

# Optical Centres Produced in Diamond by Radiation Damage

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(Received 9 January 2007; accepted 28 March 2007)

**Key words:** diamond, radiation damage, annealing, absorption spectroscopy

Optical centres produced in diamond by radiation damage and annealing, and which can be easily detected by absorption spectroscopy, are described. For annealing temperatures from 200 to 1650°C, at ambient pressure, the general behaviour is characterised by the complementary growth of one optical centre as another centre is destroyed. By 1750°C, the absorption produced by all radiation-induced optical centres has become weaker and, following annealing at high pressure and high temperature (typically 2300°C at > 5 GPa), most of these centres are present in only negligible concentrations. The roles played by the impurities (boron, single nitrogen and nitrogen aggregates), present in the majority of diamonds, are discussed in detail.

## 1. Introduction

Radiation damage has been used extensively for more than 50 years to produce defects in diamond. The principal mechanism is the production of vacancies and self-interstitials. All natural diamonds, diamonds grown by high-pressure, high-temperature (HPHT) synthesis and diamonds grown by chemical vapour deposition (CVD) contain defects introduced during growth. The interaction of these preexisting defects with vacancies and interstitials created by radiation damage has contributed to our present understanding of the defect spectroscopy of diamond.

Understanding the role of defects is important for many of the technological applications of diamond. In addition, many of the defects produce absorption in the visible region of the optical spectrum, and so influence the colour of diamond gemstones.<sup>(1)</sup> Here, too, an understanding of the optical centres produced by radiation damage is crucial in allowing gem-testing laboratories to determine whether the colour of a diamond is natural, or has been enhanced by some form of "treatment."

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Any particle with sufficient energy (electrons, neutrons,  $\gamma$ -rays, ions, etc.) can produce vacancies in diamond. Since the pioneering studies of Clark and coworkers,<sup>(2,3)</sup> electrons with energies of 1 to 2 MeV have been the preferred means of producing optical centres for fundamental studies. Such electrons produce predominantly isolated vacancies and interstitials reasonably quickly, and the penetration depth of the order of 1 mm ensures that a useful path length of material is produced for optical absorption studies. By contrast, neutrons and heavy ions produce regions of multiple damage and, although neutrons have a large penetration depth, charged particles with an energy of a few MeV penetrate only a few  $\mu\text{m}$ . A 5.5 MeV  $\alpha$  particle, for example, has a range of approximately 14  $\mu\text{m}$ .<sup>(4)</sup> A typical electron irradiation, using a linear accelerator or Van de Graaff accelerator with a beam-current density of 50  $\mu\text{A cm}^{-2}$ , would require 1 to 2 h. To achieve a similar vacancy concentration, using a powerful  $\gamma$ -ray source, takes many weeks.<sup>(2,3)</sup>

In this review, we will concentrate on the study of optical centres using absorption spectroscopy. This is a quantitative technique, which allows the relative concentrations of defects to be determined and, in cases where calibrations have been carried out, absolute concentrations of optical centres may be obtained. All spectra have been recorded with the diamond at 77 K, unless stated otherwise.

Luminescence spectroscopy can be many orders of magnitude more sensitive than absorption spectroscopy. Laser-excited photoluminescence allows semiquantitative concentrations of defects to be obtained by comparing the intensity of the luminescence from an optical centre with the intensity of the emission produced by Raman scattering. Cathodoluminescence spectroscopy generates useful complementary information, but is not a quantitative technique.<sup>(5)</sup> However, apart from a very brief mention, the many radiation-induced defects, which can be detected only by luminescence spectroscopy (and so, presumably are present in very low concentrations), will not be discussed here.

## 2. Vacancy Production — Role of Preexisting Defects

The rates at which vacancies and interstitials are introduced in diamond, and the charge state of the vacancy, depend critically on the preexisting defects in the diamond. These defects are also used to classify diamond into different “types,”<sup>(5)</sup> and the responses of the diamonds to radiation damage are subdivided here by diamond type.

### 2.1 *Type Ib diamond*

Type Ib diamond contains nitrogen on isolated substitutional lattice sites. For natural diamonds, it is believed that the nitrogen is originally incorporated in this form but that, after long periods at typical geological temperatures, the nitrogen forms aggregates characteristic of type Ia diamonds. Natural diamonds classified as type Ib are consequently rare and are frequently a mixture of type Ib and type Ia material. The single substitutional nitrogen produces an absorption in the visible region, starting at approximately 550 nm, and increasing towards shorter wavelengths.<sup>(6)</sup> This absorption can produce an attractive yellow colour in a gem diamond, sometimes described as “canary yellow.”<sup>(7)</sup> The nitrogen concentrations in such specimens are generally rather low.

