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Screening and engineering of colour centres in diamond

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Topical Review

Screening and engineering of colour centres in diamond

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Abstract

We present a high throughput and systematic method for the screening of colour centres in diamond with the aim of searching for and reproducibly creating new optical centres down to the single defect level, potentially of interest for a wide range of diamond-based quantum applications. The screening method presented here should, moreover, help to identify some already indexed defects among hundreds in diamond (Zaitsev 2001 Optical Properties of Diamond (Berlin: Springer)) but also some promising defects of a still unknown nature, such as the recently discovered ST1 centre (Lee et al 2013 Nat. Nanotechnol. 8 487; John et al 2017 New J. Phys. 19 053008). We use ion implantation in a systematic manner to implant several chemical elements. Ion implantation has the advantage of addressing single atoms inside the bulk with defined depth and high lateral resolution, but the disadvantage of producing intrinsic defects. The implanted samples are annealed in vacuum at different temperatures (between 600 °C and 1600 °C with 200 °C steps) and fully characterised at each step in order to follow the evolution of the defects: formation, dissociation, diffusion, re-formation and charge state, at the ensemble level and, if possible, at the single centre level. We review the unavoidable ion implantation defects (such as the GR1 and 3H centres), discuss ion channeling and thermal annealing and estimate the diffusion of the vacancies, nitrogen and hydrogen. We use different characterisation methods best suited for our study (from widefield fluorescence down to sub-diffraction optical imaging of single centres) and discuss reproducibility issues due to diamond and defect inhomogeneities. Nitrogen is also implanted for reference, taking advantage of
the considerable knowledge on NV centres as a versatile sensor in order to retrieve or deduce the conditions and local environment in which the different implanted chemical elements are embedded. We show here the preliminary promising results of a long-term study and focus on the elements O, Mg, Ca, F and P from which fluorescent centres were found.

Keywords: diamond, ion implantation, nitrogen-vacancy centre, ST1 centre, defect engineering, diffusion, ion channeling

(Some figures may appear in colour only in the online journal)

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Introduction

The emergence of quantum information processing and the search for suitable systems and hosts have shed light on defect-related optical centres in solid-state materials. Colour centres behave like single artificial atoms and, compared to alternative approaches such as quantum dots, they can be fabricated in a well-defined way with identical properties. To achieve long coherence times even at room temperature, it is important that the host material has a wide bandgap (to avoid free charge carriers) and a high Debye temperature (to reduce the interaction with phonons). Diamond, and more particularly, the nitrogen-vacancy (NV) centre, have been widely studied and demonstrated unique optical and spin properties [4, 5] of great interest for a wide range of applications such as quantum computing [6, 7], quantum communication [8, 9] and the quantum sensing of magnetic fields, [10–12] electric fields [13] or temperature [14–16]. More recently, the possibility of reversibly tuning the charge state of a single NV centre from NV− through NV0 to NV+ was demonstrated [17, 18], as well as the electrical readout of magnetic resonance using photocurrent measurement [19]. However, despite its outstanding properties, the NV centre has a large electron phonon coupling which leads to only 4% of the light emitted in the zero-phonon line (ZPL). Spectral diffusion is also a serious issue. On the other hand, the silicon-vacancy centre (SiV) possesses many advantages, such as the possibility of producing indistinguishable photons [20] due to an emission mostly found within the ZPL at 737 nm. A direct coherent control of the SiV spin state requires a temperature below 4K to avoid phonon scattering [21, 22]. However, with nano-photonic structures, it is possible to switch single photons and allow the achievement
of entangled SiV centres by indistinguishable Raman photons emitted into a waveguide [23]. Recently, attention has also been focused on other X-vacancy defects involving group IV elements. GeV and SnV centres were both artificially created and observed down to the single centre level. The GeV centre was successfully produced both by ion implantation [24, 25] and by high-pressure growth [26]. It has a sharp and strong photoluminescence band at room temperature with a ZPL at 602 nm and a lifetime of about 1.4 ns with photon count rates measured up to 200 kCts s\(^{-1}\). The GeV has a split-vacancy crystal structure similar to that of the SiV centre. The SnV centre shows a ZPL at 620 nm at room temperature [27]. At low temperatures, this line splits up into two peaks with an FWHM of 0.2 nm only [28]. The PbV centre is also expected, but the larger radiation damage produced by a single Pb atom due to its large mass may render the production of this centre more difficult.

A promising defect centre but which still has not been reliably reproduced, so-called ST1, shows optically detected magnetic resonance (ODMR) at room temperature, which is a rare property among optical centres in diamond [2, 3] only shared with the NV centre to date. The electronic level configuration consists of a singlet ground state and a triplet in the excited state. This is an advantage with respect to the NV centre due to the fact that the singlet spin-free ground state should prevent the spin state from decoupling with the environmental spin bath. The ST1 centre does not show hyperfine coupling, indicating a nuclear-spin-free constituent. One of the candidates for this defect is \(^{16}\)O (oxygen was involved in the etching [2] and in the implantation processes [3] which led to the discovery of the ST1 centre); however, there is no evidence regarding it. In addition, \(^{24}\)Mg or \(^{40}\)Ca might also be involved. Interestingly, the L1 defect centre (with very sharp and bright polarised emission with ZPL at 580 nm) was produced together with the ST1 centre by ion implantation [3].

The nature of these two centres is still unknown; however, they may involve the same impurity atom in different configurations. Native centres emitting in the near-infrared were also reported from commercially available diamond samples treated thermally [29] without knowing what they were made of. Note that fluorescent centres related to europium [30] and helium [31, 32] were recently reported.

Therefore, many optically active defects have been observed in diamond, establishing this material as a promising platform for exploring properties at the quantum scale. Nevertheless, the search for new defect centres [33, 34] and the identification of centres of an unknown nature is an ongoing topic. It is of particular importance to develop procedures allowing a reliable control of the formation of those defects which usually have reproducibility issues. The aim of this study is to ‘screen’ the periodic table of elements by implantation and annealing and help retrieve or discover optical centres in diamond in a systematic manner. Wide-field optical characterisation methods were first employed, and then confocal microscopy and spectroscopy, as well as sub-diffraction methods in some special cases.

One of the main challenges regarding quantum applications based on optical centres in diamond concerns the reproducibility of the diamond substrates and of the optical centre environment. Quality control at the quantum level should be considered and developed; that is, for example, fluorescence stability but also charge state control and close-by defect control, as well as the spin coherence time for ODMR-active centres. All these properties and parameters can be investigated by taking advantage of the extensive experience gained from the NV centres that can be exploited to locally probe the material quality and local environment of the optical centres that we aim to screen.

In this paper, we will first present the fabrication method used to search and create optical centres with high throughput. We will briefly recall the ion–matter interactions and discuss the main implantation defects, illustrated by the experimental results, and the effects of thermal annealing. We will then estimate the diffusion coefficient of nitrogen (N), the vacancies, carbon (C) interstitials and hydrogen (H), which are the main species found in an implanted CVD diamond. A short section will be dedicated to diamond homogeneity and quality control of the samples and the created centres. In the last part, we will present the first results of our screening method and discuss the properties of some of the newly found fluorescent centres.

1. Method for the ion implantation screening of different chemical elements

In this first section, the screening of optical centres in diamond by ion implantation will be presented. Ion implantation is the method of choice for a high throughput screening of different chemical elements. The advantages are: the possibility of selecting an atom (also an isotope) or molecule and to implant it with high spatial resolution and in a countable way [35–37], even deterministically [38, 39]. However, it induces defects which require an optimised thermal annealing to heal them out. Chemical vapour deposition (CVD) also enables the creation of some optical centres during the growth (NV, SiV, GeV), with generally better overall properties but without the possibility of screening many elements or placing them on demand [40, 41]. Due to the compact C lattice, large atoms cannot be easily accommodated by direct growth in the film. Phosphorous (P) has, for instance, a very low doping efficiency, especially on a (1 0 0) orientation [42, 43]. This explains why only relatively light elements have been routinely in situ doped so far. Moreover, the spatial localisation of the dopants during CVD growth is further complicated by memory effects or long gas residence times that do not easily allow abrupt doping profiles to be obtained. For these reasons, the screening of colour centres through an implantation procedure appears to be a more reliable way to produce specific defect centres.

The systematic study we are following here relies on ion implantation only. An ion accelerator can provide different ion species (atomic or molecular) and ensure that mass selection of the different isotopes is easily achieved. The choice of ion kinetic energy ensures control of the penetration depth. With the use of a focused beam and optical system, it is possible,
without lithography, to ‘pattern’ a periodic system of elements into a diamond sample, as illustrated in figure 1(a). In the following, the 100 kV accelerator of Leipzig University is used to provide a large range of ion species, suitable for the high-throughput screening of optical centres in diamond. The ion accelerator (figure 1(b)) consists of a cesium sputter source in which home-made cathodes of different chemical compositions can be mounted. With this setup, only negative ion species are available. More details can be found in [44]. A 90° bending electro-magnet is used for the mass selection of the desired ion species. A typical mass spectrum is shown in figure 1(c) for a Mg cathode. The different peaks are well separated which ensures a pure isotopic content for each ion species implantation. For alignment and orientation, the sample is pre-patterned with graphite spots. This is also easily done with the ion beam, implanting a spot with an ion fluence above the graphitisation threshold of about $10^{22}$ vacancies cm$^{-3}$ [45]. After annealing, the damaged regions
with defect densities exceeding this value will be transformed into graphite and become visible under an optical microscope.

