface (⟨111⟩ crystal direction). In this set-up, the contrast for NV centres aligned along the ⟨111⟩ direction is optimised, whereas NVs oriented along the other three directions make the same angle to the B-field (109.5 °), and therefore their resonance frequencies overlap. The measurement reveals only one NV orientation, namely the one along ⟨111⟩ direction and thus preferential alignment can be proven. To support this statement, figure 8.3(c) contains simulated ODMR transitions (green line) for all four NV groups. Clearly visible is the lack of the inner transitions in the measured data, which is due to preferentially-aligned NVs.

To be able to give a value for the sensitivity of the ensemble as stated in equation 7.4 it is necessary to measure the spin properties, namely the T_2 Hahn echo coherence time, of the created ensembles. The averaged T_2 values for samples A and B are (10.1 ± 2.6)µs and (6.0 ± 3.3)µs respectively. Individual measurements for several ensembles for the samples are given in table A.1 in the appendix A.2.

With these values and equation 7.4 the magnetic field sensitivity of the produced
samples can be estimated to $0.96 \frac{nT}{\sqrt{Hz \mu m^3}}$ for Sample A and $0.69 \frac{nT}{\sqrt{Hz \mu m^3}}$ for Sample B.

These values are not groundbreaking, but nevertheless, we want to increase the sensitivity even further. To do so, it is necessary to increase the NV density as well as the coherence time. A treatment which is proposed and used in several reports [244,245] which can fulfil both requirements at the same time is high-temperature annealing of diamonds containing NV centres. Inspired by the positive results from the past, this procedure was performed on our samples, and the effects and results are discussed in the next section.

8.2 Increasing the volume normalised sensitivity

Figure 8.4: Annealing process to increase the NV yield and its coherence time. (a) Annealing ramp used to induce migration of vacancies where the temperature is ramped up stepwise to keep the vacuum conditions of $10^{-7}$ mbar. (b) Increase of the creation yield for the two samples analysed with the technique described in section 7.3. The Gaussian fits of the histograms are clearly shifted to higher NV numbers after the annealing process (solid triangles).

Increasing the magnetic field sensitivity of an NV based quantum sensor means to increase contrast, density or coherence time as given in equation 7.4. Inspired by the ion implantation procedure to fabricate NV centres where thermal annealing is used to combine nitrogen ions and created vacancies to form NV centres, this high-temperature vacuum annealing procedure was performed on the overgrown samples. Note that the CVD overgrowth technique already contains an in-situ annealing treatment, as the growth happens at about 1000°C. Vacancies which are created
from imperfections of the growth are mobile and can be trapped by a substitutional nitrogen atom to form an NV centre. In previous reports [195], though, it was shown that by annealing implanted nitrogen samples to higher temperatures (>1000 °C) not only the creation yield (ratio between observed NV centres and number of implanted nitrogen ions) is increased but also enhanced coherence times are observed. This is because the NV’s environment is ‘healed’ by this procedure, and it is believed that vacancies become mobile and the crystal lattice relaxes at high temperatures. Therefore, fewer defects (mainly paramagnetic defects) are present and thus less decoherence is caused.

Samples A and B, which were introduced and characterised in the previous section are put in an annealing oven under high vacuum (<10^{-7} mbar) and are annealed at 1500 °C for 2 hours. In order to keep this high vacuum, the heating element is ramped stepwise to this temperature, as illustrated in figure 8.4(a). First, the chamber is held at 500 °C for one hour, to allow water which could have entered during the mounting of the sample to evaporate. Another step is included at a temperature of 1200 °C for one hour before the process temperature of 1500 °C is reached. It is reported that vacancies become mobile at temperatures above 650 °C [186, 187] and therefore not only the two hours but moreover the whole process has to be considered for the actual annealing process, including the cooling down step. During this entire time vacancies can diffuse, can be absorbed at the surface or be trapped by additional nitrogen atoms. The latter can be seen in the data shown in figure 8.4 (b). The analysis method from section 7.3 is employed to dissolve the shift to higher NV numbers, indicated by the Gaussian fits for the samples after the annealing treatment. The amount of NV centres increases for the two samples is by a factor of 1.23 (average numbers 66 to 81 NVs) and 4.57 (14 to 64 NVs) for Samples A and B respectively. At this point, the different enhancement factors cannot be explained entirely, as they could stem from either a limited number of nitrogen atoms or a limited number of available vacancies present in the diamond.

The second effect caused by the high-temperature treatment is an elevated coherence time $T_2$ measured by the Hahn echo sequence. Exemplary one measurement is shown in figure 8.5(a) where the increased coherence can be observed. To substantiate this statement, several Hahn echo measurements were performed over different ensembles among the two samples, and the results are summarised in table A.1 in the appendix A.2. The average increasing factors are 3.2 (10.1 µs to 32.3 µs) and 4.3
8.2 Increasing the volume normalised sensitivity

Figure 8.5: Characterisation of high temperature treated NV centres. (a) Hahn echo measurements confirm the increased coherence time after the reconstruction of the diamond lattice due to the high-temperature annealing process. The exponential decay of the annealed ensemble occurs slower (purple) and reveals a coherence time of $T_2 = 38.0\,\mu$s. (b) The increased creation yield comes with the pay-off of a lost preferential alignment since ODMR transitions from orientations other than $\langle 111 \rangle$ are observed. Note that the increase of NV yield was 23%, whereas the occurrence of the new orientations is 34%. This means that there are not only new NV centres created, but probably some of the existing ones have changed their orientation.

(6.0\,\mu s to 26.0\,\mu s) for the Samples A and B.

An increased coherence time and NV density as a result of the annealing treatment ends up in an increased magnetic field sensitivity, but this comes with the pay-off of a lost preferential NV centre alignment as proven by the ODMR measurement in figure 8.5(b). Two additional (inner) ODMR transition lines appear in the spectrum as a result of the activation of NV centres not aligned along the $\langle 111 \rangle$ direction. These are created either by diffusion of NV centres at high temperatures [246], where the vacancy is mobile and can move within the defect centre to any of the other three carbon positions or by the creation of new NV centres which were not present before annealing. This cannot be fully answered by these measurements, but nevertheless, in the latter case, the creation would happen randomly distributed among the four possible orientations as seen from ion implantation techniques as well. Analysis of the ODMR dips (comparing the area under the curves) reveals the fraction between different orientations, and for Sample A it can be concluded that still, 66% of the NV centres are preferentially-aligned along one crystal direction. In an actual sensing experiment the rest 34% are excited by the focussed laser as well, but their fluorescence signal does not carry any information, therefore lowers the ODMR contrast and consequently the magnetic field sensitivity. Despite
this loss of preferential alignment, the high-temperature vacuum annealing treatment ceases in an increased sensitivity of factors 1.3 and 2.9 for the Samples A and B, respectively. The estimated volume normalised sensitivities are calculated and shown in table 8.1.

<table>
<thead>
<tr>
<th>Volume normalised sensitivity $\eta_V$ in $\frac{nT}{\sqrt{\text{Hz} \cdot \mu m^3}}$</th>
<th>Sample A</th>
<th>Sample B</th>
<th>CVD grown$^*$</th>
<th>HPHT</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-grown</td>
<td>annealed</td>
<td>as-grown</td>
<td>annealed</td>
<td>as-grown</td>
</tr>
<tr>
<td>0.96</td>
<td>0.73</td>
<td>2.04</td>
<td>0.69</td>
<td>0.58</td>
</tr>
</tbody>
</table>

Table 8.1: Summary of the calculated ac volume normalised magnetic field sensitivities reached in Samples A and B as-grown and after the high temperature vacuum annealing procedure. + calculated from data given in [139]. (Parameters $C_O = 0.2$, $p_B = 100$ kcts/s and $\tau_L = 300$ ns were used). Additionally the value for an electron irradiated HPHT diamond [33] is given for comparison.

8.3 Determining the experimental magnetic field sensitivity

![Figure 8.6](image.png)

Figure 8.6: Method to measure the actual magnetic field sensitivity experimentally. (a) The magnetic field sensitivity is given as the highest slope of the ODMR curve. (b) Equivalent to this in the case of dc sensing, is the slope of the sine function received from a Ramsey experiment. (c) The uncertainty of a measured dc magnetic field amplitude $\delta B$ is decreased with increasing measurement time. The sensitivity in $\frac{nT}{\sqrt{\text{Hz} \cdot \mu m^3}}$ can be understood as the measurement uncertainty per unit time. Illustrated are two different NV sensors with different sensitivity (dark purple with green points and light purple with green squares.)