Measurements on one canary yellow diamond showed that the absorption coefficient at 400 nm was approximately  $10 \text{ cm}^{-1}$ , implying that the single nitrogen concentration was approximately 20 ppm.<sup>(8)</sup>

Diamond produced commercially by HPHT synthesis, on the other hand, is predominantly type Ib. The average nitrogen concentration is typically 50 to 200 ppm, but the distribution of the nitrogen is very inhomogeneous.<sup>(9)</sup> HPHT diamonds contain several different types of growth sector;  $\{100\}$  and  $\{111\}$  frequently dominate, but minor growth sectors such as  $\{110\}$ ,  $\{113\}$  and  $\{115\}$  can occupy a significant fraction of the crystal. The concentrations of nitrogen differ by at least an order of magnitude in the various growth sectors.<sup>(9)</sup> The concentration of neutral nitrogen ( $\text{N}^0$ ) in type Ib diamond can be determined from the strength of the absorption produced in the defect-induced one-phonon region, using either the intensity of the broad band at  $1130 \text{ cm}^{-1}$ <sup>(10)</sup> or the sharp peak at  $1344 \text{ cm}^{-1}$ <sup>(11)</sup> associated with a localised vibrational mode.

Several optical centres in diamond, including vacancies, can exist in more than one charge state. Isolated substitutional nitrogen behaves as an electrical donor, and, if it is sufficiently close to a vacancy, the vacancy will be in the negative charge state.<sup>(12)</sup> This is referred to as the ND1 centre, or  $\text{V}^-$ . In the absence of single substitutional nitrogen, the vacancies will be present in the neutral charge state  $\text{V}^0$ , giving rise to the GR1 absorption band.

Figure 1 shows the absorption spectrum from the  $\{115\}$  growth sector of an electron-irradiated type Ib diamond. Before irradiation, this region of the diamond contained approximately 1 ppm of isolated substitutional nitrogen. Three important features are identified in the figure; the GR1 and ND1 zero-phonon lines (ZPLs), and the peak at 666.6 nm (1.859 eV) due to a localised vibrational mode associated with the neutral self-interstitial  $\text{I}^0$  in a split  $\langle 001 \rangle$  configuration. Lines on the low-energy (long-

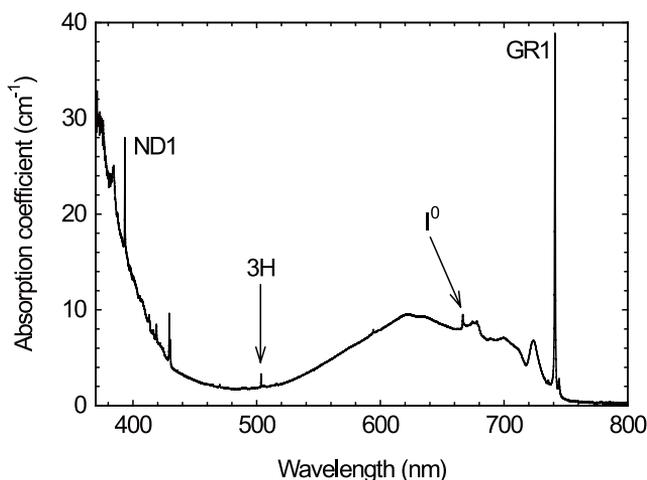


Fig. 1. Absorption spectrum of an electron-irradiated HPHT synthetic diamond containing approximately 1 ppm of single substitutional nitrogen. Absorptions by the neutral vacancy (GR1), the negative vacancy (ND1) and the self-interstitial ( $\text{I}^0$ ) are clearly visible.

wavelength) side of the ND1 ZPL are due to transitions to higher excited states (GR2 to GR8) associated with  $V^0$ . The concentrations of  $V^0$  and  $V^-$  can be determined from the integrated intensities of the GR1 and ND1 ZPLs.<sup>(13)</sup>

At high nitrogen concentrations ( $\sim 75$  ppm), in the  $\{111\}$  growth sector of the same diamond, the spectrum in the visible region is markedly different (Fig. 2). The GR1 line is now undetectable, although there is a broad unidentified band in a similar spectral region to that of the GR1 band. Two lines at 523.6 nm (2.367 eV) and 489.0 nm (2.535 eV) are present, which were not detectable in the low-nitrogen sector, and the steeply rising absorption makes it impossible to carry out measurements at wavelengths below approximately 450 nm.

At intermediate nitrogen concentrations, and with the vacancy concentration  $[V] > [N^0]$ , it is possible to see a weak GR1 ZPL. However, the line is 3 times broader than in Fig. 1. (Quantities inside square brackets are concentrations.)

Spectra in the defect-induced one-phonon region are shown in Fig. 3. Nitrogen in the positive charge state ( $N^+$ ) produces a characteristic absorption band with a sharp spike at  $1332\text{ cm}^{-1}$ .<sup>(11)</sup> Provided nickel is not used in the synthesis, the concentration of  $N^+$  in an irradiated type Ib diamond is equal to the concentration of negative vacancies. The concentration of the latter can therefore be inferred from the intensity of the absorption peak at  $1332\text{ cm}^{-1}$ .<sup>(11)</sup> As we have noted earlier, the concentration of  $N^0$  can be determined from the intensity of the peak at  $1344\text{ cm}^{-1}$ . In (a), there is no detectable  $N^0$ , and in (b), the concentrations of  $N^0$  and  $N^+$  are similar.