2. Interaction of ions with matter

2.1. Defect production and ion channeling

The main interaction of kinetic ions with matter is an interaction with the electrons of the crystal atoms. The Coulomb interaction can be calculated by the Bethe–Bloch formula and is theoretically and experimentally well understood. The energy transfer to the electrons depends on the kinetic energy and the mass of the ions. For the ion energies used in the following (up to a hundred keV), the typical energy gained by the electrons is too low to displace a crystal atom. The energy transfer is also too low to significantly heat up the ion path and no displacement takes place at all by the interaction with electrons. The heating of the sample needs to be taken into account only for high ion currents, but it is negligible in the following. However, the interaction of the ions with the electrons leads to a slowing down of the ions, referred to as electronic stopping.

Defects only occur in a direct interaction of the kinetic ions with the nuclei of the crystal atoms (so-called nuclear stopping). This process takes place most efficiently at a low ion energy (below a few tens of keV) and leads to the displacement of an atom if the kinetic energy transfer exceeds the displacement energy of the bound atom. The typical displacement energy for diamond is 40 eV. Additionally, the displaced atom can itself interact with other crystal atoms and further displace them. This effect results in a cascade of displaced atoms (see figure 2(c)). SRIM simulations (SRIM) allow us to calculate the number of vacancies produced by the implantation of an ion into a solid and take secondary displacements into account. The program assumes a random distribution of the crystal atoms and achieves very good results if the ion beam direction is tilted a few degrees out of one of the main crystal axes. The program only calculates the interaction of the ion and no annealing of the crystal. An additional source of error will be induced if the direction of the incident ion is small with respect to the crystal lattice; ion channeling can then take place. In this case, the ion can travel through atom rows or planes as guided by the electric potential, generally penetrating deeper and producing a different defect distribution along the depth [46]. This is important to consider when a high precision placement of the optical centres is required. This effect is well described in silicon [47] and it was also observed in diamond implantations [37, 48–50]. It can be modeled using the CTRIM code [51], as illustrated in the following with the example of 4 keV N, which is often used to produce shallow NV centres for magnetometry. Figure 2(a) shows the CTRIM simulations of the vacancy depth distribution (upper graph), calculated for two incidence angles of 0° and 7° with respect to a perfectly flat (0 0 1) surface. The lower graph is a plot of the depth distribution of the implanted N atom. It can be seen that channeling leads to different depth profiles, both for N and the vacancies. Indeed, ion channeling (and the number of ions effectively channeled) depends at first on the incidence angle with respect to a given channeling direction, but also on many parameters such as the ion energy, ion species, target material, crystal orientation or beam divergence. But it also strongly depends on the surface roughness, which is a parameter difficult to evaluate and is poorly reproducible. We found that the experimental implantation impurity profiles found in [37, 49] (measured by secondary ion mass spectrometry, SIMS) cannot be fitted without introducing a surface ‘roughness’ in the simulation. This has been done in the results presented in figure 2(b). Here, a 1.5 nm layer of amorphous C was introduced to account for the surface roughness. It can be seen that the channeling effect is strongly reduced. This is supported by the atomic probe tomography results conducted on diamond implanted with 5 keV N at vertical incidence onto a (1 1 1) surface [52]. However, it is important to consider the surrounding defect configuration at the end of the range where the ion finally stops within the crystal lattice, in both cases of channeled and not channeled ions. In order to study this more precisely, we have conducted molecular dynamics [53] simulations of the implantation of 4 keV N at 0° and 7° incidence onto (1 0 0) diamond. The development of the ensuing collision cascade was followed for 3 ps, which was found to be a sufficiently long time for the collision cascade to cool down and the athermal defect recombination process to stop. Naturally, within this time scale, practically no defect migration driven by equilibrium thermal activation can take place.

After defect analysis, we also calculated the distance from the N atom to the nearest vacancy and computed the statistics regarding how many vacancies and interstitials were within 1 nm of the final N atom position (the interstitial formed by the N atom itself was not counted in this statistic). The snapshots of a typical event are illustrated in figure 2(c). Most of the primary damage is in small disordered atom regions rather than isolated point defects. In the clear majority of cases, the final position of the N atom was within such a disordered cluster. In only one case out of ten off-normal impact cases simulated, and none out of the ten normal impact cases, was the final N atom separated by more than 1 nm from all intrinsic defects. The MD simulation results on the damage production show that in the primary damage state after a cascade has cooled (at 3 ps, before any thermal defect migration), the implanted N is in most cases surrounded by closely vacancies and interstitials, or, in other words, part of a damage pocket. What is important to note is that the difference between the implantations into channelled and non-channeled directions is minor. Note that all the implantations conducted in the following sections were done on (1 0 0) diamond at 0° incidence where channeling is likely to occur.

2.2. Characterisation of implantation defects

It is not the purpose of this work to review all the radiation defects; however, it will focus on some of them and on specific aspects which are of relevance for the creation and application of single optical centres in diamond for quantum-based applications. Indeed, the use of single centres in diamond for
quantum purposes imposes some requirements on the local environment of the defects. Most of the experimental demonstrations were achieved using the NV centre, which was historically seen as the most promising qubit in the solid state. Its unique optical and spin properties proved to be extremely suitable for sensing, especially using the coherence properties of single NV− centres. That can, therefore, be used in our screening purposes as a witness for other defect centres.

It is inherent in any implantation that radiation defects are produced, at first C interstitials and C vacancies, but also more complex intrinsic defects. The major problem of the ion implantation technique for quantum applications or electrical doping remains in the fact that all the radiation defects due to the ion implantation process cannot be totally annealed out. Many studies deal with this problem; however, mostly on ensembles with large numbers of defect centres. It was only recently that this topic could be brought to defects at the single level. In particular, the comparison between NV centres obtained by N implantation and annealing or by N doping during a CVD growth process showed that the coherence times of the native grown NV centres were generally better than for the implanted ones [41, 57], revealing a better environment. It is therefore of great importance to determine, control and engineer the local environment of the defect centres that we aim to produce. For example, considering the defect family of column IV elements associated with a split vacancy (SiV, GeV, SnV and PbV centres), the vacancy configuration after implantation is expected to vary strongly due to the different masses of these atoms. This is what we will consider in the next section. Attempts to create PbV centres are still ongoing. One of the possible reasons that it has not been observed yet lies in the very different atomic mass between Si and Pb, not only from a crystalline point of view, but also in terms of the efficiency of the defect production.

2.2.1. GR1 centres (single neutral vacancies). The most prominent NV and SiV centres involve vacancies, and we first discuss here the production and measurement of single vacancies. In particular, we focus on the GR1 (V0, neutral vacancy) centre, with a characteristic ZPL at 741 nm [1] which can be easily observed with a confocal microscope. A simple experiment can be conducted which consists of measuring the vacancy production depending on the mass of the implanted ion (for similar penetration depth and fluence). Figure 3(a) is a collection of confocal fluorescence scans recorded directly after the ion implantation (without annealing) of ten different elements at the same ion fluence of $1 \times 10^{12}$ cm$^{-2}$ and comparable penetration depth of 50–70 nm. The laser excitation is 532 nm and the fluorescence is filtered with a longpass filter (650 nm) to image the neutral single vacancies (GR1). (b) Fluorescence spectra of the Li, Mg, K and Sr implantations. The spectra were recorded by scanning a $10 \times 10$ μm$^2$ area at the centre of the implantation spots and subtracting it with the reference spectrum from a $10 \times 10$ μm$^2$ unimplanted area taken apart. (c) SRIM simulation for three elements Li, Mg and Sr, showing the vacancy density distribution produced by the implantation of three ions of each ion species. The unit is given in vacancies nm$^{-2}$. (d) Plot of the number of vacancies produced per implanted ion, simulated with SRIM (blue stars) and of the measured GR1 fluorescence intensity (orange dots) as a function of the ion mass.
Figure 4. Ion implantation related defects: 3H centres. (a) Widefield fluorescence image of a 550 × 700 µm² area of a screened diamond with Na, Mg, K, Rb and Cs ion implantation, recorded after annealing at 600 °C for 4h. The fluences are 1 × 10¹⁰ cm⁻², 1 × 10¹¹ cm⁻² and 1 × 10¹² cm⁻². The excitation wavelength is 488 nm. The five reference graphite spots can be recognised. A weak and green fluorescence can be seen from the heaviest ions at the highest fluence and corresponds to 3H emission as well as the halos around the graphite spots. (b) Fluorescence spectrum of 3H centres taken from the Cs spot. The inset shows the 3H intensity as a function of ion mass for the 1 × 10¹² cm⁻² fluence. The corresponding implantation energies are indicated in figure 2(a).