In this section, the dc magnetic field sensitivity for Sample B from section 8.1 is determined in an experiment. The set-up for this measurement is the regular con-
focal set-up which additionally contains a lab power supply, to generate a constant current $I$ through the copper wire. The variation of this current leads to a different effective magnetic field which can be measured by the NV centre ensembles in the sample. The sensitivity $\eta$ can be interpreted as the minimum magnetic field which can be measured per unit time. The smallest change of the magnetic field can be written as,

$$\Delta B = \frac{\partial B}{\partial C} \times \Delta C,$$

where $B$ is the external applied magnetic field which is measured, $C$ is the count rate level and $\Delta C$ the corresponding signal noise, given by the emission of the NV ensemble. The change of the magnetic field has to be measured via the change of fluorescence level, which is most sensitive at the inflexion point, marked as a green spot in the ODMR curve, illustrated in figure 8.6(a). The slope at this point is proportional to the sensitivity. In order to perform this measurement for dc fields, the fluorescence level difference can be measured at the inflexion point of a Ramsey measurement, as shown in figure 8.6(b). Therefore, a Ramsey measurement is performed with a fixed $\tau$, in the example $\tau = 472$ ns, under a variation of the external dc magnetic field. The resulting signal is a periodic oscillation, and the slope in the linear part can be fitted to receive the first term of equation 8.3. The standard deviation of the count rate $C$ can be determined by repeating this experiment or by merely dividing a 30 second measurement into 30 slots of 1 second. The value for $\Delta C$ can be determined by computing the standard deviation of these measurements. Note that smaller magnetic fields can be detected by increasing the measurement time $\tau$, as illustrated in figure 8.6(c) and scales with $\eta = \delta B \times \sqrt{\tau}$, where $\delta B$ marks the minimal, measurable magnetic field change. There are two different sensors with different magnetic field sensitivities, illustrated in figure 8.6(c). The pale purple line with green squares corresponds to the more sensitive one, but by increasing the measurement time for the other sensor (dark purple with green points), the smallest detectable magnetic field can be equal. Therefore, the definition of a fixed sensing time is an appropriate benchmark. In order to get the sensitivity, the value at one second of measurement time is considered, revealing the sensitivities to be $\eta_1 = 800 \frac{nT}{\sqrt{Hz}}$ (dark purple line with green points) and $\eta_2 = 200 \frac{nT}{\sqrt{Hz}}$ (pale purple line with green squares), respectively.

In a first experiment, the relationship between applied current $I$ and the resulting
magnetic field change $\Delta B$ has to be recorded. Therefore, a pulsed ODMR measurement is performed for different applied currents and together with the gyromagnetic ratio of the NV centre ($\gamma_{NV} = 2.8 \text{MHz G}^{-1}$) the line shifts can be transformed to magnetic field changes. This result is shown in figure 8.7(a) and the conversion factor between these two can be quantified by interpolation and fitting $\frac{\partial B}{\partial I} = 0.020833 \text{G mA}^{-1}$. In a second experiment, the Ramsey measurement, as described above, is performed for each applied current. The results are illustrated in figure 8.7(b) where the current to magnetic field conversion is already performed. The count rate $C$ is normalised for each individual detected laser pulse and to a measurement time of 1 second. The value of the highest slope of this curve reveals $\frac{\partial C}{\partial B} = -710 \frac{1}{\text{s G}}$. The noise level for this measurements can be evaluated as $\Delta C = 273.39 \frac{1}{\text{s}}$. This two values put into equation 8.3 reveals the smallest detectable field for Sample B which is given as

$$\Delta B = 802 \frac{\text{nT}}{\sqrt{\text{Hz}}}.$$  \hspace{1cm} (8.4)

The theoretical value for the volume normalised sensitivity of this sample can be calculated by changing the $\tau$ in equation 7.4 to $T_2^*$, which in the case of Sample
B after the annealing is on the order of 80 ns (data not shown) and this ends up in $39.8 \frac{nT}{\sqrt{Hz \times \mu m^3}}$. The discrepancy of the measured value from equation 8.4 and the theoretical expectation can be explained by the overhead of laser signal in the analysis of the signal. The one-second windows contain the actual sensing part and the read-out and initialisation of the NV centre, and therefore the value for sensitivity can further be optimised. Nevertheless, the measurement result is on the same order of magnitude and confirms the value of preferentially-aligned, high-density NV centre ensembles for magnetometry applications.

8.4 Atomic composition of the overgrown diamond layers

![Graph](image)

**Figure 8.8:** SIMS measurements performed on the high-density ⟨111⟩ Samples A (black) and B (purple). The nitrogen distribution within the first 500 nm of the overgrown layers are shown in (a). Hydrogen profiles with a high concentration for the same samples shown in (b).

Secondary ion mass spectrometry (SIMS) is a state-of-the-art technique to analyse the produced diamond layers regarding their atomic composition. For more details about this method, see section 5.2. The results obtained for Samples A and B are shown in figure 8.8, where the first exciting discovery is the different growth rates for the two plasma conditions. Sample A was grown with a speed of 210 nm/h whereas Sample B was grown slower at a rate of 120 nm/h, which can be explained in the following way (see also section 2.3.1). A lower microwave power leads to a lower microwave plasma density in the growth chamber, which comes with lower
growth temperature and therefore a lower diffusivity of the carbon species on the substrate’s surface. As a result, the growth rate is lower and ends up in a thinner diamond layer, if the growth time is fixed to two hours, as can be seen by the SIMS measurements of our samples.

Figure 8.8(a) displays the varying nitrogen density throughout the layer for both samples. It is known that the isotopically pure methane gas contains nitrogen on the order of 70 ppm, even though this would end up in a constant nitrogen concentration. As no nitrogen gas was added intentionally into the system, and since we observe a decaying profile, it can be assumed that a limited nitrogen source is used up during the growth. At this point, it is not possible to say where this source is situated. Some nitrogen might be incorporated inside the graphite heater or the chamber walls during the samples’ mounting process, but clear evidence is still missing. By the integration of the curves of figure 8.8, the overall nitrogen content inside the samples can be estimated to $1.07 \times 10^{12}$ and $1.02 \times 10^{12}$ atoms for Samples A and B, respectively. These values correspond to conversion efficiencies between nitrogen and NVs in the diamond layers of 0.25% and 0.21%, which is in good agreement with reports from the literature (0.33% [134]).

The hydrogen SIMS results are illustrated in figure 8.8(b), where hydrogen concentrations up to 3000 ppm are measured. Note that this corresponds to three orders of magnitude increased content with respect to the diamond substrate. It might be, that hydrogen is incorporated into the diamond lattice if many vacancies are present, meaning that the CVD growth is performed under not ideal conditions. The annealing procedure should annihilate most of the vacancies, but it could be that more complex vacancy clusters survive the high-temperature treatment of 1500°C. The hydrogen defect, where a hydrogen atom is trapped by a vacancy is called H1 centre. Another possibility is the formation of NVH centres where a hydrogen atom is caught by the NV centre. It is reported that this centre in CVD diamond is ten times more likely to be found than NVs [134]. The formation of these defects in mono-crystalline diamond is known [103, 247], and they are paramagnetic, thus limiting the coherence times of the created ensembles. Probably their concentration is that high, that the benefits of using a diminished $^{13}$C spin bath environment are negligible and therefore shortened $T_2$ times in comparison to the $^{13}$C-limit can be explained.

Optimising the growth conditions and minimising the hydrogen incorporation is an
8.5 Conclusion

In this chapter, we have seen, for the creation of a high-density diamond magnetic field sensor, it is advantageous if a ⟨111⟩ oriented diamond is chosen as a substrate for PECVD growth. This has several advantages over a regular ⟨100⟩ oriented one. The ability to preferentially align NV centres along one crystal axis together with a higher conversion yield and enhanced signal emission boosts the sensitivity of such magnetometers. Further increase by additional high-temperature vacuum annealing leads to a loss of preferential alignment, even though the benefit of elevated NV creation and increased coherence times compensates the lower measurement contrast. In the end, the annealing process improves the sensitivity of the NV centre ensembles for magnetometry applications. Imperfections of diamond growth are exposed by comparing the theoretical magnetic field sensitivity with the experimentally determined one and the analysis of the created diamond layers by SIMS technique. Other defects (NVH, P1, H1, H2 and others) than the desired NV centre are created during diamond growth which limits the sensor capabilities by decreasing its coherent interaction time with the sensing target. This point, however, is subject of the next chapter 9.
9 Optimising isotopically controlled NV ensembles for magnetometry applications

The results from the last chapter already show a high degree of control over the created NV centres, even though there are some issues which have to be addressed when talking about NV driven engineering. First, the nitrogen source which leads to incorporation into the diamond and therefore to creation of NV centres is not specified. It could stem from leakage, the methane gas or the chamber itself, as discussed briefly in the last section. No matter which is the right source of nitrogen, the NVs are created accidentally even though controlled in the way of optimised plasma conditions. Proper NV engineering requires doping of nitrogen $^{15}$N isotope instead of nitrogen $^{14}$N. Natural abundance of $^{15}$N is only 0.4% and a reasonable number of isotopically distinguishable NV centres proofs the intention of colour centre engineering. Furthermore, the $^{15}$N isotope has a nuclear spin of 1/2, which leads to additional sensing applications compared to $^{14}$N, as will be discussed in section 9.2.

A second point is the nitrogen incorporation into the diamond lattice. Only a small fraction of the nitrogen from the gas phase is actually converted into NV centres in the diamond. The biggest part form other defects, as P1, NVH, NVN, N2, N3, etc. [44]. As the NV centre has proven to be an excellent sensor, we are using created ensembles to obtain information about the nitrogen spin bath surrounding the NVs. This chapter deals with labelled NV centre ensemble creation and their characterization using introduced benchmark criteria in order to find the optimal growth strategy to enhance the magnetic field sensitivity of potential diamond magnetometers.
9 Optimising isotopically controlled NV ensembles for magnetometry applications

9.1 Creation of isotopically controlled, NV rich diamond layers

Table 9.1: Summary of the different diamond layer thicknesses of the six grown Samples I-VI. * estimated value, from SIMS measurements of identical process of Sample I.

