Chapter 1

Introduction to NV centers and their common usage

The aim of this first chapter is to introduce the tools and concepts required for the next chapters. We will start
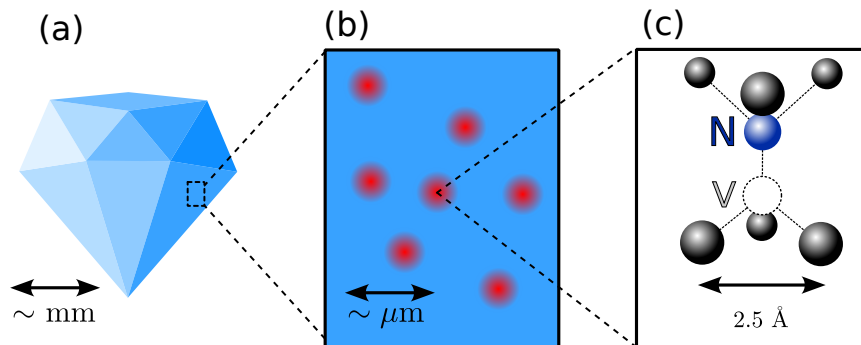
1.1 The NV center as a physical object

Figure 1.1: From the diamond to the NV center. a) Drawing of a bulk diamond. We consider a diamond to be "bulk" if it is bigger than a few 100 μm. b) Drawing representing a fluorescence microscopy image of a diamond surface. The red fluorescent spots symbolize NV centers. c) Zoom-in on the crystalline structure of an NV center. Block dots represent carbon atoms

Refaire ce paragraphe te foutre le summary après la description de la figure. Et bien parler du NV- et du charge state We will start this chapter by discussing the physical aspect of the NV center, and of its host material, the diamond. We will cover some of the basic properties of diamond and of its most common defects before addressing the creation process of both diamonds and NV centers.

Fig. 1.1 illustrates the various scales to consider in this study: we start with a diamond which for lab purposes is generally no bigger than a few mm. If we zoom-in on the surface of some diamonds, we can find bright fluorescent spots corresponding to particular crystalline defects. Standard confocal microscopy is limited in its resolution to the $\sim \mu$m range, but if we could zoom-in even further we would see the structure of the defect, illustrated here with the crystalline structure of an NV center.
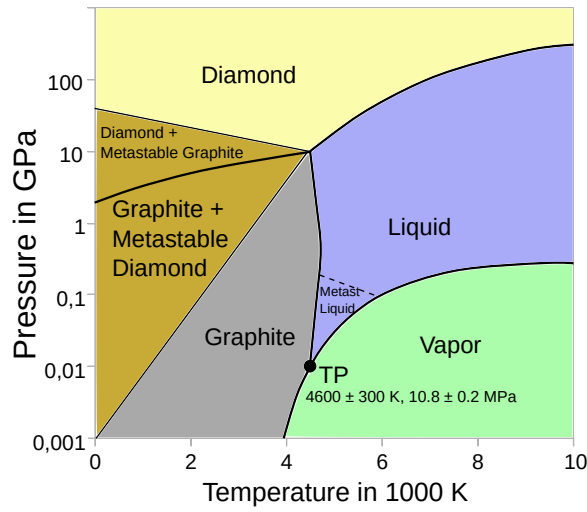
1.1.1 Diamond overview

Figure 1.2: Pressure-temperature phase diagram of elemental carbon. From wikipedia, adapted from [1, 2].

Diamond is a remarkable material in many aspects, it is famous for having the highest hardness and thermal conductivity of any natural material, and for its high optical refractive index and optical dispersion which makes it an extremely valuable crystal in jewelry.

Diamond is also famous for being extremely rare in nature, even though its only constituent, carbon, is one of the most abundant element on the Earth surface. The reason is that diamond is not the most stable phase of carbon under atmospheric pressure and temperature. This honor goes to the graphite which is found abundantly in coal.

Fig. 1.2 shows the PT phase diagram of elemental carbon. We can see that diamond becomes the thermodynamically stable phase only for pressure above a few GPa, 10^4 times higher than atmospheric pressure. Even though diamond is unstable under ambient conditions, the extremely high energy activation needed to break the sp^3 bond between two carbon atoms means that the kinematics of the $C_{\text{diamond}} \rightarrow C_{\text{graphite}}$ transition is

almost completely frozen. In many ways diamonds are more stable than graphite under ambient condition due to their relative chemical inertness.

