Electron irradiation and the formation of vacancy–interstitial pairs in diamond

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Abstract
A large number (>60) of nitrogen-containing type Ia natural diamonds, and nitrogen-free type IIa natural and synthetic diamonds, have been electron irradiated and their optical absorption spectra have been analysed in detail. The analysis reveals that the concentrations of vacancies [V] and interstitials [I^0] in type IaA diamonds increase linearly with the concentration [N_A] of the A-form of nitrogen. This increase of [V] and [I^0] with [N_A] is attributed to the trapping of vacancies and interstitials in the strain field of nitrogen. The trapping produces 'strained' vacancies and partly immobilizes interstitials, thus reducing the vacancy–interstitial recombination during electron irradiation, thereby increasing [V] and [I^0]. Those strained vacancies and interstitials recombine upon annealing at temperatures $\sim$390–420 °C. In type IaB diamonds no correlation has been found between [V] and the concentration [N_B] of the B-form of nitrogen; furthermore [I^0] was found to *decrease* linearly with [N_B]. In both type IaA and type IaB diamonds the width of the GR1 zero-phonon line, associated with the neutral vacancies [V^0], increases with nitrogen concentration. A new, more appropriate and accurate formula to calculate [V^0] is proposed based on measuring the height H of the GR1 absorption band at 2.0 eV.

1. Introduction

This paper complements and greatly expands a previous study (Davies *et al* 1992) of vacancies and nitrogen-vacancy-related centres in electron-irradiated nitrogen-free (type IIa), and nitrogen-containing (type Ia), natural diamonds. Here, instead of annealing at 600–800 °C, as done in Davies *et al* (1992), we have isothermally annealed the irradiated specimens at 390–420 °C and studied the changes in the concentrations, [V] and [I^0], of vacancies and interstitials, respectively. Additional information can be obtained in this way because, at these lower temperatures, only the interstitials are mobile and not the vacancies. This allows us to

study the role of the interstitials in the first stage of the annihilation of the vacancies, in all the types of diamond, avoiding the formation of N-vacancy centres.

Type Ia diamonds may be divided into two types: type IaA diamonds contain A-centres (two adjacent substitutional nitrogen atoms, N_s–N_s) and type IaB diamonds contain B-centres (four substitutional nitrogen atoms surrounding a vacancy, $4N_s + V$). Diamonds having the extreme type IaA or type IaB properties are relatively rare; the majority of natural type Ia diamonds are type IaA/B, which contains both A-and B-centres.

The carbon atoms, ejected when the B-centres are formed, aggregate to form small precipitates called platelets. These platelets produce an infrared (IR) absorption peak near 1365 cm^{-1}; in diamonds that are described as *regular* (Woods 1986) the intensity of this peak is proportional to the concentration of B-nitrogen. A minor fraction of type IaA/B diamonds has a platelet peak which is less intense than that expected from the general trend described above, and these specimens are described as *irregular* (Woods 1986). In some irregular type IaA/B diamonds the platelet peak is undetectably weak.

The vacancy-related centres studied by Davies *et al* (1992) were: GR1 (zero-phonon line ZPL at 1.673 eV, due to neutral vacancies V^0), ND1 (ZPL at 3.150 eV, due to negatively charged vacancies V^-), H3 (ZPL at 2.463 eV, vacancy trapped at an A-centre) and H4 (ZPL at 2.499 eV, vacancy trapped at a B-centre). Their results were based on monitoring the changes, induced by isothermal annealing at 600–800 °C, in the optical absorption features associated with these centres. They established that: (1) the annealing occurs in two stages, an initial fast process followed by a slower one—the fast process in type IIa diamonds was attributed to vacancies 'possibly' being recombined with moving interstitials, and in the type Ia diamonds by the capture, by the nitrogen-related centres, of vacancies located in the immediate proximity of these centres; (2) the annealing of vacancies at these temperatures in type IIa diamonds follows both first-and second-order kinetics. Davies *et al* attributed the first-order kinetics to the capture of vacancies by dislocations and the second-order kinetics to the formation of di-vacancies. They observed the fast and slow processes in type IaA diamonds as well. All their results were based on the fact that the vacancies are mobile at the annealing temperatures.

For two diamonds irradiated under the same conditions, Davies *et al* (1992) found that the concentration of vacancies in a type IaA diamond was 40% higher than in a type IIa diamond. In order to check the validity of this result, we have investigated the dependence of [V] and [I^0] on the concentration of nitrogen [N] in a large number of samples, well characterized with respect to their type, with a wide range of [N].