<table>
<thead>
<tr>
<th>Sample</th>
<th>N/H</th>
<th>Growth temp</th>
<th>Buffer layer</th>
<th>Buffer growth time</th>
<th>NV layer</th>
<th>NV layer growth time</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.1%</td>
<td>1005°C</td>
<td>50 nm</td>
<td>10 min</td>
<td>190 nm</td>
<td>30 min</td>
</tr>
<tr>
<td>II</td>
<td>1.0%</td>
<td>1005°C</td>
<td>155 nm</td>
<td>30 min</td>
<td>875 nm</td>
<td>120 min</td>
</tr>
<tr>
<td>III</td>
<td>5.0%</td>
<td>1005°C</td>
<td>25 nm</td>
<td>10 min</td>
<td>66 nm</td>
<td>30 min</td>
</tr>
<tr>
<td>IV</td>
<td>0.1%</td>
<td>1005°C</td>
<td>50 nm*</td>
<td>10 min</td>
<td>190 nm*</td>
<td>30 min</td>
</tr>
<tr>
<td>V</td>
<td>0.1%</td>
<td>965°C</td>
<td>66 nm</td>
<td>10 min</td>
<td>235 nm</td>
<td>30 min</td>
</tr>
<tr>
<td>VI</td>
<td>0.1%</td>
<td>1035°C</td>
<td>78 nm</td>
<td>10 min</td>
<td>320 nm</td>
<td>30 min</td>
</tr>
</tbody>
</table>

In order to investigate the creation of NV rich diamond layers, a total of six samples is produced during this chapter, whereby several parameters which influence the quality of the NV ensembles are studied. Among these are the growth time (Sample I and Sample II), nitrogen gas phase concentration (Samples I, II and III) and growth temperature (Samples IV, V and VI). A reproducibility check can be performed by comparing Samples I and IV. A summary of these samples is shown in table 9.1. In a first study, we produce three different high-density NV samples

Table 9.2: Parameters for the nitrogen isotope controlled growth for high density NV layer production. Note that the isotopically $^{12}$CH$_4$ has an enrichment of 99.99%, according to suppliers data sheet (Eurisotop).

<table>
<thead>
<tr>
<th>$^{12}$CH$_4$/H$_2$</th>
<th>Power P</th>
<th>Pressure p</th>
<th>Temperature T</th>
<th>H$_2$ Flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1%</td>
<td>1.92 kW</td>
<td>52.5 mbar</td>
<td>1005°C</td>
<td>400 sccm</td>
</tr>
</tbody>
</table>

with a varying but controlled $^{15}$N nitrogen concentration by using the PECVD overgrowth technique. Note that the isotopic enrichment of the used $^{15}$N$_2$ gas is 98%, according to the suppliers’ data sheet (Sigma Aldrich). Diamond substrates are $\langle111\rangle$ oriented single crystal plates from supplier New Diamond Technologies (see table 4.1 for details) and the identical growth parameters for the three Samples I-III are summarised in table 9.2. Only growth time and nitrogen gas concentration are different, and theses are, together with further results of this chapter, summarised
9.1 Creation of isotopically controlled, NV rich diamond layers

All samples are analysed using SIMS technique (explained in detail in section 5.2) in table 9.1.

Figure 9.1: $^{12}\text{C}$, $^{13}\text{C}$, $^{14}\text{N}$ and $^{15}\text{N}$ profiles received from SIMS measurements of (a) + (c) Sample I and (b) + (d) Sample II.

and exemplary the results for Samples I and II are presented in figure 9.1 (results for Sample III are shown in appendix A.3). The pale grey-coloured area depicts the diamond substrate, whereas the grey one represents the buffer layer and the coloured one the nitrogen-doped layer.

The first remarkable feature from the two sets of measurements is that different growth time leads to differently thick diamond layers. The buffer layer of Sample I (compare the grey-coloured area of figure 9.1(a)) is exposed to the plasma for 10 minutes which leads to a layer thickness of 50 nm. The growth rate $\nu_{\text{gr}}$ can therefore be calculated, according to equation (5.2), and is found to be 5 nm/min. Since the buffer layer conditions are identical for Sample II, it can be stated that the growth rate scales linear with time, since the 30 minute process leads to a layer thickness of 155 nm (see the grey-coloured area of figure 9.1(b)). The growth rate
of 5.16 nm/min is slightly higher than for the first buffer layer, but nevertheless, a reproducible and scalable PECVD diamond growth process is developed. It has been shown before (see also section 5.2), that different nitrogen concentrations during the growth process lead to different growth rates. Sample I was grown at a speed of $\nu_{\text{gr}}^I = 6$ nm/min, which lead to a carbon $^{12}\text{C}$ enrichment of over 99.9% in respect to the $^{13}\text{C}$ content. Sample II shows a similar enrichment ratio, even though an elevated growth speed ($\nu_{\text{gr}}^{II} = 7.2$ nm/min). Both samples show that the isotopic enrichment of the source gas is imprinted in the grown diamond layer. Furthermore, the data implies that a ten times increased nitrogen gas content during the growth leads to a growth rate speed-up by a factor of 1.2.

Nitrogen investigations of the two Samples I and II are shown in figures 9.1(c) and (d), respectively. Both nitrogen isotopes $^{14}\text{N}$ and $^{15}\text{N}$ are monitored during the controlled etching of the SIMS measurement, where the $^{14}\text{N}$ content in the diamond substrate is higher than the $^{15}\text{N}$ content. In the grown layer though, the opposite is the case, namely the desired $^{15}\text{N}$ isotope is more present, indicating the intentional doping, even tough the isotopic purity of the source gas (98%) is not reached. This is an indication, that background nitrogen is present in the gas mixture and its origin, at this point, is not clear. Note, that this statement holds for both Samples I and II. Even though the ratio between the two isotopes is equal among the samples, the absolute nitrogen content is more than five times higher for Sample II. The average $^{15}\text{N}$ content reaches $3.9 \times 10^{19} \text{cm}^{-3}$ whereas Sample I reaches a value of $7.08 \times 10^{18} \text{cm}^{-3}$. So, a ten times increased amount of nitrogen in the gas phase $[N_G]$ of the CVD chamber results in a 5.5 times increased nitrogen content inside the diamond $[N_D]$. Another critical parameter for PECVD diamond growth and the incorporation of nitrogen and the resulting production of NV centres, is the growth temperature. In order to study this effect, three additional samples are produced with varying growth temperature. The growth parameters are identical to the ones for Sample I-III, but this time the nitrogen content is fixed to N/H=0.1 %, and the temperature is varied from 1005 °C (Sample IV), over 965 °C (Sample V) to 1035 °C (Sample VI). The temperature is measured with an infrared pyrometer as presented in section 4.2. Diamond substrates are also $\langle 111 \rangle$ oriented plates, but this time from supplier Applied Diamond Inc. In order to test the reproducibility of the developed growth process depending on the diamond substrate, Samples I and IV are pro-
9.1 Creation of isotopically controlled, NV rich diamond layers

duced under the same growth conditions. The other two samples (V and VI) are subject of SIMS measurements (data shown in the appendix A.3). The effect on the diamond growth rate is further illustrated in figure 9.2(a). Note that the addition of nitrogen decreases the growth rate for Sample III. Probably a critical nitrogen content is reached by this sample which influences the growth conditions and the underlying growth dynamics in a non-favourable way. Figure 9.2(b) contains the nitrogen $^{15}$N content of the individual samples, averaged over the layer thickness which is used to calculate the doping efficiency for the six produced samples, by using equation (5.3). A variation between $\zeta^{VI} = 3.84 \times 10^{-5}$ and $\zeta^{III} = 4.32 \times 10^{-6}$

![Figure 9.2](image)

Figure 9.2: (a) Diamond growth rate for the non-doped and doped layers produced in chapter 9. The addition of nitrogen leads to an elevated growth rate, whereas a higher N/C ratio accounts for a higher growth rate. (b) $^{15}$N content calculated from SIMS measurements. A high $^{15}$N gas concentration leads to a high incorporation rate.

can be determined. It is interesting to note that SIMS measurements suggest that Sample II is a more promising sample, due to the high nitrogen content, whereas the doping efficiency emphasises the growth processes underlying Sample I as the more promising approach. In order to rank the received doping efficiencies, they are compared with reports from the literature and plotted in figure 9.3(a). They are separated depending on the production technique where the reported doping efficiencies for $\langle 111 \rangle$ oriented diamond substrates are higher than for $\langle 100 \rangle$ oriented ones.