Figure 5. Cathodoluminescence (CL) spectra at 85 K of the N implantations carried out at three different depths using the implantation energies of 5.0, 2.5 and 1.0 keV (with a fluence of 1 × 10¹⁰ cm⁻²). The CL measurement is conducted with an electron beam of 5 keV energy. The spectra are dominated by the NV centres. The radiation defects at 389 nm and 441 nm are also present. The spectra of the unimplanted diamond and of the CCD dark counts are also plotted for comparison.

Figure 2(c) in the case of heavier ions, which explains the observed fluorescence quenching (as already reported on NV centres [60, 61]). This highlights the fact that very different defect distributions surround implanted atoms of different masses such as N, Si, Ge, Sn or Pb, possibly leading to multiple complex configurations. For example, the creation efficiency of NV centres is highly dependent on the energy of the N atoms [60], as will be recalled in figure 6(b). Furthermore, by looking in detail at the K and Ca implantation spots, even though the fluence of 1 × 10¹² cm⁻² is moderate, we observe a ‘dose’ nonlinear effect on the GR1 emission: the centre of the spot is darker than the edge (illustrating the non-uniform implantation fluence which is maximal at the centre). The GR1 fluorescence decreases while the fluence increases. Not only the mass of the ion but also this dose effect indicates that there is a possible overlap between the vacancy ‘clouds’ produced by each ion and that, again, the fluorescence begins to be quenched or that more complex defects build. The corresponding vacancy concentration for these K and Ca implantations is locally about 7 × 10¹⁰ cm⁻², still at least two orders of magnitude below the graphitisation threshold, but with an average V–V distance of about 2.4 nm. For the Mg spot, which does not show such an effect, the average V–V distance is about 3.06 nm. It is therefore an effect with a sharp threshold does not show such an effect, the average V distance of about 2.4 nm. For the Mg spot, which does not show such an effect, the average V–V distance is about 3.06 nm. It is attributed to (1 0 0) split self-interstitial [1, 62, 63]. The 3H centre generally efficiently forms above temperatures of 300 °C–400 °C and anneals out at different temperatures depending on factors such as the N concentration or the doping level.

Figure 4(a) is an optical widefield fluorescence image of an area of the screened diamond implanted with Na, Mg, K, Rb and Cs and annealed for 4h at 600 °C in vacuum. The green fluorescence of the 3H centres is visible for the highest fluence spots of the three heaviest atoms. A fluorescence spectrum from the Cs spot is plotted in figure 4(b). In contrast to the GR1 centres, it can be seen here that the intensity of the 3H centre increases with ion mass (inset in figure 4(b)). In addition, a green corona of 3H centres is also present around each graphite spot. During the implantation process, the ion beam is slightly scattered at the masking aperture, leading to a tail around each spot, having a decreasing fluence with the increasing distance from the centre of the spot. There is, however, a nonlinear fluence dependence again: the 3H fluorescence intensity is maximum within a narrow fluence range, as indicated by the relatively sharp edges of the fluorescence and decreases in the centre of the spot. The evolution of the 3H signal on the temperature range is shown in figure 6(a).

2.2.3. The 2.807 eV and 3.188 eV centres. These two defect centres are often observed together after ion implantation processes in diamond. They are believed to be related to N and interstitial C atoms [1, 64]. They present a ZPL at 441 nm (2.807 eV) and 389 nm (3.188 eV) respectively, accompanied by a significant phonon sideband. We have prepared a sample (ultrapure CVD growth of 100 µm on top of a (1 0 0) HPHT substrate) with a set of N implantations at different ion energies (0.8 keV–5 keV) and ion fluences (10¹⁰ cm⁻² to 10¹³ cm⁻²). The sample was annealed at 800 °C for 2h in vacuum to form NV centres and to check the appearance of the 2.807 eV and 3.188 eV defect lines. It was characterised by standard confocal scanning fluorescence microscopy for imaging and spectroscopy of the NV centres (laser excitation
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532 nm, detection with a bandpass filter 660 nm – 735 nm) and by cathodoluminescence (CL).

The CL fluorescence spectra recorded at $T = 85 \text{ K}$ from three different implantation spots (energies of 5, 2.5 and 1 keV and the same fluence of $10^{13} \text{ cm}^{-2}$) and from the unimplanted diamond are plotted in figure 5. As expected, the spectra are dominated by the emission of the NV centres. Note that only the contribution from the neutral charge state NV$_0$ with a ZPL at 575 nm (and not from the NV$^-$, ZPL at 638 nm) is present, as already observed in CL [1] and EL with pin diodes [65, 66]. Note also that the ion energy dependence of the NV centre creation yield is here again observed as in [60] (see also figure 6(b)). The 3.188 eV defect (389 nm) together with its characteristic phonon sideband can be seen and is therefore not annealed out at 800 °C. It has the same intensity for the three implantations and therefore does not appear to have any ion-energy dependence. The emission is only one order of magnitude weaker than the NV centre at 5 keV (about $5 \times 10^{11} \text{ NV cm}^{-2}$); however, it is of comparable intensity with the NV centres implanted at 1 keV. In addition, the 2.807 eV defect (441 nm) together with its phonon sideband is visible but with a weaker intensity than the 3.188 eV defect. It can be seen that its intensity increases with the ion energy, as the NV centre emission does, but not as strongly. The observation of the 3.188 eV and 2.807 eV defects under N implantation and 800 °C annealing is in agreement with the proposed nature found in [1, 64] of a N atom and C interstitial. It will be of interest to follow their temperature behavior at different implantation fluences in further studies. Furthermore, there is a peak at 470 nm which points out at the emission wavelength of the TR12 centre, another often observed radiation defect [1, 67]. However, it is believed that it is the replica of the free exciton emission (noted X$_{2nd}$), because it is also present in the unimplanted region. Interestingly, no signal from the GR1 or the 3H centres can be found, although the implantation fluence was relatively high. This indicates that they have likely annealed out or are present as vacancy complexes (the sample was annealed only to 800 °C). Note the very weak contribution from H$_3$ centres (involving two N atoms, ZPL at 503 nm) which is expected to arise from the HPHT substrate.

3. Thermal treatment

As discussed above, different kinds of defects can form depending on the implantation energy and fluence or doping level in the diamond. It is also relevant to estimate the influence of the annealing treatment on the colour centre formation. The best example of this is N. The classification of diamond was historically determined from whether N is present (type I) or not (type II) and in which form: type Ib (isolated single N impurities) and type Ia (aggregated N impurities) subdivised into type IaA (aggregated N pairs) and type IaB (aggregated 4N + V). Thermal (and pressure) treatments are widely used in jewelry in order to change the colour or look of gemstones.

Figure 6. Thermal stability and creation yield of NV centres. (a) Fluorescence intensity versus annealing temperature of different defects: NV, H3, GR1 and 3H. The NV centres correspond to implantations of N at 45 keV and $1 \times 10^{15} \text{ cm}^{-2}$ (orange dots) and to 300 keV and $1 \times 10^{13} \text{ cm}^{-2}$ (red dots). (b) NV centre creation yield versus ion implantation energy for two different samples annealed at 800 °C in vacuum for 2h. The hollow circles account for the NV$^-$ fluorescence (using a longpass 650 nm filter) and the filled circles for the NV$^0$ + NV$^-$ fluorescence. (c) NV fluorescence versus annealing time at a temperature of 1600 °C in vacuum, measured from an implanted area with 45 keV N ions at a fluence of $1 \times 10^{15} \text{ cm}^{-2}$. (d) Fluorescence confocal scan of an ‘electronic grade’ sample annealed for 4h at 1600 °C in vacuum. Although no single NV is found before annealing, the thermal treatment induces the formation of single NV centres at a density of about 0.1–1 NV $\mu$m$^{-2}$. (e) Confocal fluorescence scan of a low-fluence implanted diamond with 5 keV N after a 2h annealing at 900 °C. (f) Scan of the same region after a 90 min annealing at 1150 °C. Almost none of the approximately 200 NV centres have disappeared. (g) ODMR spectra of five single NV centres recorded before (red) and after (blue) the 1150 °C treatment. A weak magnetic field is applied in order to distinguish between the four different possible orientations of NV centres due to different Zeeman splittings. At least four of the five studied NV centres did not change the orientation of the NV bond during the thermal treatment.
and increase their commercial value [68]. The first goal of a thermal treatment after any ion implantation process is, however, to heal the radiation defects as much as possible. Our aim for the screening study is furthermore to perform different annealing steps and to characterise the implanted areas after each of these steps in order to follow the defect production evolution related to each implanted element. Several optically active radiation defects, such as the ones presented above (GR1, 3H, 3.188 eV and 2.807 eV), can be followed to control the healing process. In addition, we will use, for example, the dissociation of NV centres into H3 (N–V–N) centres to estimate the diffusion coefficient of N at a given temperature.