Defect concentrations for the  $\{115\}$  and  $\{111\}$  growth sectors are listed in Table 1, and an interesting conclusion that emerges from this analysis is that the vacancy production rate is 3 to 5 times higher in a type Ib diamond containing a few hundred ppm of  $N^0$  than in a nitrogen-free specimen.<sup>(14)</sup>

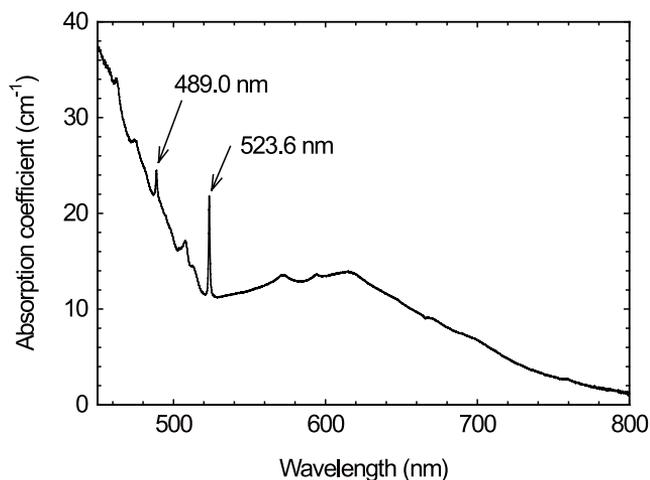


Fig. 2. Absorption spectrum from the  $\{111\}$  growth sector of an electron-irradiated HPHT synthetic diamond, containing approximately 75 ppm of single substitutional nitrogen.

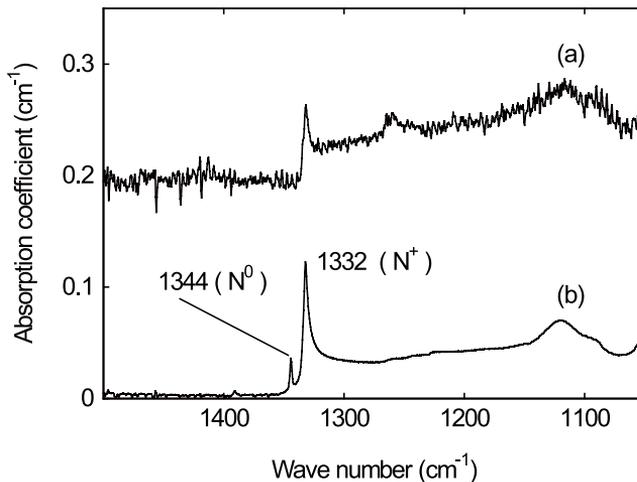


Fig. 3. Optical absorption spectra in the defect-induced one-phonon region, recorded with the diamond at room temperature, for two different growth sectors of an electron-irradiated HPHT synthetic diamond: spectrum (a) from {115}, multiplied by 10; spectrum (b) from {111}. The spectra have been adjusted vertically to avoid curves intersecting.

Table 1

Concentrations of neutral nitrogen ( $N^0$ ), positive nitrogen ( $N^+$ ), neutral vacancies ( $V^0$ ) and negative vacancies ( $V^-$ ) in two different growth sectors of an electron-irradiated type Ib synthetic diamond.

Growth sector	$N^0$ (ppm)	$N^+$ (ppm) (from 1332 $\text{cm}^{-1}$ peak)	$N^+$ (ppm) (from ND1 peak)	$V^0$ (ppm)	$V^-$ (ppm)	$V^0 + V^-$ (ppm)
{111}	$45 \pm 4$	$29 \pm 5.3$	—	0	$29 \pm 5.3$	$29 \pm 5$
{115}	0	$1.7 \pm 0.5$	$0.8 \pm 0.1$	$6.9 \pm 1.8$	$\sim 1.1$	$8 \pm 2$

For all other types of diamond, the absorption spectra in the visible region, following a 2 MeV electron irradiation, are similar to that shown in Fig. 1, subject to the minor variations described below. In all cases, the strength of the ND1 ( $V^-$ ) peak is weaker than that shown in Fig. 1.

## 2.2 Type Ia diamond

In type IaA diamonds, the nitrogen is present as nearest-neighbour substitutional pairs (A aggregates). The A aggregate is a very deep donor with an ionisation energy of  $\sim 4$  eV. However, there is relatively little evidence of charge compensation; most of the

vacancies produced by irradiation are in the neutral charge state. For a given irradiation,  $[V^0]$  increases by approximately 50% and  $[I^0]$  increases by approximately 25%, as  $[N_A]$  increases from zero to 1200 ppm.<sup>(15)</sup>

In type IaB diamonds, the nitrogen is present as B aggregates (4 substitutional nitrogen atoms symmetrically surrounding a vacancy). Again, most of the vacancies are generated in the neutral charge state, but for a given irradiation, there is no increase in  $[V]$  with the concentration of nitrogen. By contrast, with type IaA diamonds, the intensity of the  $I^0$  peak decreases with increasing  $[N_B]$ .<sup>(15)</sup>

For both type IaA and type IaB diamond, the width of the GR1 ZPL increases by approximately a factor of 3 as the nitrogen concentration increases from zero to 1200 ppm.<sup>(15)</sup>