It can be seen that the samples presented here, have a very low nitrogen doping efficiency compared to previously reported samples. A high doping efficiency,
Figure 9.3: (a) Nitrogen doping efficiency received for the six samples (green points) compared between several works depending on the diamond substrate orientation \((\langle 111 \rangle\) purple squares \[31, 138, 139, 228, 248\] and \(\langle 100 \rangle\) blue triangles \[227–229\]). Image based on Osterkamp et al. \[249\]. (b) NV creation efficiency for the six samples (green points) is compared as well for the same \((\langle 111 \rangle)\) samples (purple squares) and additionally electron irradiated \((\langle 100 \rangle)\), nitrogen doped CVD layers (red triangles) \[240, 250\].

though is not the goal of this work. Instead, the creation of NV centres and their surrounding spin bath is of significant interest. Therefore, the quantity of interest, namely the amount of generated NV centres, should be part of the figure of merit for benchmarking the samples. For this purpose, figure 9.3(b) contains the NV creation efficiency, which is calculated by dividing the amount of NV centres by the amount of nitrogen present in the diamond layer. Creation efficiencies up to 5% are reported for CVD grown samples \[31\]. Higher values are achieved by additional electron irradiation of the samples with a subsequent annealing step, but they come at the cost of a loss of preferential alignment. Note, that the diamond layers which are reported in \[31\] and \[240\] are produced in the facilities reported in this thesis. As part of a collaboration, however, the samples were measured by the corresponding colleagues who have published the respective papers and therefore this data is not part of this dissertation.

Not all of the comparison works of figure 9.3(a) contain investigations of NV centres related information as the yield for example and therefore cannot be included in figure 9.3(b). It can be seen that the order of the Samples I-VI is different for the two benchmark criteria presented in figure 9.3(a)+(b). Therefore, benchmark methods are discussed in more detail in the next section, emerging a key figure for categorizing diamond samples containing NV centres with potential use in magnetometry.
9.2 $^{15}$NV ensembles and spin bath control

![Diagram](image)

**Figure 9.4:** Characterisation of the $^{15}$N doped samples. In order to verify the presence of $^{15}$NVs in the diamond layers, the hyperfine coupling to the NV’s electronic spin is measured via pulsed ODMR (a) to resolve the splitting of 3.1 MHz (b) Image based on Osterkamp et al. 249. (c) Ramsey sequence to perform FID measurements (d) without (purple) and with P1 spin bath driving (green) shows the limitation due to the bath interaction and their decoupling via resonant driving. (e) The $^{15}$N type P1 spectrum is measured for all the samples via a DEER measurement during which the bath frequency is swept. (f) Experimental data are plotted as green dots, whereas the solid purple line represents simulated transitions for the $^{15}$N type P1 centres. The dashed purple line shows simulated transitions for the $^{14}$N type P1 centres, which are not visible in the experimentally measured spectrum. Image based on Ref. 249. (g) The solid purple line is a simulation which shows the expected P1 spectral linewidth dependent on its density, whereas the green curve simulates the expected NV dephasing time under a given P1 spin bath concentration. The red squares mark the measured linewidth and the corresponding P1 concentration, whereas the orange dots indicate the experimentally determined $T_2^*$ time. The P1 linewidth estimation is used to derive the values presented in table 9.4.

All Samples I-VI show preferentially-aligned NV centres along the $\langle 111 \rangle$ crystal axis, but different concentrations of the isotopically controlled type $^{15}$NVs. Pulsed ODMR measurements (pulse sequence shown in 9.4(a)) are performed to determine the hyperfine splitting (3.1 MHz) caused by the nitrogen nuclear spin associated with the NV centre (see figure 9.4(b)). The presence of $^{15}$NVs was proven in all
samples (if T_2* time is too short (<300 ns), other techniques can be used to prove the presence of ^{15}NV [251]). FID measurements using the Ramsey sequence, as introduced in section 3, are performed on the NV ensembles exemplary shown for Sample I. The signal observed from this measurement is shown in purple in figure 9.4(d). This relatively short decay time of 40 ns is due to the interaction with the surrounding spin bath of P1 centres.

The spin bath is investigated in the next experiment, where a spin-echo double resonance (SEDOR) technique is used [252]. A Hahn echo is performed on the NV’s electronic spins, and the bath spins are flipped at the same time as the NVs. The spin bath flips cause decoherence of the NV, and the signal will show a dip at the resonant frequencies. The resulting spectrum is shown in green in figure 9.4(f) and contains the characteristic spectrum of neutrally charged ^{15}N impurities (P1 centres). The purple lines represent the simulated P1 spectra for ^{15}N (solid) and ^{14}N (dashed) according to [253], where clearly the first one matches the experiment. In order to understand the characteristic spectra shown in figure 9.4(f) it is necessary to look into the P1 centre in more detail. P1 centres are considered as substitutional nitrogen atoms, replacing a carbon atom directly at its lattice site. In fact, it has been found that nitrogen expands to about 10-40% into the direction of one of the neighbouring carbon atoms [254,255]. By aligning the magnetic field along the ⟨111⟩ crystal axis, one orientation is parallel with the applied B field vector, whereas the other three orientations cover the same angle of 109.5°. The ^{15}N isotope P1 centre possesses an electron spin of S_{N15} = 1/2 and a nuclear spin of I_{N15} = 1/2, resulting in four eigenstates and therefore two allowed dipole transitions. For four orientations of P1 centres, this gives a total of eight resonances, which under the conditions from above reduce to four with intensity ratios of 1:3:3:1. Moreover, this can be seen in the spectrum of figure 9.4(f). In the case of ^{14}N isotope, which possesses electronic and nuclear spins of S_{N14} = 1/2 and I_{N14} = 1, the overall number of resonances is twelve. In the special case of the aligned magnetic field along the ⟨111⟩ direction, they are reduced to five, as shown in the simulated spectrum with intensity relation of 1:3:4:3:1 (dotted purple line in figure 9.4(f)).

Details on the P1 centre related parameters used for the simulations, which are performed for a magnetic field of 0.3 mT, are summarised in table 9.3. Furthermore, the gyromagnetic ratio of P1 centres \( \gamma_{P1} = g \times \mu_B / h = 2.8 \text{ MHz/G} \) is used where, \( g = 2.0024, \mu_B = 9.274 \times 10^{-24} \text{ J/T} \) and \( h = 6.626 \times 10^{-34} \text{ Js} \), are the electronic
g-factor, the Bohr magneton and the Planck constant respectively.

Since the P1 transition frequencies are known at the applied magnetic field of Table 9.3:

Table 9.3: Overview of the characters used for the simulation in figure 9.4(f), values for the P1 centre taken from [256–258].

<table>
<thead>
<tr>
<th></th>
<th>$^{14}$N</th>
<th>$^{15}$N</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{</td>
<td></td>
<td>}$</td>
</tr>
<tr>
<td>$A_{\perp}$</td>
<td>Hyperfine</td>
<td>114.2 MHz</td>
</tr>
<tr>
<td>$P$</td>
<td>Quadrupole Splitting</td>
<td>-3.97 MHz</td>
</tr>
</tbody>
</table>

300 G perpendicular to the diamond surface, it is possible to drive these transitions to suppress NV-P1 interactions (only valid, if the driving rate of $\Omega_{P1}$ is faster than the average coupling strength $\Gamma_{NV-P1}$ [31]). This driving is averaging the heterospin dipolar interactions and prolongs the NV’s coherence or dephasing time. This effect is illustrated in green in figure 9.4(d).

The advantage of this decoupling is that it increases the magnetic field sensitivity of a potential NV based diamond magnetometer to dc magnetic fields. In this work, however, we are mainly interested in the nature of nitrogen inside the diamond and its form within the lattice. Therefore, the NV sensors are used to estimate the P1 density in the sample. The interacting P1 spin bath causes local fluctuations seen by the sensor NVs and leads to a dephasing time $T_2^* = \frac{1}{2 \times \pi \times \frac{\Gamma}{ppm}}$, where $\Gamma = 9.1 \text{ kHz/ppm}$ represents the electronic spin interaction strength [259].

This interaction is illustrated in figure 9.4(g) where the purple line displays the P1 concentration at a given P1 linewidth and the green curve the corresponding dephasing time at a known P1 spin concentration. From a fitted, not power broadened linewidth of $\sim 6$ MHz, we estimate a P1 density of approximately 100 ppm for Sample I. The NV density is measured by optical emission signal and can be estimated to 200 ppb, which gives a conversion efficiency of 0.2% regarding the P1 spin bath, which is in good agreement to previous work [134]. The values for the other Samples II-VI are illustrated in the summary table 9.4. It is interesting to note, that the experimentally determined $T_2^*$ dephasing time is slightly shorter than expected from the simulation, which has to be studied in more detail.

The main advantage in using $^{15}$N instead of the commonly used $^{14}$N, besides the fact that it proofs the intentional engineering due to the low natural abundance, can be seen in figure 9.4(f) as well. The strongest transition of $^{14}$N is the central one
which overlaps with the position for electronic spins with a g-factor close to $g = 2$. Therefore, it is difficult to distinguish signals stemming from the P1 spin bath or other bath impurities as for example, NVH$^-$ [247]. Since $^{15}$N has a nuclear spin of $1/2$ the central line is not present in the spectrum and enables sensing of other spin species. In fact, there is a small dip in the spectrum of figure 9.4(f) which is close to the position of $g = 2$, shifted by 10 MHz though. Further analysis is necessary to confirm the presence of NVH$^-$, which, due to the $^{15}$N properties, is possible now. At least to our knowledge, this is the first time such a study can be performed with preferentially aligned, isotopically controlled $^{15}$NVs confined to a thin diamond layer and created during a PECVD diamond growth process.