### 3.1. Diffusion of vacancies

The creation of NV centres by N ion implantation requires an annealing step to ensure the positioning of the N atom in a substitutional place and the diffusion of vacancies (produced by the kinetic N ion along its path) until one of them is captured to form the NV centre. The efficiency of this statistical process is often given as the NV creation yield (the number of observed NV centres with respect to the number of implanted N atoms). It depends mainly on the annealing temperature [1, 60] and on the implantation energy [60]. The typical ‘yield versus energy’ dependence is plotted in figure 6(b) for two different samples of high purity. It shows that the yield is only in the percent range at energies of a few keV to produce shallow NV centres (a few nm depth). The use of such low energies is necessary for applications such as magnetometry [12] (sensitivity proportional to (1/d²) where d is the NV-object distance) or high spatial resolution implantation (to avoid ion straggling into the material) [69]. Therefore, over the last few years, efforts have been made to improve the NV creation yield [70–73] and to better understand the mechanisms at play. The annealing temperature (or time) necessary to form the NV centres needs to be sufficient so that the vacancies become mobile. A double exponential behaviour is generally observed in the annealing out of vacancies, due typically to the recombination of vacancies and C interstitial starting at 600 °C, and to the diffusion of vacancies becoming significant at about 800 °C [74]. In figure 6(a), the temperature dependence of the NV fluorescence is plotted as a function of the annealing temperature for two different ion fluences (10¹³ cm⁻² orange dots, 10¹⁵ cm⁻² red dots) of N implantation into two type-IIa diamond samples. At temperatures around 1000 °C, a plateau is reached and when the temperature is further increased, the NV centres tend to dissociate and possibly form other defects. This is supported by figure 6(c), showing the fluorescence decrease as a function of time from an ensemble of implanted NV centres heated at 1600 °C. Interestingly, we found that the same thermal treatment at 1600 °C applied to electronic grade diamonds with [N] < 1 ppb also causes NV centres to form, but from the native N. This was measured several times and is shown in figure 6(d) for a sample from which no single NV could be found before the 1600 °C treatment. The dispersed bright spots in the scan are single NV centres which can be found within the whole diamond (with an average distance of 1–5 µm, corresponding to an NV density of 10¹⁰–10¹² cm⁻³). This effect cannot be observed in optical grade material due to the too large amount of native N and NV centres already present. We attribute it to the thermal generation of vacancies. These are unstable in a perfect lattice and recombine with their adjacent interstitials during cooling down, but able to form a stable NV defect when generated close to a native N atom.

Not only is the creation yield important, but also the removal of all the surrounding implantation defects which is a key issue for quantum applications based on the spin of the NV⁻ centre. It was shown in [59] that the most suitable annealing temperature to remove paramagnetic defects is about 1100 °C. At such a temperature, most of the (Vₐ)⁰ defects anneal out, which can be followed by measuring the coherence time of single NV centres [59]. In this context, we have checked the stability of single NV centres at a slightly higher temperature of 1150 °C. This experiment is based on the con-focal imaging of single NV centres and on ODMR spectra to check whether the vacancy moves around the N atom, possibly leading to a new orientation of the NV centre within the diamond crystal. This can be followed by applying a low magnetic field and measuring the Zeeman splitting between the two resonances between the m₁ = 0 and m₁ = ±1. For a misaligned B field, each of the four possible (1 1 1) orientations of NV centres will provide a different Zeeman splitting. The first test consisted of imaging an area of a diamond randomly implanted with 5 keV N (figure 6(e)). The same zone was then imaged again (figure 6(f)) after a 90 min annealing at 1150 °C in vacuum. It can be seen that none of the approximately 200 single NV centres have disappeared and no additional NV has appeared. At the scale of the optical setup, it seems that no diffusion of the NV as a whole occurred. To further examine whether the vacancy may have changed place about the N atom, five single NV centres were selected and their ODMR spectra were taken before and after 90 min thermal treatment. The results are plotted in figure 6(g). The orientation of four NV centres is the same, whereas this cannot be concluded for NV5. What is important to note here is that the NV centres are extremely stable at 1100 °C which is the most suitable temperature to remove as many vacancy complexes as possible and to obtain the best coherence times.

The increase of the NV yield with increasing implantation energy shown in figure 6(b) is always observed. It can be explained by the number of vacancies per ion which increases with the ion energy (and therefore the probability to build an N–V complex during annealing) together with the increased probability to lose vacancies at the diamond surface. Moreover, due to surface proximity and band bending, a significant amount of the very shallow NV centres may be present in the NV⁺ charge state which is optically inactive, reducing the apparent NV yield. This is supported by the increasing NV⁺/NV⁻ ratio observed for both samples in figure 6(b) and in [73] when the implantation energy is reduced below 5 keV. Note that it was shown in [71] that a p-type doped layer leads to charging single vacancies positively as V⁺, which, in turn, precludes the formation of di-vacancies by Coulomb repulsion. Neutral single vacancies can more easily
form divacancies, which are more difficult to anneal out and which do not contribute to the formation of NV centres.

In addition, H diffusion is known to induce the passivation of NV centres by the formation of stable NVH complexes (only visible in electron paramagnetic resonance (EPR) or Fourier transform infrared spectroscopy (FTIR) depending on its charge state) and we will discuss it in the following.

3.2. Diffusion of N atoms

The very low diffusion of impurities in diamond makes it difficult to precisely estimate it experimentally. In the case of diamonds in which N is the dominant impurity (in the range 100 ppb to several ppm), the relative amount of NV and H3 centres can, however, be used to estimate N diffusion at the nanometer scale. Indeed, with increasing temperature, N atoms tend to aggregate and build more complex defects [75]. We can use this effect to determine the diffusion coefficient of N following the fluorescence of both these defects in a simple experiment. To this end, we implanted different areas of an optical grade quality diamond from element 6 with N ions, at fluences between $10^{12}$ cm$^{-2}$ and $10^{15}$ cm$^{-2}$, and set the kinetic energy to 45 keV (average depth of 60 nm). The corresponding local N densities are in the range $2 \times 10^{17}$ cm$^{-3}$ to $2 \times 10^{20}$ cm$^{-3}$, which in turn corresponds to the average closest N–N distances in the range 17 nm–1.7 nm. Subsequently, the diamond was annealed in vacuum at increasing temperatures from 500 °C–1600 °C (see figure 6(a)), staying about 20 s at each target temperature. Afterwards, the sample was heated further at 1600 °C for a total annealing time of 320 s and 1520 s respectively. The fluorescence intensities of the NV and H3 centres were then studied as a function of annealing temperature and annealing time using a confocal microscope. For the $10^{12}$ cm$^{-2}$ fluence (figure 7(a)), only the NV centres are observed, whatever the annealing temperature during this time. In such conditions, the 7.9 nm N–N distance is too large to enable the building of H3 centres. For the $10^{14}$ cm$^{-2}$ fluence (figure 7(b)), the spectral signature of the H3 centres appears for the highest treatment temperature of 1600 °C, indicating that some N diffused as far as the closest N atom, expected here to be 3.7 nm apart. To analyse these spectra, the reference emission spectra of single H3, NV$^0$ and NV$^-$ centres (figure 7(d)) were used. The time dependence of the NV/H3 ratio was studied for the highest temperature of 1600 °C. The fluorescence spectra presented in figure 7(c) (fluence of $10^{15}$ cm$^{-2}$) reveal that most of the implanted NV centres have disappeared and that the H3 centres became the dominant species after 1520 s at this temperature. In addition, this is shown in figure 7(f), where the NV and H3 fluorescence were normalised to their respective fluorescence after 20 s annealing at 1600 °C. Assuming that the diffusion length is now roughly equal to the average distance

Figure 7. N diffusion revealed by the evolution of the NV/H3 ratio. (a) Fluorescence spectra of a N implantation at a fluence of $1 \times 10^{13}$ cm$^{-2}$, recorded after different thermal treatments between 1300 °C and 1600 °C. (b) Fluorescence spectra of a N implanted region with a ten times higher fluence ($1 \times 10^{14}$ cm$^{-2}$) recorded after different thermal treatments between 1300 °C and 1600 °C. (c) Fluorescence spectra of a highly N implanted region ($1 \times 10^{15}$ cm$^{-2}$) recorded after different annealing times of 20, 320 and 1520 s at a temperature of 1600 °C under vacuum. (d) Reference spectra of H3, NV$^0$ and NV$^-$ used for fitting the data. (e) Fluorescence intensity versus annealing temperature for the NV and H3 centres. (f) Fluorescence intensity versus annealing time at 1600 °C for the NV and H3 centres.
the growth conditions such as temperature, pressure, growth rate or crystal orientation. Nevertheless, it can be estimated indirectly through its involvement in many known defects (and possible important role in their formation). For example, the NVH concentration can be estimated by EPR (NVH⁻) or FTIR experiments (NVH⁺) [77] and compared to the concentration of substitutional N and NV centres. Besides, it is known that the V⁻H and impurity-V⁻H complexes are very stable [78]. As a consequence, it is important to take H diffusion into account when aiming to create and use optical centres in CVD diamond. Conversely, the study of optical centres and their temperature behavior may be a way to gain better insight into the H concentration and homogeneity.