Where the thermodynamic equilibrium really matters is for the crystallization process. The higher pressure needed to reach the diamond-stable region can only be found naturally deep under the earth crust, typically between 150 and 240 km below sea level [3], which explain their rarity. It also explains why, despite many previous efforts, diamonds were synthetically produced for the first time only in 1953 [4], more than 50 years after the first synthetic sapphires. To this day, artificial diamond synthesis remains an active field of research [5, 6].

Diamonds, either natural or artificial, are used in the lab and in industry for their extreme sturdiness, with applications ranging from abrasive to diamond anvil cells [7]. More recently, diamonds have been the object of optics and electronics applications. For both of these fields however, the focus is no longer solely on the diamond but also on the defects found inside it.
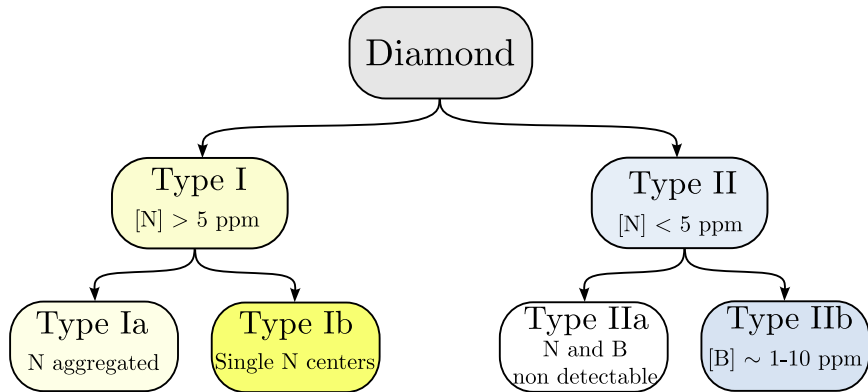
1.1.2 Point defects in diamond

Figure 1.3: Traditional classification of diamonds, based on [3]

Diamond in its intrinsic form is an insulator with a bandgap of of $\sim$ 5.47 eV and is transparent from far infrared to deep UV. As any crystal however, diamond is prone to defects. We will concentrate here on 0D point-like defects and omit structural defects such as dislocations, even though those too can affect the optical properties of the diamond [8].

Point-like defects can be constituted by the absence of a carbon atom ("vacancies"), an interstitial defect between two carbon atoms or the substitution of a carbon atom with another atom. These impurities result in unpaired electron or holes localized around the impurity site. This localization causes discrete energy levels for the holes or the electrons, some of which will lie inside the diamond bandgap and will impact the crystal optical and electrical properties.

Defects with electronic transitions in the optical range are called "colored centers" as they are responsible for the coloring of the gems. H, He, Li, B, N, O, Ne, P, Si, As, Ti, Cr, Ni, Co, Zn, Zr, Ag, W, Xe and Tl are known to form colored centers when introduced in diamond [5, 9], and each of these elements can form several defects. Nitrogen alone can form more than 50 different colored centers [10, 11].

Nitrogen, and to a lesser extant boron, are the most commonly found extrinsic elements in natural diamond. The traditional classification of diamond is presented in Fig. 1.3. It is based on the N and B concentration, with a threshold of a few ppm (part per million) for each species as this was the smaller amount easily detectable through IR absorption. Type Ia diamonds contain clustered N defects such as the B-center which is the N_4V defect. In contrast, type Ib diamond mostly contains C-center which are single substitutional N_s defects, also referred to as P1 centers in the spin community. Type IIb diamond contains B impurities which give them a blueish-grey color, and type IIa diamond contains no detectable impurities via IR absorption [11].

Nitrogen-vacancy centers are a rare occurrence in both natural diamonds and untreated synthetic diamonds, but we will see later that the much more common N_s defects can be converted in NV centers. When working with NV centers, the starting crystal is therefore often a type Ib if one wants to work with ensemble, or a type IIa if one wants to work with single NV centers.