Since the amount of NVH, present in CVD diamond, is an order of magnitude higher than the amount of NV centres [134, 227], it is essential to understand its formation to get a decent picture of the nitrogen dynamics during the growth process. This knowledge could lead to potentially exploiting conversion of P1 and NVH to NV centres and drive the sensitivity of a possible diamond magnetometer to its maximum. Another possible application lies in the field of detecting superparamagnetic particles if the NV rich layers are produced in very close proximity to the diamond surface [260].

With this analysis method, it is possible to redefine the benchmark criterion for high-density NV ensembles used for magnetometry applications. Instead of correlating the number of nitrogen inside the diamond to NV centres, the P1 centres should be taken as a reference. Such a number contains more physical information about the system since the coherence times of the NV ensembles, in an otherwise spin free environment ($^{12}$C), is mainly limited by P1 centres. Therefore, the NV/P1 ratio depicts an excellent key figure for benchmarking produced diamond samples and the emergence of relevant growth improving parameters. The non-destructive detection of such P1 noise sources is a non-trivial task on the nano-scale of thin diamond layers (conventional EPR is not sensitive to the low number of spins), and the number of comparison works is limited. Nevertheless, the samples produced under varying nitrogen content and varying growth temperature are illustrated in figure 9.5(a) as well as two reference samples from the literature.
Clearly visible is that the produced Sample I performs best in this graph, and it can be concluded, that growth parameters for Sample I are superior in comparison to the other ones. Especially a low nitrogen gas phase content (N/H=0.1%) leads to an enhanced NV/P1 ratio. Furthermore, the variation of temperature in our PECVD diamond growth chamber decreases the NV/P1 ratio and the intermediate temperature of 1005°C seems favourable for optimising growth conditions for NV generation.

By adding up the NV and P1 concentrations within the produced diamond layers and comparing this value with the overall nitrogen content, it is possible to estimate the amount of nitrogen of unknown form. This can be seen in figure 9.5(b), where the percentage of untraceable nitrogen is marked (bar with the palest colour). Probably this nitrogen is present in forms of NVN$^0$, A-centres or H4 which are not tracked by the used methods. Further analysis is necessary to fully understand the dynamics of nitrogen incorporation during PECVD diamond growth in order to optimize the NV centre formation. Converting as much nitrogen as possible to NV centres would bring two advantages at once, namely an increased NV density and a reduced influence of the spin bath surrounding the NV. Both would end up in an increased magnetic field sensitivity. Note that nitrogen of Samples I and IV seems to be completely converted to NV or P1 centres, therefore represent the most promising samples.
All comparisons (figure 9.3 and figure 9.5) show the necessity to define a gold standard for NV fabrication using the PECVD method to compare different studies and evaluate superior growth strategies reliably. This could lead to synergy effects and a speed-up in the comprehension process of NV generation for magnetometry applications.

### 9.3 Dynamical decoupling of $^{15}$NV ensembles

![Dynamical decoupling experiment](image)

**Figure 9.6:** Dynamical decoupling of the $^{15}$NV electronic spin ensembles: (a) XY8 pulse sequence to prolong the NVs electronic spin coherence time. $\pi$-pulses around x and y-axes refocus the influences from the spin bath and therefore preserve the coherence. (b) Dynamical decoupling experiment for one ensemble of NVs in Sample II. The Hahn echo coherence time, the lower bond of this experiment, is approximately 1 $\mu$s. By increasing the XY8-N order, the coherence time decay is pushed to higher $\tau_{tot}$ values. Solid lines are fitted values to the decoherence envelope of the form $\exp[-(\tau_{tot}/T_2)^n]$, where n is free parameter dependant on the dynamics of the spin environment. Image based on Osterkamp et al. 249. (c) Power-law scaling of the measured NV ensemble coherence times with respect to the total number of $\pi$-pulses used in the decoupling sequence. The solid lines represent fit functions (with error marked as coloured areas), from which the power scaling factor k was extracted: $k_I = 0.59$, $k_{II} = 0.59$, $k_{III} = 0.60$, $k_{IV} = 0.58$, $k_{V} = 0.66$ and $k_{VI} = 0.59$ suggesting Lorentzian distributed spin baths for all samples.

In the last section, it has been shown that a highly sensitive NV magnetometer benefits from a large number of preferentially aligned NV centres. Unfortunately, not all nitrogen present in the diamond lattice is used to create this desired point defect. In fact, the creation yield of CVD produced NV centres is on the order
of a few per cent. It is believed that most nitrogen incorporated in the diamond lattice is present in the form of a neutrally charged substitutional single nitrogen atom. It is reported that the ratio between P1 and NV centres is on the order of (300:1) [134,227]. In a spin-free $^{12}$C diamond host lattice these P1 centres build the primary source of decoherence for the NV centres. A higher P1 concentration should lead to a shorter NV coherence time. As this source is known, it is possible to protect the NV’s electron spin by decoupling.

Several so called Dynamical Decoupling sequences have been proposed in the literature as CPMG [168,169], XY8 [170] or AXY [171]. Here the XY8 pulse sequence (shown in figure 9.6(a)) is used for decoupling, which in principle constitutes an expansion of the Hahn echo sequence presented in the theory part, section 3, where a series of temporally equally spaced $\pi$-pulses are used instead of one central $\pi$-pulse. These are also alternated around different axes (x and y) to prevent the accumulation of errors. The main block consists of eight pulses which are spaced with a waiting (sensing) time $\tau$ in between. The whole block can be repeated $N_{XY8}$ times, where $N_{XY8}$ represents the XY8 order. Note that the total number of pulses is $N_{XY8}$ times 8, so an XY8 measurement of the order 2 (XY8-2) consists of a total of 16 $\pi$-pulses.

The coherence time $T_2$ measured with the Hahn echo sequence is on the order of 1 µs for the ensembles in Sample II. This relatively low value, in comparison with NVs in $^{12}$C enriched diamond samples, can be explained by the nitrogen-rich spin bath, as discussed above. Dynamical decoupling by using different orders of the XY8-N sequence prolongs this coherence time, and the NV ensemble’s spin coherence is measured in respect to the full sensing time $\tau_{tot}$. Figure 9.6(b) shows the coherence time measurements where each measurement is fitted with an exponential function of the form $\exp[-(\tau/T_2)^n]$. Clearly visible is the prolongation of the decay time where a 15 times improvement is measured by using a sequence (XY8-16) with a total of 128 $\pi$-pulses. The effect is similar for the Samples I (14 x improvement), III (10 x), IV (15 x), V (11 x) and VI (12 x) and their prolonged coherence time are summarised in table 9.4.

It is reported [261] that the type of noise bath can be exploited by fitting the total coherence time versus the number of applied $\pi$-pulses with a power law of the form,

$$T_2^n \propto (8 \times N_{XY8})^k.$$  \hspace{1cm} (9.1)
These power laws, including the fit errors, are illustrated in figure 9.6(c) for the six Samples I-VI produced under varying nitrogen gas content and different temperatures. It is interesting to note that despite the different overall coherence times, the fitting factors are nearly the same $k \approx 0.60$. This allows the assumption that the limiting spin bath is dominated by Lorentzian distributed noise, which in theory results in a scaling factor of $k = 2/3$ [261,262]. The interpretation of this factor could be that there is one noise source present in the environment of the NV centres, which we identify, in the confirmed absence of $^{13}$C, as P1 centres. The strong dependence of the NV centres coherence times on the presence and density of P1 centres underlines the feasibility of the above-defined criterion. The NV/P1 ratio is an excellent figure of merit for the improvement of colour centre creation techniques. Note, that this is not only limited to PECVD diamond growth methods using delta doping but holds for the whole variety from HPHT pressing to ion implantation techniques which specialise on the fabrication of NV centres.

Table 9.4: Summary of all samples used during this chapter. * estimated value, SIMS results of identical process of Sample I are used.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_2$</th>
<th>$T_2$</th>
<th>$T_2$</th>
<th>$T_2$</th>
<th>NV density</th>
<th>P1 $^{15}$N density</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>3.2 µs</td>
<td>44 µs</td>
<td>180 ns</td>
<td>900 ns</td>
<td>464 ppb</td>
<td>40 ppm</td>
</tr>
<tr>
<td>II</td>
<td>1.0 µs</td>
<td>15 µs</td>
<td>40 ns</td>
<td>190 ns</td>
<td>109 ppb</td>
<td>100 ppm</td>
</tr>
<tr>
<td>III</td>
<td>1.3 µs</td>
<td>13.5 µs</td>
<td>42 ns</td>
<td>-</td>
<td>447 ppb*</td>
<td>100 ppm</td>
</tr>
<tr>
<td>IV</td>
<td>2.6 µs</td>
<td>38.7 µs</td>
<td>31 ns</td>
<td>-</td>
<td>290 ppb*</td>
<td>41 ppm</td>
</tr>
<tr>
<td>V</td>
<td>2.4 µs</td>
<td>26.1 µs</td>
<td>200 ns</td>
<td>-</td>
<td>181 ppb</td>
<td>50 ppm</td>
</tr>
<tr>
<td>VI</td>
<td>2.5 µs</td>
<td>31.1 µs</td>
<td>57 ns</td>
<td>-</td>
<td>69 ppb</td>
<td>42 ppm</td>
</tr>
</tbody>
</table>

9.4 Conclusion

The ability to preferential align NV centre ensembles along one crystal axis is a powerful feature towards the sensitivity optimisation of a quantum-enhanced diamond magnetometer. The lack of understanding the colour centre creation process limits engineering capabilities and gives rise to a new benchmark to analyse diamond samples containing NV centres. Improving the NV properties at a concurrent control of the nitrogen-based spin bath environment during the PECVD process is
indispensable. In order to identify key parameters which influence the NV/P1 ratio, it is necessary to rank several growth procedures to highlight the most promising growth strategy. This task is fulfilled in this chapter, where several PECVD diamond growth processes are investigated, and the best one revealed a NV/P1 ratio of 0.5%. It is shown furthermore, that a low nitrogen gas concentration of N/H=0.1\%, during diamond growth, is advantageous as well as the choice of intermediate growth temperature of approx 1000°C.
10 Conclusion and Outlook

10.1 Conclusion

Nitrogen-vacancy (NV) colour centre research has proven to be very promising regarding the implementation of industrial applications as magnetic imaging on the nanoscale or highly sensitive magnetometers. The fabrication processes aiming for optimised NV content and coherence times, though, are still in their infancy and production of suitable synthetic diamond samples is challenging and requires accurate examination.