More specifically, it was reported by Stacey et al [79] that H can diffuse over several tens of micrometers at 800 °C with a diffusion coefficient as high as $0.6 \times 10^{-8}$ cm² s⁻¹. This was obtained by applying H plasma (at different temperatures and times) to an electronic grade diamond sample and measuring the fluorescence of NV centres as a function of the depth to deduce the diffusion length. The disappearance of the NV signal was accounted for by their passivation and the formation of NVH complexes which are not optically active. Deuterium diffusion was also previously reported [80, 81] and estimated in boron doped diamonds to study the passivation of boron acceptors. Much lower diffusion coefficients of about $5 \times 10^{-14}$ cm² s⁻¹ were reported at 550 °C, which could be increased up to $1.6 \times 10^{-11}$ cm² s⁻¹ under bias-assisted deuteration applying 80 V [82].

We have also studied the passivation of NV centres using implanted N into a (1 0 0) electronic grade single crystal sample at different ion energies and fluences, as seen in figure 8(a). After an 800 °C annealing to form NV centres, the sample was cleaned in a boiling acid mixture to prepare an O-termination of the surface. PL images of the whole sample were acquired with a DiamondView™ setup that uses UV light (200 nm–230 nm) to excite the luminescence. The 25 µm diameter NV ensemble spots are clearly visible. The detection limit of the setup is estimated to be $1.5 \times 10^{10}$ NV cm⁻² from the least visible NV spot. Figure 8(b) shows the image of the sample as prepared, where the NV patterning can be easily recognised. The sample has then been hydrogenated in a CVD reactor for 30 min under a H plasma at a low temperature of 500 °C and low power (1000 W) to avoid any surface etching. The PL image after the H plasma annealing can be seen in figure 8(c) using the same measurement conditions. Surprisingly, an intense blue fluorescence is observed, but not at the position where the NV centres are present, which appear as dark spots quenching this blue fluorescence. The origin of this fluorescence is not yet understood but near surface strain induced by polishing might be involved. The diamond surface was then re-oxygenated, placing the sample twice for 3 min in a plasma cleaner under oxygen and then using an ozonation treatment (30 min under O₃ using a UV excimer lamp at 172 nm) which is routinely used to ensure a good O-termination. The result is shown in figure 8(d). Compared to figure 8(b), the NV fluorescence is reduced for most of the implantation spots, although the surface termination and measurement parameters are the same. This is attributed to H diffusion which leads to the formation of stable NVH defects. The loss of NV centres depends between the implanted N atoms at this fluence of $10^{15}$ cm⁻², which is about 1.7 nm, we can estimate the diffusion coefficient of N. Using Fick’s second law of diffusion

$$\frac{\partial C(\vec{r}, t)}{\partial t} = D \nabla^2 C(\vec{r}, t)$$

where $C(\vec{r}, t)$ is the N concentration, in one dimension the diffusion coefficient $D$ can be estimated to be

$$D = \frac{x^2}{t} = 1.7 \times 10^{-17} \text{cm}^2 \text{s}^{-1}.$$  

This is supported by the results in figures 7(a) and (b), which show that at a ten times lower fluence of $10^{14}$ cm⁻², some H3 centres appear, while none are formed at $10^{13}$ cm⁻².

### 3.3. Diffusion of H—passivation of NV centres

H is likely the most common impurity in high purity CVD diamonds (with boron and N concentrations of a few $10^{14}$ cm⁻³ or less) due to the use of H plasma for growth. It is, however, difficult to estimate the total H concentration. Methods such as SIMS or nuclear reaction analysis have both typical ppm sensitivity for H, limiting the lowest measurable concentration to $\approx 10^{17}$ cm⁻³ [76]. The [H] concentration may depend on
on the ion energy and ion fluence used during the implantation process. This is shown in figure 9(e) (sample 1, blue squares and triangles). It is found that the lower the ion fluence, the more the NVs are passivated. Therefore, in a ‘cleaner’ diamond lattice, the NVs are preferential traps for diffusing H, whereas in a more defected lattice, H can be trapped at other impurities or defects. Besides, at a given ion fluence, the 5 keV implanted NVs are less passivated than the 2.5 keV ones which are shallower. Note that the depth of the NV centres here is up to 25 nm only, which is orders of magnitude less than the NV passivation due to H diffusion reported for distances of several tens of µm in [79]. The question of H diffusion in diamond is still open and we discuss it further in the next section in which overgrowth experiments were conducted. This is an important issue to consider for the engineering of defects in diamond, especially with the presence of impurity dopants or other point defects.

3.4. Diffusion of H—CVD overgrowth

For diamond-based quantum information processing, the optical centres used as quantum bits need to be placed precisely and close to each other within the diamond lattice. This is a challenging task when the requirement for inter-distance is about 30–50 nm. It was, however, shown that the high-resolution ion implantation of NV centres below 20 nm is possible [35], as revealed by sub-diffraction STED microscopy (see section 5.4). Nevertheless, it implies the use of low ion energy of a few keV (to minimise ion straggling [69]) which leads to the creation of very shallow centres that are sensitive to surface defects. One possible method consists of overgrowing the implanted centres by CVD in order to bury them and improve their properties, as already demonstrated for the enhancement of the spin coherence time [83] and the charge state stabilisation [73]. However, due to the use of CVD overgrowth, H diffusion may take place and passivate the shallow implanted optical centres. We have conducted several overgrowth experiments using three types of diamond samples (one ‘optical grade’ and one ‘electronic grade’ from element 6, and one as-grown CVD layer) which were previously implanted with NV centres at different shallow depths (between 1 keV and 5 keV). Typically, a few µm of diamond was overgrown in the standard growth conditions for high-purity material (850 °C, 3000 W, 1 h).
200 mbar, 4% CH₄). Figures 9(a) and (b) present the result of the overgrowth on the optical grade sample which contains NV centres within the whole diamond volume. No passivation of NV centres was observed after the overgrowth at the µm depth scale: the characteristic inclined layers richer in N and NV centres are still present after the overgrowth. This is different from the results of [79] for which NV passivation is observed several tens of µm below the surface. However, at the nm depth scale (figure 9(c)), the implanted NV centres have been passivated in different amounts, depending on the NV density, as shown in figure 9(e) (violet triangles, sample 2). This figure plots the ratio of NV centres measured after overgrowth with respect to the initial density. For the fluence of 3 × 10¹² and 1 × 10¹³ cm⁻², 83% and 59% respectively of the NV centres have 'disappeared'. For the higher fluxes, we observe an apparent increase in the NV density which we attribute to an improvement of the diamond quality during the overgrowth. Figure 9(d) shows confocal scans of patterns of NV centres implanted at different depths. The surprising effect here is that the shallower NV centres survived the overgrowth whereas most of the deeper ones have disappeared. This is due to the strong ion-energy dependence of the NV creation yield (see figure 6(b)) which imposes the use of much higher N fluxes for 1 keV implantation than for 5 keV in order to obtain the same number of NV centres.

For the same NV density, the passivation generally increases with depth for the three overgrowths. This is to be understood by taking into account the N density. Taking the creation yield NV/N into account, a 5 keV NV-centre is surrounded by about 25–100 N, whereas the creation of one 1 keV NV-centre required the implantation of at least ten times more N. We believe that this excess in N (and unhealed implantation defects) provides more traps for the diffusing H, therefore effectively reducing the passivation of the NV centres when the implantation energy is decreased. Furthermore, a fluence dependence is also observed in figure 9(e) for the two other samples too. A slight etching of the initial diamond surface during the overgrowth cannot be excluded and might be the reason for the highest loss of NV centres in the fluence range 10¹²–10¹³ cm⁻². Nevertheless, these results suggest that H diffusion takes place, at least on several tens of nm in our conditions, and that it needs to be taken into account, especially for CVD layers.

An annealing at 1100 °C for 2h was conducted and no NV centre could be found after they had been passivated. This confirms that NVH centres are very stable and cannot be easily dissociated. It would be of interest to check what happens for other kinds of optical centres such as SiV, SnV, ST1 or L1 centres.

4. Screening of alternative colour centres in diamond

This section is dedicated to the preliminary results of the screening study, concerning more particularly the elements O, F, Mg, Ca and P, which were all found to produce optically active defects. The nuclear-spin-free elements ¹⁶O, ²⁴Mg and ⁴⁰Ca were particularly of interest in the context of the search for the ST1 centre [2, 3].