### 2.3 Type II diamond

Substitutional boron is the major impurity in type IIb diamond and forms an acceptor centre with an ionisation energy of 0.37 eV. Natural type IIb diamonds are extremely rare, and have boron concentrations of typically  $< 0.5$  ppm. Because single nitrogen and the A-aggregate of nitrogen are electrical donors, it is only those diamonds with  $[N] < [B]$  that have the characteristic type IIb (semiconducting) properties, and this explains why natural specimens are so rare. It is relatively straightforward to produce type IIb diamond by HPHT synthesis, by removing the nitrogen and doping with boron, and much higher concentrations of boron (1000 ppm, or more) can be obtained.<sup>(9)</sup> As with nitrogen, the distribution of B in HPHT type IIb diamond is very inhomogeneous;  $[B]$  is highest in the  $\{111\}$  sectors and lowest in the  $\{100\}$  and  $\{113\}$  sectors.<sup>(9)</sup>

When type IIb diamond is subjected to irradiation damage, the boron acceptors are charge-compensated by the radiation-induced defects, and the characteristic absorption produced by boron is progressively reduced with increasing amounts of irradiation. It is only when the acceptors have been fully compensated that there is a significant growth in the intensity of the GR1 absorption.<sup>(16,17)</sup> This behaviour implies that vacancies are being produced in the positive charge state. Figure 4 shows that there are absorption lines in the near-infrared spectrum of electron-irradiated type IIb diamond that are not observed in other types of diamond. It has been proposed that the line at  $11023\text{ cm}^{-1}$  (1.367 eV) is a transition at the positive vacancy,<sup>(18)</sup> but confirmation is still being awaited. Charles *et al.* have suggested that the ZPLs observed in photoluminescence at 636 and 666 nm, from electron-irradiated boron-doped synthetic diamond, are transitions at  $V^+$ ,<sup>(19)</sup> but again this conclusion needs to be confirmed by further investigations. It is worthy of note that no  $I^0$  absorption is detected before the acceptors are fully compensated, suggesting that either the self-interstitial can also act as a donor (and so exist in a positively charged state), or that  $I^0$  is not stable in the absence of  $V^0$  or  $V^-$ .

Type IIa diamonds are those specimens for which no absorption due to boron or nitrogen can be detected by conventional infrared spectroscopy. Again, such specimens are rare in nature; furthermore, many natural type IIa diamonds have a “mosaic” structure and are heavily dislocated. Thus, although a natural type IIa diamond contains a negligible concentration of impurities, the width of the GR1 ZPL can be comparable to that in a high-nitrogen type Ia specimen.<sup>(15)</sup>

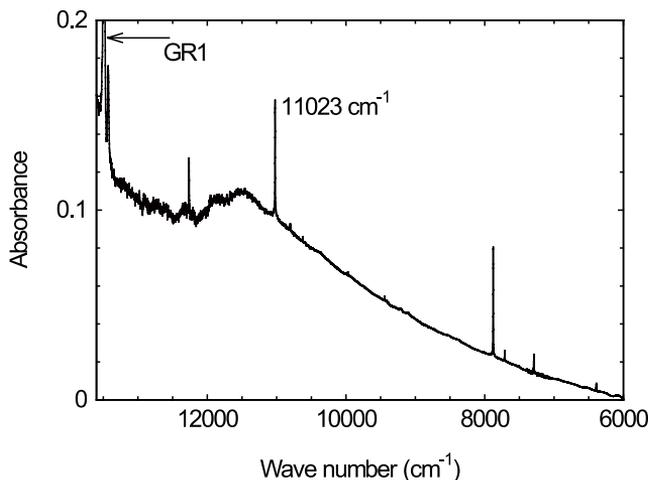


Fig. 4. Near-infrared absorption spectrum of an electron-irradiated natural type IIb diamond. The line at  $11023\text{ cm}^{-1}$  has been attributed to the positive vacancy.<sup>(14)</sup>

Type IIa diamond with excellent crystal perfection can be grown by HPHT synthesis by removing nitrogen (using nitrogen “getters” in the growth capsule) and also by the homoepitaxial growth of CVD diamond. The sharpest GR1 ZPLs are produced by radiation damage in this type of material. Because boron is a very common element, albeit at low concentrations, nominally type IIa HPHT diamonds may sometimes have regions with a type IIb character, due to the presence of sub-ppm levels of B.<sup>(9)</sup>

### 3. Annealing of Radiation Damage

#### 3.1 *Interstitial-related centres*

When type Ia diamond is heated for typically 1 h at  $800^\circ\text{C}$ , the GR1 absorption is mostly destroyed, and new absorption bands appear, associated with vacancies trapped at the various forms of nitrogen.<sup>(20)</sup> These changes do not occur at a significant level until temperatures above  $600^\circ\text{C}$  are used, and it is therefore assumed that substantial changes that occur at temperatures below  $600^\circ\text{C}$  are associated with the migration of interstitials. The precise temperature at which a particular change occurs depends on the nitrogen concentration and the crystal perfection, as well as, of course, the heating time. In a high-nitrogen diamond, the GR1 line is completely destroyed after heating at  $800^\circ\text{C}$  for 1 h, whereas in a low-nitrogen single-crystal CVD specimen, heating above  $900^\circ\text{C}$  is required.