In this thesis, the general principles of NV centre creation by nitrogen incorporation during a PECVD diamond growth process were studied. Successful fabrication of shallow, single NV centres approximately 5 nm below the diamond surface was reported, which were used to perform a nanoscale NMR experiment in order to confirm the shallowness. Crucial point during this magnetic resonance experiment was the primal charge state stabilisation by fluorine surface termination since NVs suffer from charge fluctuations and traps on the diamond surface. Several stabilisation processes were tested where the stabilisation by SF$_6$ plasma treatment for a duration of 4 minutes yields the most promising results.

Quantum sensing is one of the big promising fields, nowadays, which is treated as the new shooting star to unite the quantum with the macroscopic world. High-density NV centre ensembles are very sensitive to magnetic fields, and their sensitivity scales with the ensemble’s size. The fabrication of such ensembles (density up to 1 ppm) and new routes to define the sensitivity from a material scientist’s point of view are the central part of this thesis. Introduction of the volume normalised sensitivity and ways to improve it by high-temperature annealing are presented for preferentially-aligned NV centre ensembles, where the latter treatment increases the volume normalised sensitivity $\eta_V$ by a factor of up to 2.9. The

131
discrepancy between theoretical and experimental value is found to be on the order of 60 ($\eta^B_{\text{theo}} = 0.69 \frac{nT}{\sqrt{Hz/\mu m^3}} \leftrightarrow \eta^B_{\text{exp}} = 39.8 \frac{nT}{\sqrt{Hz/\mu m^3}}$). However, the increase caused by an additional annealing step comes at the cost of the loss of preferential alignment (34% of the measured NV ensembles are not aligned along ⟨111⟩ crystal direction).

Engineering of NV centres requires control of the nitrogen content in diamond and consolidated knowledge of the NV creation process during PECVD diamond growth. Usage of isotopically controlled source gases limits the influences from unwanted side effects and proofs the intention of the engineering action. High-density, along one crystal axis aligned NV ensembles were successfully produced under varying nitrogen and temperature conditions. In order to benchmark the different growth procedures, a new key figure is introduced, namely, the NV/P1 ratio, which contains information about the NV sensor density and the primary source of decoherence to it. For the reported samples, this ratio is on the order of 1.1%.

Additionally, investigations regarding the NV centres coherence times and their prolongation, by the usage of dynamical decoupling techniques, is found to be on the order of 15 and 5 respectively for $T_2$ and $T^*_2$. Studying the saturation behaviour of applied decoupling protocols reveals information about the complexity of the underlying spin bath, which is found to be similar for all samples (scaling constant for XY8 dynamical decoupling, $k \approx 0.6$). Application of these benchmark criteria leads to the identification of promising growth strategies for enhanced NV centre creation, which in our case are a decent nitrogen content in respect to hydrogen of N/H=0.1% and an intermediate growth temperature of 1005 °C.
10.2 Outlook

Quantum computation, quantum cryptography, quantum metrology and quantum simulation based on defect centres is diamond would benefit from an enhanced and superior fabrication process. The lack of suitable NV samples limits the community from the much sought-after breakthrough in quantum technology. Optimisation of the electron spins coherence properties by controlling the environment of the NV centres together with an elevated creation efficiency is key to such quantum grade diamond material (in the style of E6 electronic grade). Many research groups are persuading this task [263], mainly on large diamond crystals to make use of the conventional EPR technique [32,264]. Precise control of the nitrogen incorporation is a difficult task since nitrogen can be present in many configurations which are partially dark in the sense of fluorescence or magnetic response [44]. Their formation though has to be understood in order to steer the creation towards NV centres. The NV density should ideally be increased to reach a value of NV/P1=1, which would end in a configuration where NV-NV coupling is the dominant decoherence source. Naturally, there are also approaches to improve the NV sensitivity post-growth, for example by enhancing the photon collection efficiency via nano-structuring [232,265] or suppressing the limited time of coherent interaction by using techniques like correlation spectroscopy [181] or quantum heterodyne detection (Qdyne) [182].

Finally, in order to create an added value in the field of quantum technology the integration of optimised, even if not perfect yet, NV centre containing diamond samples into devices is of major importance [266,267]. These integrated magnetometers draw attention to the field and fortify the breakthrough potential of NV centre based devices as pioneers in applicable quantum technology.
Appendix
A Appendix

A.1 Growth recipes - Overview

A.1.1 Layers for the first SIMS measurements

The diamond layers described in chapter 5 are grown on Ib type ⟨111⟩ oriented diamond substrates. The plasma conditions are set to MW power $P = 1.2$ kW, MW frequency $f = 2.46$ GHz, pressure $p = 25$ mbar and growth temperature of $T = 750$ °C, measured with a thermocouple. A hydrogen termination is performed for 5 minutes prior to the growth.

Sample X

Diamond substrate: HPHT crystal, polished, ⟨100⟩ oriented
Sumitomo, multisectorial, 3.5 mm x 3.5 mm x 1 mm
Specific parameters: For the buffer layer, the flow rates are adjusted to $\text{flow}_{H_2} = 200$ sccm and $\text{flow}_{CH_4} = 1$ sccm. Growth time is $t_{\text{buff}} = 6$ hours.
For the N doped layer, the flow rates are adjusted to $\text{flow}_{H_2} = 600$ sccm, $\text{flow}_{CH_4} = 0.3$ sccm and $\text{flow}_{15N_2} = 5$ sccm. Growth time is $t_{N-\text{layer}} = 5$ hours.

Sample Y

Diamond substrate: HPHT crystal, polished, ⟨100⟩ oriented
Sumitomo, multisectorial, 3.5 mm x 3.5 mm x 1 mm
Specific parameters: For the N doped layer, the flow rates are adjusted to $\text{flow}_{H_2} = 600$ sccm, $\text{flow}_{CH_4} = 0.3$ sccm and $\text{flow}_{15N_2} = 0.3$ sccm. Growth time is $t_{\text{buff}} = 0$ hours $t_{N-\text{layer}} = 24$ hours.
A.1.2 Shallow NV centre experiments

Shallow and buried NV centres

The diamond layers described in chapter 6 are grown on Ib type ⟨100⟩ oriented diamond substrates. The plasma conditions are set to MW power $P = 1.2\,\text{kW}$, MW frequency $f = 2.46\,\text{GHz}$, pressure $p = 20\,\text{mbar}$ and growth temperature of $T = 750\,\text{°C}$, measured with a thermocouple. A hydrogen termination is performed for 5 minutes prior to the growth.

Diamond substrate: HPHT crystal, polished, ⟨100⟩ oriented Sumitomo, multisectorial, 3.5 mm x 3.5 mm x 1 mm

Specific parameters: The flow rates are adjusted to $\text{flow}_{H_2} = 200\,\text{sccm}$, $\text{flow}_{CH_4} = 1\,\text{sccm}$ and $\text{flow}_{15N_2} = 5\,\text{sccm}$. The growth times are $t_{buff}^1 = 47\,\text{hours}$, $t_{N\text{-layer}}^1 = 5\,\text{minutes}$, $t_{buff}^2 = 45\,\text{hours}$, $t_{N\text{-layer}}^2 = 5\,\text{minutes}$.

Off-angle experiment

The diamond layers described in section 7.4 are grown on IIa type ⟨100⟩ oriented diamond substrates with several off cut regions. The plasma conditions are set to MW power $P = 1.2\,\text{kW}$, MW frequency $f = 2.46\,\text{GHz}$, pressure $p = 22.5\,\text{mbar}$ and growth temperature of $T = 750\,\text{°C}$, measured with a thermocouple. A hydrogen termination is performed for 5 minutes prior to the growth.