As described in section 1, our method consists of implanting different chemical elements within the same sample and using, at first, wide-field techniques for high throughput, and then confocal fluorescence microscopy (or
To this end, we have built a home-made and versatile wide-field fluorescence microscope, as shown in figure 10(b). The laser source, the objective and the imaging lens can be easily changed and adapted to the sample and fluorescent centres in order to obtain fluorescence images in one shot. The sample used here is a single crystal (100) CVD ‘electronic grade’ from element 6 presented in section 1. Due to the lower sensitivity of the wide-field setup (compared to scanning confocal fluorescence microscopy) high implantation fluences are used to ensure strong fluorescence signals ($10^{12}$ cm$^{-2}$, $10^{13}$ cm$^{-2}$ and $10^{14}$ cm$^{-2}$). N was also implanted as a reference ($30$ keV, $10^{14}$ cm$^{-2}$). Three graphite spots were produced for orientation using $16$O ions at a very high fluence of $10^{16}$ cm$^{-2}$. The implantation through an aperture placed a few mm away from the diamond surface (figure 1(b)) induces a

**Figure 11.** (a) Fluorescence spectra at room temperature of single ST1 and L1 centres of a still unknown nature (laser excitation 532 nm). The dip around 532 nm in the ST1 spectrum is due to the Notch filter (532 nm) used to suppress the reflection of the laser. (b)–(f) Fluorescence spectra of the different ensemble implantations found in figure 10(a) (after annealing at 1600 °C for 4 h in vacuum), all recorded using the same acquisition conditions and 488 nm laser excitation (488 nm Notch filter and 50/50 beamsplitter instead of a dichroic mirror). The spectra are measured during the scan of a 10 × 10 µm$^2$ area at the centre of each spot. The spectra are background corrected using a reference spectrum taken away from the implantation. (b) Oxygen (depth 50 nm, fluence $1 \times 10^{15}$ cm$^{-2}$) after the removal of graphite. The remaining effective oxygen fluence is expected to be in the range $10^{13}$–$10^{14}$ cm$^{-2}$, comparable to the fluence in the corona (the same effect is also seen for 3H centres in figure 4, where the graphite has not been removed). (c) N, depth 50 nm, fluence $1 \times 10^{14}$ cm$^{-2}$. By analogy to the oxygen implantation, the N spot shows H3 fluorescence, confirming the high temperature treatment at 1600 °C. (d) Fluorine, depth 50 nm, fluence $1 \times 10^{14}$ cm$^{-2}$. (e) Calcium, depth 50 nm, fluence $1 \times 10^{14}$ cm$^{-2}$. (f) Mg, depth 50 nm, fluence $1 \times 10^{14}$ cm$^{-2}$. 

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fluence gradient around the spots, allowing us to study the fluorescent centres at the single centre level in case they are bright enough. The sample was annealed for 4 h at 1600 °C in vacuum. The surface was cleaned in an oxygen plasma chamber, which removed most of the graphite from the oxygen spots. A typical wide-field image of this screened diamond with the elements N, O, F, Mg and Ca is shown in figure 10(a) in real colours. It was recorded in one shot (20 s acquisition time) with a commercial photo camera. The wide-field image shows that each implanted element produces fluorescence and provides rough but rapid insight into their brightness and spectral emission before more precise measurement methods are employed.

4.1. Oxygen

One of the aims of the screening method is to try to reproduce the defects of a still unknown nature. It was recently shown that the so-called ST1 and L1 centres (figure 11(a)) were created together within the same sample and ion implantation run [3].

The ST1 centre is promising since it shows ODMR at room temperature. No hyperfine coupling was found in the ODMR spectra, indicating that the constituent atom likely possesses no nuclear spin. One of the candidates is 16O, supported by the fact that the two creation methods of ST1 involved oxygen: (i) RIE etching [2] and ion implantation using a cathode with B, C, N, and O in it [3]. We have recently implanted oxygen at low fluence and annealed the sample at 800 °C in order to find single centres. No L1 or ST1 could be found. Here we have used a much higher ion fluence with a gradient up to $1 \times 10^{16}$ cm$^{-2}$ and an annealing temperature of 1600 °C. Indeed, we observe the creation of O-related colour centres with an intense orange fluorescence (figure 10(a)) with a ZPL likely at 584.5 nm and a broad phonon sideband of about 120 nm (figure 11(b)). The same spectra are found both in the corona and in the centre (after removal of the graphite of the O-spots). This centre has already been reported in [84] in the case of O$^+$ implantation and after annealing above 1600 °C only. Another line at 598.4 nm was also attributed to the O implantation but we do not observe it here. This high-density high-temperature treatment of oxygen can be put in parallel with N. At low fluence and low temperature annealing (800 °C), NV centres are mostly produced. However, at higher fluences and higher temperatures, it becomes more likely to form H3 centres (ZPL at 503 nm) due to the diffusion of N (see section 3.2). As a reference, we have also implanted N at high fluence to check whether H3 centres also form. The green–yellow fluorescence seen in figure 10(a) reveals the presence of H3 centres in majority, which is confirmed by the spectrum shown in figure 11(c). These O-related centres may be due to O complexes. However, neither the optical spectra of the ST1 (ZPL at 546 nm and broad phonon sideband) nor of the L1 (sharp and strong ZPL around 580 nm) resemble the O-centre shown here.

4.2. Calcium

The most naturally occurring isotope of calcium, 40Ca with 97% abundance, is free of nuclear spin. The orange fluorescence observed in figure 10(a) from the Ca spot might be a candidate to correspond with the ST1 fluorescence. However, the brightness of the Ca-related fluorescence is weak and no single centres could be found. The fluorescence spectrum taken from the spot of the highest fluence is shown in figure 11(e). It possesses a ZPL at 557.2 nm and a broad phonon sideband which do not correspond to the ST1 centre.

4.3. Fluorine

The red fluorescence observed in figure 10(a) from the fluorine spot is about 30 times brighter than the Ca-related emission. The fluorescence spectrum taken from the spot of highest fluence is shown in figure 11(d). A broad emission peak centered
at 680nm is observed without any visible ZPL. At the edge of the implanted areas (figure 12(a)), single emission spots can be found with the same fluorescence spectra as the ensemble fluorescence of figure 11(d), indicating that they are fluorine-related. This is shown in figure 12(b) for the centre circled in figure 12(a). The single-quantum-emitter behavior of these spots has been checked by measuring the $g(2)(\tau)$ autocorrelation function using a Hanbury-Brown and Twiss setup. The photon antibunching ($g(2)(\tau = 0) < 0.5$ at zero time delay) observed in figure 12(c) is proof that these are indeed single fluorine centres. The lifetime of the excited state is estimated to be $(7 \pm 2)$ ns, deduced from the single-exponential fit. Note that the 28% uncertainty is due to a measurement artefact (peak at $t = 2.5$ ns). The creation yield of the optically active F centres is estimated to be about $8 \times 10^{-4}$, which is about two orders of magnitude weaker than for the NV centres at the same implantation energy. The (background-corrected) saturation curve of one of these centres is plotted in figure 12(d). The raw data (without background correction) has been fitted as follows

$$I = I_\infty \frac{1}{1 + P_s/P} + bP$$

where $I_\infty$ is the saturation count rate, $P_s$ is the saturation power and $b$ is the linear contribution of the background fluorescence. We obtain $I_\infty = 3.0 \times 10^{5}$ counts s$^{-1}$, a saturation power of 8.1 mW and $b \approx 8 \times 10^2$ counts s$^{-1}$ mW$^{-1}$.

4.4. Magnesium

The isotope $^{24}\text{Mg}$ (abundance of 79%), free of nuclear spin, is also a potential candidate involved in the ST1 defect. The fluorescence spectrum of an ensemble of Mg-related centres is shown in figure 11(f). It possesses a sharp and intense ZPL at 557.4 nm and the vibronic sideband presents features at 66 meV and 154 meV. Although some single ST1 centres were reported with ZPL emission above 550 nm, the sideband is rather different. The Mg fluorescence is strong and a weak peak was already observed directly after implantation without annealing. Figure 13(a) is a confocal fluorescence close view (15 $\times$ 15 $\mu$m$^2$) taken at the edge of the Mg-implanted area with an excitation wavelength of 532 nm and an oil immersion objective of NA = 1.35. (b) Fluorescence spectrum of a single Mg-related centre (excitation power 4 mW, 125 s integration time). (c) Saturation curve of a single Mg centre. (d) Photon autocorrelation function $g(2)(\tau)$ measured at a laser power of 1.44 mW. The curve is background corrected and normalised. The dip going to zero at zero-time delay proves the single quantum emitter behavior of the defect. The exponential fit gives a lifetime of 2.4 ns for the excited state. The inset shows the $g(2)(\tau)$ function for longer times.
antibunching observed in the photon autocorrelation function $g^2(\tau)$ plotted in figure 13(d). The curve is fitted with a three-exponential function. The lifetime of the excited state can be deduced from the fit and we obtain about 2.3 ns, shorter than the 9 ns of the ST1 centre. The bunching behaviour indicates the presence of two shelving states with time constants of about 150 ns and 2.4 $\mu$s. A typical saturation curve for a single Mg centre is shown in figure 13(c). We obtain $I_\infty = 3.3 \times 10^5$ counts s$^{-1}$, a saturation power of 5.1 mW and $b \approx 3.82 \times 10^4$ counts s$^{-1}$ mW$^{-1}$.