The boron defects are mainly studied in the context of p-doped diamond semi-conductor: a concentration of $[B] \approx 1000$ ppm is needed to achieve a significant overlap between the impurity sites, which turns the diamond into a semi-metal [12].Other defects of interest, generally not present naturally but introduced voluntarily, include P and S defects to create n-doped diamond [13] (still an active field of research), as well as group IV-vacancy defects (SiV, GeV, SnV, PbV) for quantum optics application [14].

The NV center however remains by far the most studied defect in diamond due to its unique spin properties which will be explained below.

1.1.3 Creation of synthetic diamond for optics and electronics applications

We will now focus on the creation process of the diamonds. Almost all diamonds used in optics or electronics experiments today are synthetic, due to the higher control of the growth process required for these applications. There are two main competing technologies for the growth of large (μm $\sim$ mm) single crystal diamonds: High pressure high temperature growth (HPHT) and chemical vapor deposition growth (CVD). Both of these processes have their own specificities which we will detail below.
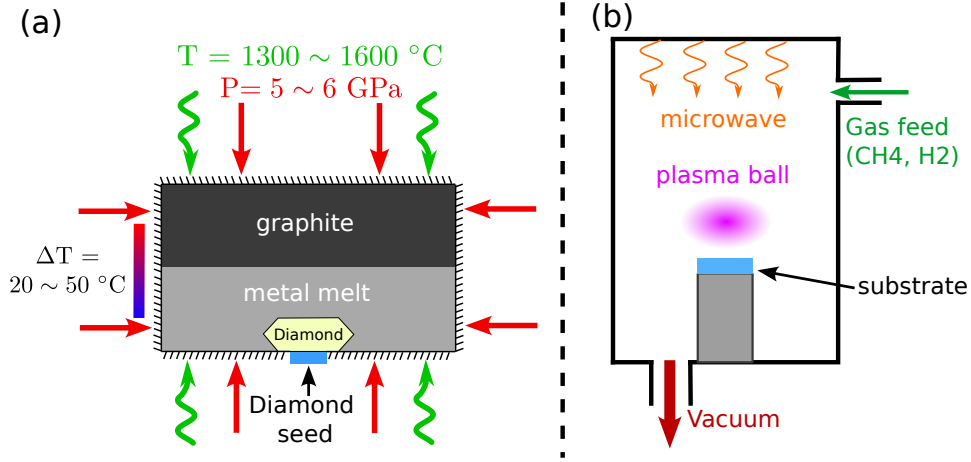
Figure 1.4: Schematics of HPHT (a) and CVD (b) growth process as detailed in main text

HPHT growth

HPHT was the first commercially viable process for synthetic diamonds, starting from the 1950s [4, 15]. The basic idea of HPHT synthesis is to reconstruct an environment where diamond is the thermodynamically stable phase of carbon, similarly to the growth process of natural diamond below the earth crust.

Fig. 1.4-a) illustrates the apparatus of HPHT synthesis: a carbon source (graphite) and a solvent metal composed of transition metals (Fe, NI, Co typically [16]) are put under $5 \sim 6$ GPa pressure in a press and heated to temperatures ≥ 1300 °C. A diamond crystal seed is put in the metal catalyst and a temperature gradient insures that the carbon migrates from the graphite to the diamond.

The first synthesis of HPHT diamonds were all of type Ib due to unwanted nitrogen pollution in the metal melt. The first HPHT type IIa diamonds were produced in the late 90s by adding other elements to the metal melt (Ti, Al, Zr) which would react preferentially with nitrogen and prevent its incorporation in the diamond [17, 18].

CVD growth

CVD growth for diamond was first demonstrated convincingly in the 80s [19–21]. Unlike HPHT, CVD operates in a regime where diamond is not the thermodynamically stable phase. It relies therefore heavily on catalysts to stabilize the diamond phase versus the graphite one.

The main catalyst used is atomic hydrogen, which can both create the free radicals required to form the $C - C$ diamond bonds, and which etches sp^2 bonds (graphite) faster than it does sp^3 bonds (diamond) [22]. Hydrogen

5

is by far the most abundant element in the gas phase: the precursor gases used for the growth are typically CH_4 and H_2 in proportions of $1-5\%$ and $95-99\%$ respectively [6].