Diamond substrate: CVD crystal, off angle polished, base material ⟨100⟩ oriented Element Six, monosectorial, 2 mm x 2 mm x 0.5 mm

Specific parameters: The flow rates are adjusted to $\text{flow}_{H_2} = 600\,\text{sccm}$, $\text{flow}_{CH_4} = 0.3\,\text{sccm}$ and $\text{flow}_{15N_2} = 0.3\,\text{sccm}$. The growth times are $t_{buff} = 2\,\text{hours}$, $t_{N\text{-layer}} = 2\,\text{hours}$.

A.1.3 Dense NV ensemble experiments

The diamond layers described in the chapter 7 are grown on IIa type ⟨111⟩ oriented diamond substrates. The plasma conditions are set to MW frequency $f = 2.46\,\text{GHz}$ and pressure $p = 22.5\,\text{mbar}$. A hydrogen termination is performed for 5 minutes prior to the growth. The flow rates are $\text{flow}_{H_2} = 200\,\text{sccm}$, $\text{flow}_{12CH_4} = 1\,\text{sccm}$.
Sample A

Diamond substrate: CVD crystal, polished, ⟨111⟩ oriented
Applied Diamond Inc., monosectorial, 2 mm x 2 mm x 0.5 mm
Specific parameters: The microwave power for Sample A is $P = 1.2$ kW which results in a growth temperature of $T = 930 \, ^\circ C$ measured with a pyrometer. The growth times are $t_{N-layer} = 2$ hours. Note that the intrinsic nitrogen of the chamber was used for the NV creation.

Sample B

Diamond substrate: CVD crystal, polished, ⟨111⟩ oriented
Applied Diamond Inc., monosectorial, 2 mm x 2 mm x 0.5 mm
Specific parameters: The microwave power for Sample B is $P = 0.72$ kW which results in a growth temperature of $T = 875 \, ^\circ C$ measured with a pyrometer. The growth times are $t_{N-layer} = 2$ hours. Note that the intrinsic nitrogen of the chamber was used for the NV creation.

A.1.4 $^{15}$NV ensembles experiments

The diamond layers described in the chapter 9 are grown on IIa type ⟨111⟩ oriented diamond substrates. The MW plasma conditions for these experiments are fixed to $(P = 1.92 \, \text{kW}, \, p = 52.5 \, \text{mbar}, \, f = 2.46 \, \text{GHz})$. The hydrogen termination is performed by applying a microwave (MW) plasma in a hydrogen atmosphere with a constant flow rate of $flow_{H_2} = 400 \, \text{sccm}$ for 5 minutes. $^{12}\text{CH}_4$ is applied at flow rate of $flow_{\text{CH}_4} = 0.4 \, \text{sccm}$. The intrinsic growth is performed for a certain time $t_{buff}$ before nitrogen was added to the system. The growth time for the nitrogen rich diamond layer was set to $t_{N-layer} = 30 - 120$ minutes, depending on the process.

Sample I

Diamond substrate: HPHT crystal, polished, ⟨111⟩ oriented
New Diamond Technology, monosectorial, 2 mm x 2 mm x 0.5 mm
Specific growth parameter: $flow_{N_2} = 0.4 \, \text{sccm}$, $t_{buff} = 10 \, \text{min}$, $t_{N-layer} = 30 \, \text{min}$, growth temperature $T=1005 \, ^\circ C$. 
Sample II
Diamond substrate: HPHT crystal, polished, $\langle 111 \rangle$ oriented
New Diamond Technology, monosectorial, 2 mm x 2 mm x 0.5 mm
Specific growth parameter: $flow_{N_2} = 4$ sccm, $t_{buff} = 30$ min, $t_{N-layer} = 120$ min, growth temperature $T=1005^\circ C$.

Sample III
Diamond substrate: HPHT crystal, polished, $\langle 111 \rangle$ oriented
New Diamond Technology, monosectorial, 2 mm x 2 mm x 0.5 mm
Specific growth parameter: $flow_{N_2} = 20$ sccm, $t_{buff} = 30$ min, $t_{N-layer} = 120$ min, growth temperature $T=1005^\circ C$.

Sample IV
Diamond substrate: CVD crystal, polished, $\langle 111 \rangle$ oriented
Applied Diamond Incorporation, monosectorial, 2 mm x 0.61 mm x 0.3 mm
Specific growth parameter: $flow_{N_2} = 0.4$ sccm, $t_{buff} = 30$ min, $t_{N-layer} = 120$ min, growth temperature $T=1005^\circ C$.

Sample V
Diamond substrate: CVD crystal, polished, $\langle 111 \rangle$ oriented
Applied Diamond Incorporation, monosectorial, 2 mm x 0.61 mm x 0.3 mm
Specific growth parameter: $flow_{N_2} = 0.4$ sccm, $t_{buff} = 30$ min, $t_{N-layer} = 120$ min, growth temperature $T=965^\circ C$.

Sample VI
Diamond substrate: CVD crystal, polished, $\langle 111 \rangle$ oriented
New Diamond Technology, multisectorial, 2 mm x 2 mm x 0.5 mm
Specific growth parameter: $flow_{N_2} = 0.4$ sccm, $t_{buff} = 30$ min, $t_{N-layer} = 120$ min, growth temperature $T=1035^\circ C$. 
A.2 Hahn echo coherence times

In this section, several Hahn echo measurements are shown which were performed on preferentially-aligned NV ensembles presented in chapter 8. The results for measurements performed on the samples before and after the annealing process are summarised in table A.1.

Table A.1: Summary of the coherence times measured on ensembles of Samples A and B before and after the high temperature annealing procedure.

<table>
<thead>
<tr>
<th>Ensemble</th>
<th>Sample A</th>
<th>Sample B</th>
<th>Sample A annealed</th>
<th>Sample B annealed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ensemble 01</td>
<td>7.9 µs</td>
<td>8.0 µs</td>
<td>29.4 µs</td>
<td>24.0 µs</td>
</tr>
<tr>
<td>Ensemble 02</td>
<td>11.4 µs</td>
<td>13.0 µs</td>
<td>31.0 µs</td>
<td>22.0 µs</td>
</tr>
<tr>
<td>Ensemble 03</td>
<td>9.4 µs</td>
<td>4.4 µs</td>
<td>40.0 µs</td>
<td>30.0 µs</td>
</tr>
<tr>
<td>Ensemble 04</td>
<td>11.0 µs</td>
<td>8.5 µs</td>
<td>29.0 µs</td>
<td>24.5 µs</td>
</tr>
<tr>
<td>Ensemble 05</td>
<td>15.0 µs</td>
<td>5.3 µs</td>
<td>33.0 µs</td>
<td>22.6 µs</td>
</tr>
<tr>
<td>Ensemble 06</td>
<td>10.0 µs</td>
<td>3.1 µs</td>
<td>38.0 µs</td>
<td>21.5 µs</td>
</tr>
<tr>
<td>Ensemble 07</td>
<td>12.5 µs</td>
<td>2.8 µs</td>
<td>28.3 µs</td>
<td>35.0 µs</td>
</tr>
<tr>
<td>Ensemble 08</td>
<td>11.4 µs</td>
<td>5.2 µs</td>
<td>29.0 µs</td>
<td>33.0 µs</td>
</tr>
<tr>
<td>Ensemble 09</td>
<td>9.6 µs</td>
<td>3.4 µs</td>
<td>33.0 µs</td>
<td>23.1 µs</td>
</tr>
<tr>
<td>Ensemble 10</td>
<td>10.2 µs</td>
<td>-</td>
<td>-</td>
<td>22.0 µs</td>
</tr>
<tr>
<td>Ensemble 11</td>
<td>9.5 µs</td>
<td>-</td>
<td>-</td>
<td>24.0 µs</td>
</tr>
<tr>
<td>Ensemble 12</td>
<td>9.1 µs</td>
<td>-</td>
<td>-</td>
<td>26.8 µs</td>
</tr>
<tr>
<td>Ensemble 13</td>
<td>2.8 µs</td>
<td>-</td>
<td>-</td>
<td>29.0 µs</td>
</tr>
<tr>
<td>Ensemble 14</td>
<td>10.3 µs</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ensemble 15</td>
<td>11.7 µs</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>10.1 µs</strong></td>
<td><strong>6.0 µs</strong></td>
<td><strong>32.3 µs</strong></td>
<td><strong>26.0 µs</strong></td>
</tr>
</tbody>
</table>
A Appendix

A.3 SIMS measurements

Figure A.1: $^{15}$N profiles of Samples I, II, III, V and VI from chapter 9. The lines are shifted vertically in order to increase the visibility. A higher nitrogen content in the gas phase leads to an increased layer thickness, as well as a higher growth temperature.