With the measurement of single Mg centres, it becomes possible to estimate the creation yield of the Mg centres with respect to the number of implanted Mg atoms. Taking an average fluorescence intensity in the implantation spot of fluence $10^{13}$ cm$^{-2}$, we obtain a creation yield of about 12%. Note that this corresponds to an annealing done at 1600 °C for 4 h. Further study is required to follow the temperature evolution of the Mg-related fluorescence.

The optical properties of these Mg-related centres measured in an intrinsic region of the diamond sample indicate that it is a different defect than the ST1 centre. Finally, we have searched for ODMR within the microwave frequency range 0.5–4 GHz with 1 MHz resolution and did not find any resonance.

4.5. Phosphorous

Phosphorous is one of the possible donors in diamond, but with a deep level placed 0.57 eV below the conduction band. This means that at room-temperature, no free carriers can be found in the conduction band. However, the charge state of optical centres can be influenced by way of compensation by the presence of donors in their vicinity [85, 86]. Ion implantation and annealing are generally less efficient in producing active substitutional P donors compared to CVD growth due to the presence of radiation defects acting as compensation centres [49], as can be measured with bound exciton spectroscopy in CL [87]. Note that up to 70% of substitutional P was reported by implantation and annealing, as measured by the emission channeling technique [88].

Here, we found that the implantation of P followed by high temperature annealing (4 h at 1600 °C) in vacuum leads to the formation of luminescent centres with a very low creation yield. This can be seen in figure 14(a), where the border between the P-implanted area and the unimplanted area (covered with aluminum foil) is imaged with confocal microscopy. Single spots with an average density of about 1.5 $\mu$m$^{-2}$ are visible. The P implantation conditions were determined to obtain P atoms at an average depth of 50 nm with a total fluence of $1.6 \times 10^{13}$ cm$^{-2}$. This indicates a creation yield of about $10^{-5}$ with respect to the number of implanted P atoms. Moreover, two kinds of centres are observed as plotted in figures 14(b) and (c), with ZPL at 557 nm or with a doublet of lines at 579.4 nm and 597.2 nm. These centres were visible only after the annealing and might involve vacancies. It is not yet clear what these likely P-related centres can be. It was, however, theoretically predicted that PV$^-$ centres do not possess an optical transition and act as compensation centres of n-type doping [89]. The high temperature and long annealing time used, together with the relatively high P density of about $3 \times 10^{18}$ cm$^{-3}$ might imply more complex defects than PV, by analogy with the H3/NV ratio studied in section 3.2. Note that most of the P-related centres are turned off when the excitation power is increased, typically above 200 $\mu$W.

5. Quality control of implanted colour centres and diamond substrates

The applications of optical centres in diamond for quantum information processing or quantum sensing push the requirements of the material quality and the reproducible and nanometer placement of these centres to their limits. The multi-purpose sensing capabilities of the NV centre (magnetic and electric fields, chemical potential, temperature, stress) can be used to sense the material quality and homogeneity. Therefore, in our screening study, we always implant N as a reference or witness of the diamond matrix hosting the other defects that we create by implantation.
Figure 15. Time trace analysis for charge state and fluorescence stability. (a) Confocal fluorescence scans (1 × 1 μm²) of three different L1 centres implanted into an electronic grade CVD diamond (laser excitation at 532 nm and detection within 575–630 nm). The centres are separated by only a few μm but show different stability/blinking under the same excitation conditions. (b) Time trace of one of the moderately blinking L1 centres at a laser power of 800 μW. (c) Power dependence of the ionising and recharging rates of the moderately blinking L1 centre at 594 nm excitation. Reproduced from [3]. © IOP Publishing Ltd. CC BY 3.0. (d) Time trace of a single NV centre in an electronic grade CVD diamond enabling a charge-state single-shot readout (excitation 594 nm, 5 μW, detection 660–735 nm). With the 594 nm laser used here (5 μW), fluorescence is observed only when the NV centres are negatively charged. The charge state jumps are photo-induced by the laser [101]. (e) Power dependence of the ionising and recharging rates of the single NV centre. (f) Fluorescence image of a single native NV centre within a HPHT sample with [N] of 10 ppm. (g) Fluorescence image of a single NV centre implanted into a boron-doped CVD layer with [B] about 1 × 10¹⁸ cm⁻³ (6 ppm). For both scans, the laser excitation is 594 nm and the detection window is 660 nm–735 nm. (h) and (i) Time trace analysis of the two centres with P = 800 μW for the centre in (f) and P = 230 μW for the centre in (g). The charge state changes between NV⁺ and NV⁰ are due to the boron (acceptor) doping.

In this section, we discuss four methods that we propose to apply complementarily in order to improve reproducibility in the creation of the different optical centres:

- Time trace analysis of the fluorescence (or single-shot charge-state readout) of single NV (or other) centres in order to sense the electrical environment through the stability or blinking dynamics.
- NV-based ODMR to sense the magnetic and electric environment as well through the measurement of the coherence time T₂ or T₁ of the electron spin of single NV± centres.
- Cross-polarisation analysis in transmission in order to visualise the residual stress within the diamond sample, as well as extended defects such as dislocations.
- Stimulated emission depletion (STED) microscopy: in the context of building scalable arrays of qubits based on NV, ST1 or other centres, their relative distances can be confirmed optically by sub-diffraction imaging techniques such as STED [90]. In this section, we show that STED can also be successfully applied to the recently discovered and promising ST1 centres [2, 3]. Additionally, we discuss its potential application to GR1 centres (neutral vacancies) which would be of high interest for defect engineering in diamond.

5.1. Charge state and fluorescence stability—time trace analysis

The fluorescence and charge state stability of defect centres is an important issue for their reliable use as sensors, qubits or single-photon sources. Although they can be seen as artificial atoms in the solid-state, the close environment of implanted centres may vary from one to the other due to many process steps, to diamond quality, homogeneity and impurity level, or due to the surface state and/or preparation. In diamond, no general chemical potential can be defined as in standard semi-conductors [91], thus the optical centres can be found in different charge states at different locations within a diamond sample. This is illustrated in figure 15(a) which shows three implanted L1 centres (separated by only a few μm) in an electronic grade CVD (1 0 0) diamond sample. The confocal fluorescence scans are all taken under the same excitation conditions (excitation laser 532 nm, 500 μW, scan speed 5 μm s⁻¹) and it can be seen that the three L1 centres show drastically different stability and blinking properties. The charge states of the L1 are not yet known, however the blinking is likely due to surface states or neighbouring donor or acceptor states. The fluorescence stability and/or blinking dynamics can be followed by recording the time-trace of the fluorescence as in figure 15(b). A stable L1 centre would be useful as a single photon source whereas a fast-blinking L1 would be suitable for stochastic sub-diffraction imaging such as stochastic optical reconstruction microscopy (STORM) [92] or photoactivated localisation microscopy (PALM) [93]. The ionising and charging rates can be deduced and plotted as a function of the laser power (figure 15(c)) or excitation wavelength. They can therefore be used as a footprint for the centre’s environment and we propose to use this technique for the quality control of optical centres.

Much effort was made to stabilise [85, 86] and/or tune and control the charge state of colour centres, especially with the NV centre: chemically [94–97], optically [98], and electrically [17, 18, 99, 100]. It was shown by a single-shot charge-state readout that the NV centre charge state is constantly ‘jumping’ between NV⁺ and NV⁰ under light excitation due to photo-induced ionisation and recharging [101]. These rates depend on the laser excitation power and wavelength. This is
illustrated in figures 15(d) and (e) for a single NV centre into an electronic grade CVD diamond. In addition, the presence of donors or acceptors is expected to strongly modify the charge state dynamics. This is shown for single NV centres in the case of an N-rich HPHT diamond (figures 15(f) and (h)) and of a B-rich CVD-grown diamond (figures 15(g) and (i)). The NV\textsuperscript{−} state is stabilised by the presence of the N-rich surrounding, which acts as a deep donor (1.7 eV) that can be ionised by the laser excitation and provide free electrons. In addition, the presence of boron (0.37 deep acceptor niveau) induces the blinking of the NV centre. A model was proposed in [101] in good agreement with the two-photon processes observed in the quadratic variation of the ionisation and recharging rates as a function of the excitation power.