In Fig. 1, the absorption is seen to be rising rapidly as the ultraviolet spectral region is approached. This band is referred to as the “ultraviolet continuum.” In type II diamonds, it is possible to detect absorption features superimposed on this continuum, namely, a complex series of closely spaced lines centred at  $311\text{ nm}$  ( $3.99\text{ eV}$ ) known as R11,<sup>(2)</sup> and the ZPL at  $270.5\text{ nm}$  ( $4.582\text{ eV}$ ) of the 5RL system, together with sharp local

vibrational modes at 261.0 (4.749 eV) and 259.1 nm (4.784 eV).<sup>(21)</sup> In principle, these ultraviolet features may be visible in an electron-irradiated purely type IaB diamond, but in type IaA and type Ib diamonds, the absorption produced by the nitrogen precludes their observation.

The annealing of the R11 centre will be discussed below. The 5RL system is present immediately after irradiation, reaches a maximum at an annealing temperature of approximately 500°C, and then decreases almost to zero at 800°C.<sup>(21)</sup> There is some indication that the 3H centre, which has a ZPL at 503.6 nm, and is clearly visible in Fig. 1, and the 5RL centre are different charge states of a defect having the structure I-C-I, where I represents a self-interstitial and C represents a carbon atom on its normal lattice site.<sup>(22)</sup>

The final centre to be discussed here, which is believed to involve interstitials,<sup>(23)</sup> produces a ZPL at 594 nm in nitrogen-containing diamonds. During isochronal annealing measurements, it first becomes apparent at approximately 275°C, and reaches a maximum at approximately 800°C. The behaviour of this centre will be discussed again in the section on annealing at temperatures above 900°C.

### 3.2 Annealing at temperatures below 500°C

#### 3.2.1 Type Ib diamond

At low annealing temperatures, the behaviour of type Ib diamond is different from that of the other diamond types.<sup>(14)</sup> For isochronal annealing between 175 and 275°C, the 523.6 nm (2.367 eV) line (Fig. 2) disappears and the 489.0 nm (2.535 eV) line increases in strength. The 489.0 nm line itself is annealed out between 275 and 400°C, and at the same time, the 666.6 nm (1.859 eV) line associated with I<sup>0</sup> increases. In addition, there is a progressive loss of N<sup>+</sup> absorption (Fig. 3) for annealing temperatures between 275 and 400°C, equivalent to a reduction in the concentration of V<sup>-</sup> by approximately 30%. These phenomena have been interpreted in two different ways. Originally, it was proposed that the 2.367 and 2.535 eV centres were different configurations of a defect involving a nitrogen atom and one or more self-interstitials.<sup>(14)</sup> More recently, the centres have been attributed to different configurations of a self-interstitial and a negative vacancy.<sup>(24)</sup>

Annealing out of the 666.6 nm line occurs between 400 and 450°C, and is observed in all diamond types over a similar temperature range (see below).

#### 3.2.2 Type II and type IaA diamonds

On annealing, typically at 400°C, it becomes clear that there is a broad band, with a maximum near 620 nm (2 eV),<sup>(15,22)</sup> underlying the GR1 vibronic band shown in Fig. 1. Following annealing, the total absorption at 620 nm decreases by approximately 40% and the intensity of the GR1 ZPL decreases by approximately 20%. Furthermore, the 666.6 nm peak, due to I<sup>0</sup>, disappears. During the annealing, there is a correlated reduction in the intensities of the features associated with I<sup>0</sup> and the R11 centre.<sup>(25)</sup> These effects are attributed to the recombination of the self-interstitial with vacancies; the vacancies most likely to anneal are those “strained” by the presence of nearby interstitials. It is the strained vacancies which produce the broad-band absorption underlying the GR1 band. The width of the GR1 line is also reduced following such an annealing.<sup>(15)</sup>

### 3.2.3 Type IaB diamonds

The behaviour of type IaB diamonds is slightly different for annealing at 400°C. There is a reduction in the absorption at 620 nm by typically 25%, and complete disappearance of the  $I^0$  peak, but there are no detectable changes in the intensity or the width of the GR1 ZPL.<sup>(15)</sup>

### 3.3 Annealing at temperatures up to 900°C

The major change observed in all diamond types for annealing at temperatures up to 900°C is the disappearance of the vacancy-related absorption, and the appearance in nitrogen-containing diamonds of the vacancy-nitrogen complexes.<sup>(20)</sup> A vacancy trapped at single nitrogen atom produces N-V centres. The N-V centres can exist in the negative charge state, giving rise to the optical centre with a ZPL at 637.2 nm (1.945 eV), or in the neutral charge state (N-V)<sup>0</sup>, giving rise to the optical centre with a ZPL at 575.0 nm (2.156 eV).<sup>(26)</sup> As with the vacancy in type Ib diamond (section 2.1), the charge state of the N-V centre will depend on its proximity to a single nitrogen atom.<sup>(12)</sup> This, in turn, depends on the nitrogen concentration. For high concentrations of nitrogen (> 100 ppm), most of the N-V centres are in the negative charge state, whereas in a diamond containing  $9 \pm 1$  ppm of nitrogen, and irradiated to produce approximately 6 ppm of vacancies, Lawson *et al.* found that, after annealing, 40% of the N-V centres were in the neutral charge state.<sup>(11)</sup> Figure 5 shows the spectrum for a diamond in which absorption peaks due to both the (N-V)<sup>0</sup> and (N-V)<sup>-</sup> transitions are visible, together with the 594 nm peak discussed above.