In order to conclude the set of SIMS measurements, presented in section 9.1, the $^{15}$N profiles which are extracted from SIMS measurements are presented in figure A.1. Here, all five samples which were subject of SIMS measurements are compared regarding the nitrogen incorporation and the resulting layer thicknesses. Two results can be seen in this figure. First, the layer thickness depends on the nitrogen concentration, where a thicker layer is achieved by an elevated nitrogen gas content (compare Samples I-III). The second result targets the growth temperature, which was set to 1005 °C for Samples I, II and III. Sample V was grown at 965 °C and Sample VI at 1035 °C. Naively one would expect that the growth rate increases with higher temperature and decreases with a lower one (compare also figure 2.6). In fact, both times the layer thickness and therefore, the growth rate increases.
## B Abbreviations and Symbols

### B.1 Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3D</td>
<td>three dimensional</td>
</tr>
<tr>
<td>4Cs</td>
<td>colour, clarity, cut, carat weight</td>
</tr>
<tr>
<td>ac</td>
<td>alternating current</td>
</tr>
<tr>
<td>ADI</td>
<td>Applied Diamond Incorporation</td>
</tr>
<tr>
<td>APD</td>
<td>avalanche photodiode</td>
</tr>
<tr>
<td>AWG</td>
<td>arbitrary waveform generator</td>
</tr>
<tr>
<td>BEN</td>
<td>bias-enhanced nucleation</td>
</tr>
<tr>
<td>CIL</td>
<td>Cambridge Isotope Laboratories</td>
</tr>
<tr>
<td>CPMG</td>
<td>Carr, Purcell, Meiboom, Gill sequence</td>
</tr>
<tr>
<td>CVD</td>
<td>chemical vapour deposition</td>
</tr>
<tr>
<td>dc</td>
<td>direct current</td>
</tr>
<tr>
<td>DD</td>
<td>dynamical decoupling</td>
</tr>
<tr>
<td>DEER</td>
<td>double electron-electron resonance</td>
</tr>
<tr>
<td>E6</td>
<td>Element Six</td>
</tr>
<tr>
<td>EPR</td>
<td>electron paramagnetic resonance</td>
</tr>
<tr>
<td>fcc</td>
<td>face-centred cubic</td>
</tr>
<tr>
<td>FID</td>
<td>free induction decay</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>FWHM</td>
<td>full width at half maximum</td>
</tr>
<tr>
<td>GIA</td>
<td>Gemological Institute of America</td>
</tr>
<tr>
<td>GPS</td>
<td>global positioning system</td>
</tr>
<tr>
<td>HPHT</td>
<td>high pressure high temperature</td>
</tr>
<tr>
<td>ICP</td>
<td>inductively coupled plasma</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
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</table>
### B Abbreviations and Symbols

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>MCD</td>
<td>micro-crystalline diamond</td>
</tr>
<tr>
<td>MFC</td>
<td>mass flow controller</td>
</tr>
<tr>
<td>MRI</td>
<td>magnetic resonance imaging</td>
</tr>
<tr>
<td>MW</td>
<td>microwave</td>
</tr>
<tr>
<td>NA</td>
<td>numerical aperture</td>
</tr>
<tr>
<td>NCD</td>
<td>nano-crystalline diamond</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>NDT</td>
<td>New Diamond Technologies</td>
</tr>
<tr>
<td>NV</td>
<td>nitrogen-vacancy centre</td>
</tr>
<tr>
<td>ODMR</td>
<td>optically detected magnetic resonance</td>
</tr>
<tr>
<td>PECVD</td>
<td>plasma-enhanced chemical vapour deposition</td>
</tr>
<tr>
<td>PL</td>
<td>photoluminescence</td>
</tr>
<tr>
<td>ppb</td>
<td>parts per billion</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>PSB</td>
<td>phonon sideband</td>
</tr>
<tr>
<td>PTFE</td>
<td>polytetrafluoroethylene</td>
</tr>
<tr>
<td>REF</td>
<td>reference</td>
</tr>
<tr>
<td>RIE</td>
<td>reactive ion etching</td>
</tr>
<tr>
<td>Qdyne</td>
<td>quantum heterodyne</td>
</tr>
<tr>
<td>SCD</td>
<td>single-crystalline diamond</td>
</tr>
<tr>
<td>SEDOR</td>
<td>spin echo double resonance</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscope</td>
</tr>
<tr>
<td>SFG</td>
<td>step flow growth</td>
</tr>
<tr>
<td>SIMS</td>
<td>secondary ion mass spectrometry</td>
</tr>
<tr>
<td>SQUID</td>
<td>superconducting quantum interference device</td>
</tr>
<tr>
<td>Sumi</td>
<td>Sumitomo</td>
</tr>
<tr>
<td>UHV</td>
<td>ultra high vacuum</td>
</tr>
<tr>
<td>UNCD</td>
<td>ultra-nano-crystalline diamond</td>
</tr>
<tr>
<td>UV</td>
<td>ultra-violet</td>
</tr>
<tr>
<td>UV-vis</td>
<td>ultra-violet visible spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>ZFS</td>
<td>zero-field splitting</td>
</tr>
<tr>
<td>ZPL</td>
<td>zero phonon line</td>
</tr>
</tbody>
</table>
B.2 Symbols

\( A_\parallel \) parallel hyperfine constant
\( A_{\perp} \) perpendicular hyperfine parameter
\( \vec{B} \) external magnetic field vector
\( \beta \) diamond off cut angle
\( c_m \) methane concentration
\( D \) diffusion coefficient
\( D_{\text{es}} \) = 1.42 GHz, zerofield splitting in the NV excited state
\( D_{\text{gs}} \) = 2.87 GHz, zerofield splitting in the NV ground state
\( d_{\text{layer}} \) diamond layer thickness
\( E_a \) diffusion activation energy
\( \eta \) magnetic field sensitivity
\( \eta_V \) volume normalised magnetic field sensitivity
\( f \) microwave frequency
\( F_{\text{single}} \) fluorescence level of a single NV
\( g \) = 2.0024, electronic g-factor
\( g^{(2)} \) autocorrelation function
\( \gamma \) gyromagnetic ratio
\( \Gamma \) electron spin interaction strength
\( h \) = 6.626 \times 10^{-34} \text{Js}, Planck constant
\( I(t) \) light intensity at a time \( t \)
\( k \) power law scaling constant of XY8 dynamical decoupling protocols
\( \kappa_B \) = 1.38 \times 10^{-23} \text{J/K}, Boltzmann constant
\( L \) terrace width
\( \lambda \) wavelength
\( m_s \) spin quantum number
\( \mu_B \) = 9.274 \times 10^{-24} \text{J/T}, Bohr magneton
\( N \) number of NV centres
\( n \) NV centre density
\( N/C \) nitrogen to carbon ratio
\( N/H \) nitrogen to hydrogen ratio
\( N_{\text{av}} \) average number of NV centres
\( [N_D] \) nitrogen content in diamond
### B Abbreviations and Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
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<tbody>
<tr>
<td>( N_{em} )</td>
<td>number of single photon emitters</td>
</tr>
<tr>
<td>( [N_G] )</td>
<td>nitrogen content in gas phase</td>
</tr>
<tr>
<td>( \nu_{gr} )</td>
<td>growth rate</td>
</tr>
<tr>
<td>( NV/P1 )</td>
<td>NV to P1 ratio</td>
</tr>
<tr>
<td>( P )</td>
<td>microwave power</td>
</tr>
<tr>
<td>( p )</td>
<td>pressure during PECVD growth</td>
</tr>
<tr>
<td>( Q_L )</td>
<td>leakage rate</td>
</tr>
<tr>
<td>( \rho_C )</td>
<td>carbon deposition rate</td>
</tr>
<tr>
<td>( S_x, S_y, S_z )</td>
<td>electronic spin vectors</td>
</tr>
<tr>
<td>( T )</td>
<td>temperature</td>
</tr>
<tr>
<td>( t )</td>
<td>time</td>
</tr>
<tr>
<td>( T_1 )</td>
<td>relaxation time</td>
</tr>
<tr>
<td>( T_2 )</td>
<td>coherence time (after Hahn-Echo)</td>
</tr>
<tr>
<td>( T_2^* )</td>
<td>dephasing time</td>
</tr>
<tr>
<td>( t_C )</td>
<td>diffusion time of carbon atoms</td>
</tr>
<tr>
<td>( t_{growth} )</td>
<td>diamond growth time</td>
</tr>
<tr>
<td>( \nu_{step} )</td>
<td>step growth velocity</td>
</tr>
<tr>
<td>( \zeta )</td>
<td>doping efficiency</td>
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   URL: https://doi.org/10.1038/s41598-019-42314-7
5. Magnetic-field-learning using a single electronic spin in diamond with one-photon-readout at room temperature
Physical Review X 9, 021019 (2019)
URL: https://doi.org/10.1103/PhysRevX.9.021019

6. Single Si-V− Centers in Low-Strain Nanodiamonds with Bulklike Spectral Properties and Nanomanipulation Capabilities
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* these authors contributed equally to this work
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  Advanced Quantum Technologies **3**, 2000074 (2020)
  URL: [https://doi.org/10.1002/qute.202000074](https://doi.org/10.1002/qute.202000074)

- **dc magnetometry with engineered nitrogen-vacancy spin ensembles in diamond**
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Curriculum Vitae

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Erklärung

Ich versichere hiermit, dass ich die vorliegende Arbeit selbständig angefertigt habe und keine anderen als die angegebenen Quellen und Hilfsmittel benutzt, sowie die wörtlich und inhaltlich übernommenen Stellen als solche kenntlich gemacht habe.

Weiterhin erkläre ich, dass die vorliegende Arbeit weder vollständig noch in Auszügen einer anderen Fakultät mit dem Ziel einen akademischen Titel zu erwerben vorgelegt worden ist. Ich bewerbe mich hiermit erstmalig um den Doktorgrad der Naturwissenschaften der Universität Ulm.

Ulm, den 26. November 2020

Christian Osterkamp