Fig. 1.4-b) illustrates the apparatus of a microwave plasma reactor: it consists in a modified vacuum chamber which acts as a microwave resonator. The microwave creates a plasma ball from the the precursor gases with a temperature $T_{\text{plasma}} \geq 3000°C$ [11], enough to dissociate the H_2 gas in atomic hydrogen [23]. The plasma acts as the carbon source for the diamond growing on top of the substrate, and as the catalyst to favor the diamond phase. The substrate is kept at a temperature $700 \sim 1100$ °C during the growth.

Other sources can be used to create the high temperature required for atomic hydrogen, such as a tungsten hot filament [24], electrical discharge (arcjet) [25] or even an oxygen-acetylene combustion flame [26].

For a good CVD reactor, the main sources of extrinsic impurities the diamond comes from the source gasses [23]. The commercial availability of source gases containing less than $\sim$ ppm impurities made possible the growth of high purity type IIa CVD diamonds [27–29].

Both HPHT and CVD processes can produce diamonds of high quality for quantum optics or electronics application, each with their pros and cons. HPHT offers better scalability for thick crystals ($\sim$ mm) and allows the incorporation of heavy atoms (Ge [30] , Sn [31]) which can be hard to incorporate from a gas phase. CVD on the other hand allows more versatility in the control of the impurities introduced in the crystal, including an isotopic control on both the impurities and the carbon itself. A particular advantage of CVD growth is the possibility of δ-doping where a specific defect is grown only within a thin layer of the crystal, as low as 5 nm [32–34].
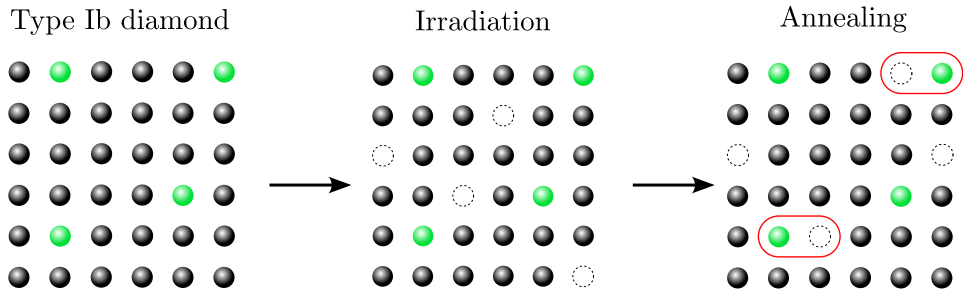
1.1.4   Optimizing NV center formation

Figure 1.5: Illustration of the formation of NV centers. Black dots represents carbon atoms and green dots nitrogen atoms

NV centers are a relatively rare impurity in untreated diamonds. In CVD diamond for instance, the proportion of nitrogen atoms forming an

NV center in an untreated crystal is at best of $2 - 3\%$ [35] and sometimes much less. While this ratio can sometimes be enough to work with single NV centers, applications such as sensing that require dense ensemble need a higher conversion rate. We will discuss here the usual techniques used to improve the formation of NV centers.

Fig. 1.5 illustrates the steps needed to maximize the number of NV centers in the crystal while keeping a relatively high crystalline purity.

The first step to create NV centers is to get individual substitutional N atoms in the crystal (N_s, C-centers or P1 centers depending on the literature). This can be achieved either *in situ* by introducing (voluntarily or not) nitrogen in the crystal during the growth process [29, 36], or *ex situ* by implanting N^+ ions with ion implantation techniques [37, 38]. Because this present work focuses on dense NV ensembles, we will consider the simplest case where the starting crystal is a type-Ib diamond due to the presence of nitrogen during the growth. A starting concentration $[N_s] = 10 \sim 300$ ppm is typical for type Ib HPHT diamonds [6].

The second step is to create monovacancies in the crystal lattice. This step might be optional for crystals which already contain a large number of monovacancies, but CVD crystals in particular can have less vacancies that they have substitutional nitrogen atoms [39]. The general technique to create monovacancy is to bombard the sample with high energy particle in order to knock out carbon atoms from the crystal. Several high energy particle have been used to create vacancies, such as protons, electrons, ions, neutrons and even gamma rays [40–42]. The most common irradiation source for for bulk diamond however is electron irradiation (e-beam) [43], thanks to their ability to penetrate the crystal and to create vacancies uniformly.