For type Ia diamonds, a vacancy trapped at the A or B aggregate produces an H3 or H4 centre, respectively, which gives rise to absorption with a ZPL at 503.2 nm (2.463 eV) or 496.0 nm (2.499 eV).<sup>(20)</sup> The H3 centre has the (N-V-N)<sup>0</sup> structure, and it is

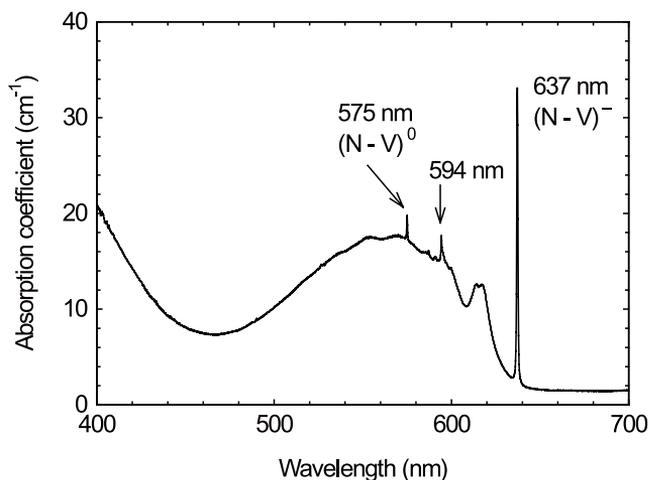


Fig. 5. Absorption spectrum of an electron-irradiated HPHT synthetic diamond after annealing at 800°C.

assumed that the H4 centre is also in the neutral charge state. Typical spectra are shown in Fig. 6, and in addition to the major absorption bands, the line at 594 nm is clearly visible in each spectrum.

### 3.4 Annealing at temperatures up to 1500°C

#### 3.4.1 Type Ia diamond

Annealing type Ia diamonds at temperatures around 1100°C destroys the 594 nm absorption and creates two lines known as H1b at 2024 nm (0.612 eV) and H1c at 1934 nm (0.641 eV). The available evidence suggests<sup>(23)</sup> that the centres giving rise to these absorption lines are formed when some, or all, of the defects that compose the 594 nm centre are trapped at the A aggregate (to form H1b) or the B aggregate (to form H1c).

Figure 7 illustrates how the relative intensities of three related optical centres change<sup>(23)</sup> in a type IaA diamond for annealing temperatures up to 1450°C. The intensity of the 594 nm line progressively decreases between 800 and 1100°C; as the 594 nm line disappears, H1b grows in intensity. The H1b line itself begins to decrease in intensity at approximately 1250°C, disappearing completely by 1500°C. As the H1b line disappears, absorption in the H2 band increases. H2 is the negative charge state (N-V-N)<sup>-</sup> of H3.<sup>(27)</sup> Annealing irradiated type IaA diamonds at temperatures above 1500°C reduces the intensities of the H3 and H2 absorption systems. Figure 8 shows the absorption spectrum of such a type of diamond after annealing at 1600°C.

The 594 nm and H1c lines in type IaB diamond are affected by annealing in a similar way to the 594 nm and H1b lines in type IaA diamond, but no H2 absorption is produced.<sup>(23)</sup>

Other absorption lines, H1d, H1e, H1f and H1g, are produced in the infrared region by various annealing procedures,<sup>(28)</sup> but the nature of these defects is not known.

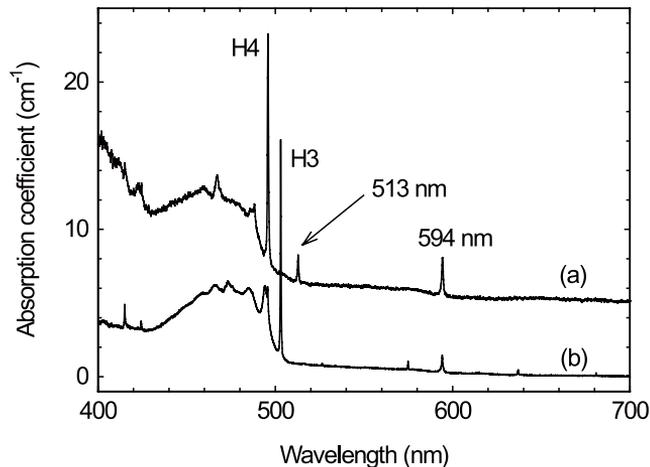


Fig. 6. Absorption spectra of (a) a type IaB natural diamond and (b) a type IaA natural diamond, after electron irradiation and annealing at 800°C. The line at 513 nm is a transition at the H4 centre.