5.2. Spin coherence time—NV-based ODMR

The spin properties of the NV centres at room temperature allow us to use the NV centre as a nanoscale and sensitive ‘multi-task’ quantum sensor. Within the screening method presented here, we always implant NV centres as well to provide insight into the diamond material into which we produce other kinds of optical centres. The NVs are well suited to measure electronic and magnetic impurities, which reveal their presence on the coherence time of the NV\textsuperscript{−} centre. For example, it was shown in [102] that the broadening of the ESR lines of single implanted NVs is dependent on the depth due to the presence of surface paramagnetic impurities. The spin coherence properties and the charge state stability of such shallow centres can be improved by diamond overgrowth [73, 83]. Isotopically \textsuperscript{13}C enriched samples with \textsuperscript{[13]}C of about 0.3\% (instead of 1.1\% natural abundance) led to long T\textsubscript{2} times of up to 1.8 ms at room temperature [103]. Furthermore, the radiation defects can be probed by NV-ODMR. The etching of a thin superficial diamond layer above the implanted NV centres revealed an improvement of the coherence time due to the removal of the vacancies induced by the ion implantation process present in this layer [71]. In addition, the correlation between the annealing temperature and the healing of vacancy complexes along (1 1 1) (measured by EPR) has been shown in [59]. Also, the study of the hyperfine couplings to the electron spin of the NV\textsuperscript{−} centre can be used to retrieve atom species which are close by, such as that described in [104].

5.3. Diamond homogeneity—cross-polarisation analysis

The observation of a transparent material in transmission, placed between two polarisers with their axis perpendicular to each other, enables the visualisation of birefringence. Applied to an isotope material such as diamond, this method enables a direct view of the stress within the diamond substrate, as shown in figure 16(a). The strain induces a change in the refractive index of diamond and the appearance of birefringence. Even though a quantitative analysis is hardly achievable [105], this method reveals dislocations (figure 16(b)) and therefore dislocation-free regions can be easily pre-selected. The homogeneity of the diamond sample (in terms of these defects) is easily made visible with this non-invasive and fast method. Stress is, for example, responsible for shifting the ZPL emission of most of the optical centres. It is therefore important to determine the stress and sample homogeneity.

As an example, we present in figure 16(c) the results of strong variations in the creation of NV centres by N implantation. These variations cannot be explained by ion beam current fluctuations during the implantation process because the implantation pattern was scanned 100 times (with the ion beam focused down to 1 \textmu m) to reach the total fluence per point (and not one point after the other with the full fluence implanted in one shot). Interestingly, we found these spatial variations in the creation efficiency of the NV centre within a CVD diamond layer presenting the birefringence patterns observed in figure 16(b) and having the same orientation and size. We believe that stress likely plays a role during the annealing step and influences the diffusion of vacancies. This may enable the fabrication of single centers with improved creation yields; further experiments are needed to clarify this.
analysis is a very fast and non-invasive method which can be used to preselect the suitable areas of a diamond sample for quantum application using optical centres.

5.4. High-resolution implantation—STED microscopy

The fabrication of scalable structures (as a prerequisite for large scale quantum architectures) based on optical centres in diamond is highly challenging, especially because the deterministic fabrication of NV, ST1 or other centres has not yet been achieved. However, the deterministic implantation of single ions has already been demonstrated using a modified Paul trap [38], and bunches of ions can be detected on-the-fly using image charge detection [39] which could soon become a versatile deterministic ion implantation method. On the other hand, a spatial placement within less than 20 nm has already been demonstrated with NV centres [35]. To date, only two optical centres in diamond—the NV and the ST1—were found to show ODMR at room temperature [2, 3], making them the most promising candidates for QIP.

In standard confocal fluorescence imaging, the separation power \( \Delta r \) of the setup is given by Abbe’s criteria

\[
\Delta r \approx \frac{\lambda}{2NA}
\]

where \( NA \) is the numerical aperture of the objective lens and \( \lambda \) is the wavelength of the light. The point-spread function is an ellipsoid of dimensions of about 300 nm in transverse and 1 \( \mu \)m in longitudinal directions (for standard experiments with NV centres). Two point-like emitters located within this ellipsoid cannot, therefore, be optically resolved. Consequently, the single quantum bits of a quantum device with a size smaller than \( \Delta r \) cannot be individually addressed and read-out optically by classical means. With the introduction of new nanoscopy methods such as STED [90] or STORM [92]/PALM [93], it became possible to beat the diffraction limit. An improvement of more than one order of magnitude was demonstrated in the case of STED imaging of NV centres in diamond [35, 106]. This was possible thanks to the extreme robustness and optical stability of this system which is able to sustain high laser intensities without bleaching or photodamaging the sample. Indeed, the STED resolution is theoretically unlimited and is given by

![Figure 17. STED microscopy of NV and ST1 centres. (a) Confocal scan of an array of NV centres created by N implantation through a pierced AFM tip. The optical resolution of the image is limited by diffraction. (b) STED image of the same area, with an optical STED resolution of 10 nm. (a) and (b) are reprinted from [110], Copyright (2014), with permission from Elsevier. (c) Fluorescence spectra of the ST1, NV and GR1 centres. (d) Confocal scan of a diamond sample containing L1 and ST1 centres. (e) Combination of a confocal and a STED image of a single ST1 centre (shown by the red circle in figure 12(d)). (f) Lateral resolution as a function of the STED beam intensity in the focal plane for the NV and ST1 centres. The saturation intensity of the NVs is given in [106] to be 6.6 MW cm\(^{-2}\) and it was found to be in the same order of magnitude for the ST1 centre.](image-url)
where $I_{\text{STED}}$ is the intensity of the STED depletion beam and $I_{\text{sat}}$ is the saturation intensity of the optical centre. Figure 17(a) shows an implanted array of shallow NV centres imaged by confocal microscopy with $\Delta r_{\text{confocal}} \approx 250 \text{ nm}$, and figure 17(b) shows the same array imaged by STED microscopy with $\Delta r_{\text{STED}} \approx 10 \text{ nm}$. Additionally, STED proved the targeted readout of single electron spins within a small ensemble positioned in a diffraction limited volume [107].

Here, we show that STED can also be applied efficiently to the ST1 centres. Moreover, the optical properties of the ST1 enable us to use the same wavelengths for excitation and depletion as for the NV centre. The fluorescence spectra of the ST1 enable us to use the same wavelengths for excitation and to the ST1 centres. Moreover, the optical properties of the ST1 centres. This shows that STED imaging of the most promising centres for QIP is possible, moreover using the same experimental configuration.

In the context of defect engineering, it would be of interest to image single vacancies by STED in order to improve and refine the understanding of the discussion found in the first part of this work. This would imply, first, to image single vacancies by confocal microscopy, which has not been demonstrated yet due to the typically high vacancy density. However, a fluorescence lifetime of 1.4 ns [108] and an emission sideband expanding over roughly 100 nm (figure 17(c)) fulfill the technical requirements for efficient STED imaging. Only the brightness of a single GR1 centre, which has strong non-radiative decay channels [109], might challenge current photon counting devices without representing a fundamental limitation.

**Summary**

In this paper, we have presented a high throughput screening method in the search, reproducible creation and identification of single defects in diamond. We used a versatile ion accelerator to implant several chemical elements and we applied optical imaging and spectroscopy to study the defects created and their temperature evolution. Firstly, we discussed both theoretically and experimentally the distribution of C vacancies produced at the end of the range of an implanted ion, as well as the consequences for the creation of colour centres, depending on the atom mass and nature of the defect produced. We conducted molecular dynamics simulations which showed that the primary damage is in small disordered atom regions rather than isolated point defects; this is confirmed experimentally. We further observed that the relative amount of single vacancies (GR1) which are produced decreases with the ion mass, preferentially leading to more complex groups of vacancies.

We then discussed the formation and dissociation of different defects such as GR1, 3H, NV and H3 under thermal annealing. More particularly, we showed, using ODMR, that at 1150 °C, the NV centre bonds do not change orientation. At higher temperatures, we observed N diffusion through the increase of H3 fluorescence with respect to NV fluorescence and estimated the N diffusion coefficient to be $1.7 \times 10^{-3} \text{ nm}^2 \text{s}^{-1}$ at 1600 °C. We further confirmed the effect of H diffusion on the ‘irreversible’ passivation of NV centres and quantified the NV loss in different experimental conditions. Further, the first results of the long-term screening study were presented. It was found that Ca, Mg, F, O and P induce optically active defects in the visible range. A fine study was conducted on single Mg-related centres, which were still found up to 1600 °C, and which present a strong and narrow ZPL at 557 nm with a relatively weak phonon sideband at room temperature. Interestingly, single fluorescent centres were found related to the P implantation. The low creation yield and a better understanding of these centres may provide insight into the compensation of P donors. Finally, we proposed to establish the quality control of diamond material and optical centres to improve their reproducibility. In this context, we showed that STED microscopy can be applied to the ST1 centres as efficiently as for NV centres, which is promising for the scalable creation of QIP devices based on these ODMR active centres.

In future studies, the screening will be extended to other elements, combinations of elements but also to different doping and doping levels of diamond which are likely to strongly influence the diffusion and stability of the different defects. Furthermore, this screening method will be tested with nanoparticles as well.

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