The final step is to migrate the vacancies next to the nitrogen atoms. The activation energy required to move vacancy is of ~ 2.3 eV which corresponds to temperatures of $600 \sim 700°C$ [44, 45]. The most common method to move the vacancies is therefore to anneal the crystal at a temperature $800 \sim 1200°C$ for a few hours [46]. NV centers anneal out at temperature of $1400 \sim 1500°C$ [9, 47] which explains why the vacancies tend to stick to the nitrogen atoms during the annealing phase.

The final N_s to NV conversion rate can be as high as $\sim 50\%$ [35, 48], although this ratio tend to decrease for higher $[N_s]$ concentrations. Most sample studied in this manuscript had a concentration $[NV] = 1 - 10$ ppm

1.1.5 Controlling the NV center charge state

The charge state of the NV center is of crucial importance for NV applications. Only the negatively charged NV^- center shows the specific spin properties that will be detailed below, but the NV center can exist under three charge states in the diamond: NV^-, NV^0 and NV^+. The presence of NV^+ is only marginal in standard diamonds [49, 50] and we will focus here

solely on the NV^- and NV^0 charge state.

The charge state of the NV centers depends not only on the growth process of the crystal, but also on the usage made of the sample. In particular, illumination in the optical range can promote electrons in the conduction band or holes in the valence band and modify the charge state of the NV center.

On the material side, the crystal has to remain electrically neutral which means that at least as many charge donors need to be present as there are NV^- centers. For nitrogen-rich samples, the donors are mostly N^+ centers, which imposes a limit on the maximum conversion rate of N to NV in order to keep a high $[NV^-]/[NV^0]$ ratio. The possibility to introduce other donors, such as phosphorus, has been studied [51] but remains impractical so far [52].

On the experimental side, it has been shown that the ionization of NV^- to NV^0 and the reverse process depend on the intensity and wavelength of the laser used for illumination [53]. It was found that the optimal wavelength to preserve the NV^- charge state was $510 - 540$ nm. The most common wavelength used with NV centers is 532 nm (green) due to the historical importance of Nd:YAG lasers. On the other hand, it is possible to semi-permanently ionize the NV^- into NV^0 when using a red excitation, which has been used to create an optical memory [**dhomkar2016long**].

Ccl sur le fait que osef pour les échantillon en excès de N mais que ça peut avoir de l'importance avec les samples low en impurities.

Bibliography

[1] FP Bundy. "Pressure-temperature phase diagram of elemental carbon". In: *Physica A: Statistical Mechanics and its Applications* 156.1 (1989), pp. 169–178.

[2] FP Bundy et al. "The pressure-temperature phase and transformation diagram for carbon; updated through 1994". In: *Carbon* 34.2 (1996), pp. 141–153.

[3] Ralf Tappert and Michelle C Tappert. *Diamonds in nature: a guide to rough diamonds*. Springer Science & Business Media, 2011.

[4] Amanda S Barnard. *The diamond formula: diamond synthesis–a gemmological perspective*. Butterworth-Heinemann, 2000.

[5] Olga A Shenderova et al. "Synthesis, properties, and applications of fluorescent diamond particles". In: *Journal of Vacuum Science & Technology B, Nanotechnology and Microelectronics: Materials, Processing, Measurement, and Phenomena* 37.3 (2019), p. 030802.

[6] J Achard, Vincent Jacques, and A Tallaire. "Chemical vapour deposition diamond single crystals with nitrogen-vacancy centres: a review of material synthesis and technology for quantum sensing applications". In: *Journal of Physics D: Applied Physics* 53.31 (2020), p. 313001.

[7] Aiyasami Jayaraman. "Diamond anvil cell and high-pressure physical investigations". In: *Reviews of Modern Physics* 55.1 (1983), p. 65.

[8] Alan T Collins, Hisao Kanda, and Hiroshi Kitawaki. "Colour changes produced in natural brown diamonds by high-pressure, high-temperature treatment". In: *Diamond and Related Materials* 9.2 (2000), pp. 113–122.