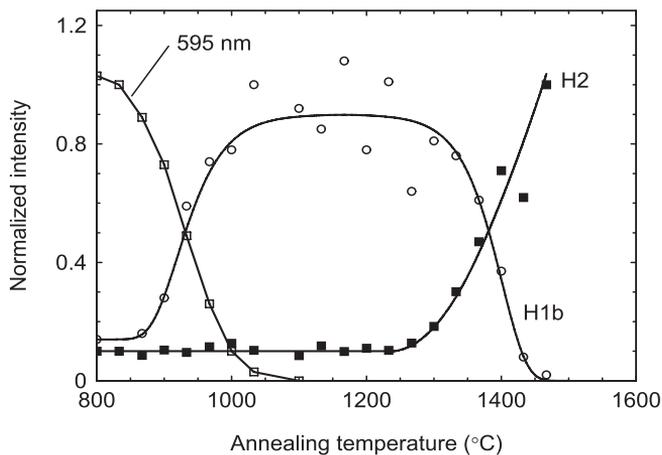


Fig. 7. Relative intensities of the 594 nm, H1b, and H2 ZPLs in a type IaA diamond as a function of the annealing temperature. The maximum for each plot has been set to unity. The H1b center is photochromic, and this partly accounts for the scatter in the data.

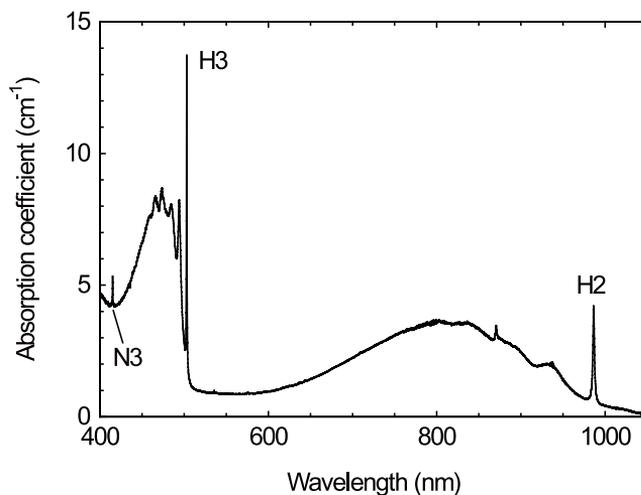


Fig. 8. Absorption spectrum of an irradiated type IaA diamond after annealing at 1600°C.

### 3.4.2 Type Ib diamond

When irradiated type Ib diamond is annealed at temperatures up to 1500°C, a large fraction of the single nitrogen is converted to A aggregates by the vacancy-enhanced aggregation mechanism.<sup>(23,29)</sup> This mechanism produces N-V-N centres, some of which are in the negative charge state because of their proximity to single nitrogen atoms that

have not formed aggregates. The intensity of the (N-V)<sup>-</sup> absorption that was present after annealing at 800°C is consequently greatly reduced, and some H3 and H2 absorption lines are produced, as illustrated in Fig. 9. (The production of H3 and H2 can first be detected after annealing at 1350°C; data in Fig. 9 are for an irradiated high-nitrogen type Ib diamond after annealing at 1600°C.)

### 3.5 Annealing at temperatures over 1500°C

Annealing studies at temperatures above 1500°C become progressively more difficult at ambient pressure in an inert gas, or in a vacuum, because of severe surface graphitisation. The practical limit is around 1750°C for 1 h.<sup>(23)</sup> However, much higher temperatures can be used if the diamonds are subjected to high pressure (> 5 GPa) to maintain conditions in the region where diamond is the stable phase of carbon.<sup>(23)</sup>

#### 3.5.1 Type IaB diamonds

The most dramatic changes in the temperature range from 1500 to 1750°C are obtained with type IaB diamonds. Figure 10 shows a comparison of the absorption spectra of a type IaB diamond after annealing at 800°C and after 1650°C.<sup>(23)</sup> After the high-temperature annealing, the H4 absorption has been destroyed, and some weak H3 absorption has been produced where none existed before. In addition, two strong absorption lines at 536.0 nm (2.313 eV) and 576.0 nm (2.152 eV) have been produced. Occasionally, these latter lines are seen together in the absorption spectra of natural brown diamonds, particularly those that exhibit pink luminescence when excited with long-wave ultraviolet radiation at approximately 365 nm.<sup>(30)</sup>

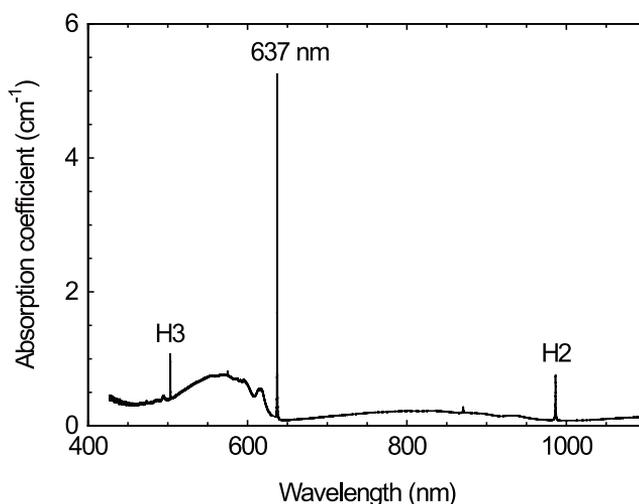


Fig. 9. Absorption spectrum of an electron-irradiated type Ib synthetic diamond after annealing at 1600°C.