[9] Alexander M Zaitsev. *Optical properties of diamond: a data handbook*. Springer Science & Business Media, 2013.

[10] Inga A Dobrinets, Victor G Vins, and Alexander M Zaitsev. *HPHT-treated diamonds*. Springer, 2016.

[11] Michael NR Ashfold et al. "Nitrogen in diamond". In: *Chemical reviews* 120.12 (2020), pp. 5745–5794.

[12]   Julie V Macpherson. "A practical guide to using boron doped diamond in electrochemical research". In: *Physical Chemistry Chemical Physics* 17.5 (2015), pp. 2935–2949.

[13]   Dhruba Das et al. "Diamond-The Ultimate Material for Exploring Physics of Spin-defects for Quantum Technologies and Diamontronics." In: *Journal of Physics D: Applied Physics* (2022).

[14]   Carlo Bradac et al. "Quantum nanophotonics with group IV defects in diamond". In: *Nature communications* 10.1 (2019), pp. 1–13.

[15]   FP Bundy, H Tracy Hall, HM Strong, et al. "Man-made diamonds". In: *nature* 176.4471 (1955), pp. 51–55.

[16]   FP Bundy. "Direct conversion of graphite to diamond in static pressure apparatus". In: *The Journal of Chemical Physics* 38.3 (1963), pp. 631–643.

[17]   RC Burns et al. "Growth of high purity large synthetic diamond crystals". In: *Diamond and Related Materials* 8.8-9 (1999), pp. 1433–1437.

[18]   H Sumiya, N Toda, and S Satoh. "Growth rate of high-quality large diamond crystals". In: *Journal of Crystal Growth* 237 (2002), pp. 1281–1285.

[19]   Seiichiro Matsumoto et al. "Growth of diamond particles from methane-hydrogen gas". In: *Journal of materials Science* 17.11 (1982), pp. 3106–3112.

[20]   Seiichiro Matsumoto et al. "Vapor deposition of diamond particles from methane". In: *Japanese Journal of applied physics* 21.4A (1982), p. L183.

[21]   Mutsukazu Kamo et al. "Diamond synthesis from gas phase in microwave plasma". In: *Journal of crystal growth* 62.3 (1983), pp. 642–644.

[22]   JJ Gracio, QH Fan, and JC Madaleno. "Diamond growth by chemical vapour deposition". In: *Journal of Physics D: Applied Physics* 43.37 (2010), p. 374017.

[23]   RS Balmer et al. "Chemical vapour deposition synthetic diamond: materials, technology and applications". In: *Journal of Physics: Condensed Matter* 21.36 (2009), p. 364221.

[24]   R Haubner and B Lux. "Diamond growth by hot-filament chemical vapor deposition: state of the art". In: *Diamond and Related Materials* 2.9 (1993), pp. 1277–1294.

[25]   J Luque et al. "Excited state density distributions of H, C, C 2, and CH by spatially resolved optical emission in a diamond depositing dc-arcjet reactor". In: *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* 16.2 (1998), pp. 397–408.

[26] Peter K Bachmann, Dieter Leers, and Hans Lydtin. "Towards a general concept of diamond chemical vapour deposition". In: *Diamond and related materials* 1.1 (1991), pp. 1–12.

[27] Makoto Kasu and Naoki Kobayashi. "High mobility and high crystalline-quality chemical-vapor-deposition grown homoepitaxial diamond". In: *Diamond and related materials* 12.3-7 (2003), pp. 413–417.

[28] DJ Twitchen et al. "High-voltage single-crystal diamond diodes". In: *IEEE Transactions on electron devices* 51.5 (2004), pp. 826–828.

[29] A Tallaire et al. "Characterisation of high-quality thick single-crystal diamond grown by CVD with a low nitrogen addition". In: *Diamond and related materials* 15.10 (2006), pp. 1700–1707.

[30] Yuri N Palyanov et al. "Germanium: a new catalyst for diamond synthesis and a new optically active impurity in diamond". In: *Scientific reports* 5.1 (2015), pp. 1–8.

[31] EA Ekimov et al. "Effect of Si, Ge and Sn dopant elements on structure and photoluminescence of nano-and microdiamonds synthesized from organic compounds". In: *Diamond and Related Materials* 93 (2019), pp. 75–83.

[32] Kenichi Ohno et al. "Engineering shallow spins in diamond with nitrogen delta-doping". In: *Applied Physics Letters* 101.8 (2012), p. 082413.

[33] Toyofumi Ishikawa et al. "Optical and spin coherence properties of nitrogen-vacancy centers placed in a 100 nm thick isotopically purified diamond layer". In: *Nano letters* 12.4 (2012), pp. 2083–2087.

[34] K Ohashi et al. "Negatively charged nitrogen-vacancy centers in a 5 nm thin 12C diamond film". In: *Nano letters* 13.10 (2013), pp. 4733–4738.

[35] Christopher Brett Hartland. "A study of point defects in CVD diamond using electron paramagnetic resonance and optical spectroscopy". PhD thesis. University of Warwick UK, 2014.

[36] MA Lobaev et al. "Influence of CVD diamond growth conditions on nitrogen incorporation". In: *Diamond and Related Materials* 72 (2017), pp. 1–6.

[37] J Meijer et al. "Generation of single color centers by focused nitrogen implantation". In: *Applied Physics Letters* 87.26 (2005), p. 261909.

[38] Jason M Smith et al. "Colour centre generation in diamond for quantum technologies". In: *Nanophotonics* 8.11 (2019), pp. 1889–1906.

[39] A Mainwood. "Point defects in natural and synthetic diamond: What they can tell us about CVD diamond". In: *physica status solidi (a)* 172.1 (1999), pp. 25–35.

[40] Gordon Davies and MF Hamer. "Optical studies of the 1.945 eV vibronic band in diamond". In: *Proceedings of the Royal Society of London. A. Mathematical and Physical Sciences* 348.1653 (1976), pp. 285–298.

[41] CE Ashbaugh. "Gemstone irradiation and radioactivity". In: *Gems & Gemology* 24.4 (1988), pp. 196–213.

[42] Ed E Kleinsasser et al. "High density nitrogen-vacancy sensing surface created via He+ ion implantation of 12C diamond". In: *Applied Physics Letters* 108.20 (2016), p. 202401.

[43] Victor M Acosta et al. "Diamonds with a high density of nitrogen-vacancy centers for magnetometry applications". In: *Physical Review B* 80.11 (2009), p. 115202.

[44] Gordon Davies et al. "Vacancy-related centers in diamond". In: *Physical Review B* 46.20 (1992), p. 13157.

[45] ME Newton et al. "Recombination-enhanced diffusion of self-interstitial atoms and vacancy–interstitial recombination in diamond". In: *Diamond and related materials* 11.3-6 (2002), pp. 618–622.

[46] J Botsoa et al. "Optimal conditions for N V- center formation in type-1b diamond studied using photoluminescence and positron annihilation spectroscopies". In: *Physical Review B* 84.12 (2011), p. 125209.

[47] H Pinto et al. "On the diffusion of NV defects in diamond". In: *physica status solidi (a)* 209.9 (2012), pp. 1765–1768.

[48] C Grezes et al. "Storage and retrieval of microwave fields at the single-photon level in a spin ensemble". In: *Physical Review A* 92.2 (2015), p. 020301.

[49] Moritz V Hauf et al. "Addressing single nitrogen-vacancy centers in diamond with transparent in-plane gate structures". In: *Nano Letters* 14.5 (2014), pp. 2359–2364.

[50] Matthias Pfender et al. "Protecting a diamond quantum memory by charge state control". In: *Nano letters* 17.10 (2017), pp. 5931–5937.

[51] Yuki Doi et al. "Pure negatively charged state of the NV center in n-type diamond". In: *Physical Review B* 93.8 (2016), p. 081203.

[52] John F Barry et al. "Sensitivity optimization for NV-diamond magnetometry". In: *Reviews of Modern Physics* 92.1 (2020), p. 015004.

[53] Nabeel Aslam et al. "Photo-induced ionization dynamics of the nitrogen vacancy defect in diamond investigated by single-shot charge state detection". In: *New Journal of Physics* 15.1 (2013), p. 013064.