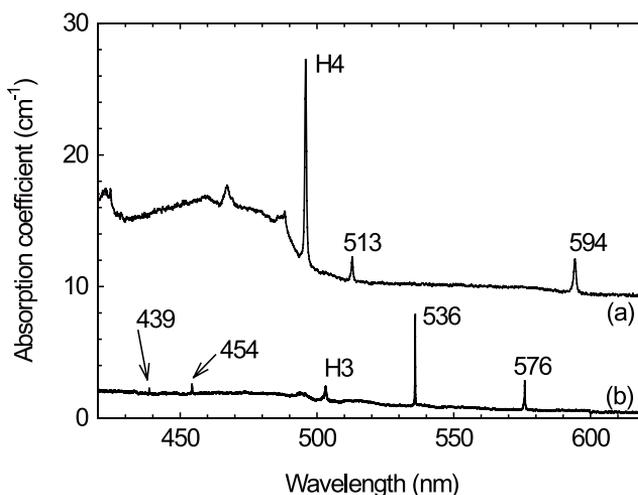


Fig. 10. Absorption spectra of an electron-irradiated type IaB diamond after annealing at (a) 900°C and (b) 1650°C. Spectra have been displaced vertically for the sake of clarity.

Figure 11 illustrates the growth and decay of the major absorption systems in type IaB diamond as a function of the annealing temperature. The behaviour of H1c is similar to that of H1b in type IaA diamond, reaching a maximum as the 594 nm absorption is annealed out (not shown in Fig. 11), and then H1c itself disappears at 1600°C. The H4 absorption is approximately constant until 1300°C, is dramatically reduced in intensity after annealing at 1600°C and is destroyed after annealing at 1650°C. The intensities of the H3, 536 nm and 576 nm lines increase until H4 is destroyed, and then decrease for higher annealing temperatures. (Note: in the original version of this figure in ref. 23, the H4 intensity was approximately 75 units at 1500°C. However, this is assumed to be an error resulting from inhomogeneity in the diamond; earlier work<sup>(31)</sup> showed a complementary reduction in the H4 intensity as the H3 intensity increased. The datum point for H4 at 1500°C has therefore been moved to 50 units in Fig. 11 to reflect the previous investigation.)

### 3.5.2 Type IaA and type Ib diamonds

After annealing at 1750°C, the H3 and H2 absorptions in a type IaA diamond decrease to approximately 15% of the maximum value reached at lower annealing temperatures.<sup>(23)</sup>

In type Ib diamond, the intensity of the 637 (N-V)<sup>-</sup> line is greatly reduced after annealing at 1650°C, and the dominant absorption resulting from radiation damage is due to H2. This becomes progressively much weaker after annealing at 1750°C.<sup>(23)</sup>

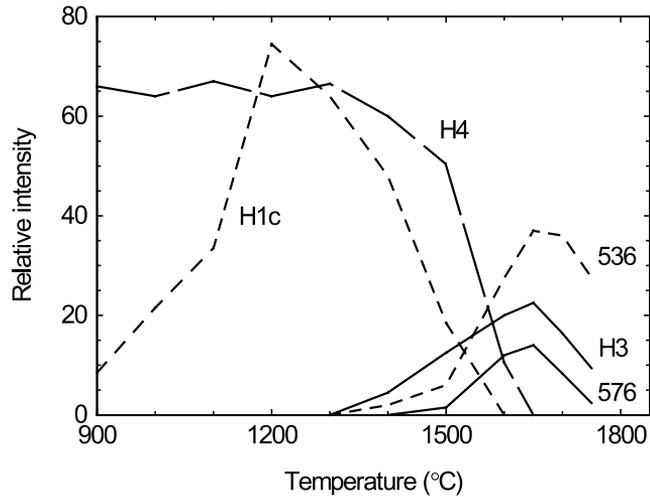


Fig. 11. Relative intensities of the H4, H1c, H3, 536 nm and 576 nm ZPLs in an electron-irradiated type IaB diamond as a function of the annealing temperature. To aid comparison, data for the H3, 536 nm and 576 nm lines have been plotted on a different vertical scale from the data for H4.

### 3.6 Annealing at high pressure and high temperature (HPHT)

Natural brown diamonds can have their colour enhanced by HPHT annealing.<sup>(32)</sup> In a typical annealing, the capsule containing the diamonds is subjected to a pressure of > 5 GPa; the temperature is increased to 2300°C over a period of 140 s and the heating power is then shut off.

When irradiated type Ib, type IaA and type IaB diamonds are subjected to this same annealing schedule, the H3, H2 and 637 nm absorption lines are either extremely weak or undetectable.<sup>(23)</sup> Further work is necessary to determine whether the absorption lines at 536 and 576 nm (Fig. 10) survive after such an annealing.

## 4. Summary

The major optical centres produced by electron irradiation and annealing of diamond have been described. The discussion has been restricted to those centres that are easily detected by optical absorption. Many more absorption features can be detected using very sensitive spectrometers and/or using heavier irradiations than those employed in the work described here. Far larger numbers of ZPLs can be detected by photoluminescence and cathodoluminescence spectroscopies (most of those known in 2001 are documented in ref. 33). A reasonable understanding exists for the major optical centres; brief details have been given here, and further information can be found in the original sources.

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