2. Experimental details

Various types of diamonds were examined. The numbers of samples and their types are shown in table 1. Here HPHT and CVD refer to high-pressure high-temperature growth and chemical vapour deposition, respectively. Note that the CVD samples used in this study were the highest-quality single crystals with an extremely low concentration of impurities (Isberg *et al* 2002).

The N content of all the N-containing samples was determined by measuring the IR absorption spectra at room temperature, using a Nicolet Avatar 360 Fourier-transform spectrometer with a beam condenser, and decomposing the absorption in the one-phonon region into the various components, using the proper conversion factors (Boyd *et al* 1994, 1995). We will denote the concentrations of the A and B forms of nitrogen by [N_A] and [N_B], respectively, throughout this paper. Absorption in the visible spectral region was measured at 77 K using a PerkinElmer Lambda 800 double-beam grating spectrometer. To reduce the effects of possible inhomogeneity in nitrogen concentration, we chose samples where the optical window is less

Table 1. Details of the specimens studied in this work.

Number of samples	Type	Origin
18	IaA/B	Natural
21	IaA[a]	Natural
23	IaB regular[a]	Natural
7	IaB irregular[b]	Natural
1	Type IIa	Natural
5	Type IIa	HPHT
2	Type IIa	CVD

[a] A small number of the pure type IaA and type IaB samples contained, respectively, a small fraction (<4% of total N) of B-or A-centres.
[b] The IR spectra of these diamonds do not show the platelet peak (Woods 1986).

than 1 mm^2 and thickness is typically $\leqslant$1 mm. Nevertheless, we topographically measured the N content of some of the samples and the results showed that most are fairly homogeneous to within $\pm$5%. Initially, the concentrations of vacancies [V^0], [V$^-$] and interstitials [I^0] were calculated from the measured areas A, expressed in meV cm^{-1}, of the GR1 ZPL, the ND1 ZPL and of the 1.859 eV peak, respectively, using the appropriate conversion factors: for neutral vacancies $A = (6 \pm 1) \times 10^{-17}$ [V^0] (Iakoubovskii *et al* 2003), for negative vacancies $A = (4.8 \pm 0.2) \times 10^{-16}$ [V$^-$] (Davies 1999) and for interstitials $A = (1.1 \pm 0.2) \times 10^{-17}$ [I^0] (Hunt *et al* 2000). However, as discussed in section 4, the method for calculating the [V^0] needs to be revised.

Electron irradiation was performed using three different Van de Graaff type accelerators providing electron beams of energies 1.5, 2 and 3 MeV. Samples were mounted in indium metal on a heavy copper block cooled by streaming water at $\sim$10 °C. This mounting minimized the sample heating by the beam. Apart from the natural type IIa and the irregular type IaB diamonds, all the samples in table 1 were irradiated by 3 MeV electrons to a dose of 2×10^{18} e cm^{-2}. The natural type IIa and type IIb samples were irradiated with 2 MeV electrons to a dose of $\sim 1 \times 10^{18}$ e cm^{-2}. The irregular type IaB diamonds were irradiated with 1.5 MeV electrons to a dose of 2.2×10^{17} e cm^{-2}.

3. Results

3.1. Relationship of the presence of N and the characteristic absorption due to vacancies

3.1.1. Neutral vacancies V^0. We observed visually what seems to be an increase in [V^0] with [N$_A$]. The GR1 absorption side band has a maximum near 2 eV; therefore electron-irradiated type Ia diamonds have a green–blue colour. Figure 1 shows a micrograph of a heavily irradiated (10^{19} e cm^{-2}) type IaA diamond. Although the electron beam was uniform over the sample surface, the irradiation-induced colouration is not homogeneous; most of the sample is dark greenish-blue, but it contains a window of light colouration (smaller [V^0]). Topographic IR absorption spectra showed that the [N$_A$] of the lightly coloured volume of this sample is much lower (380 ppm) than that in the dark region (780 ppm).

From studying a large number of type Ia diamonds (table 1) we found a poor correlation between the nitrogen concentration and the integrated intensity (area) of the GR1 ZPL; the correlation coefficient (CC) is only 0.29. However, a better correlation (CC = 0.7) exists for [N$_A$] $\leqslant$ 620 ppm. The area of the ZPL was measured after subtracting a third-order polynomial baseline, and is widely assumed to be proportional to [V^0]. Figure 2(a) shows the results of 18 type IaA specimens, and for [N$_A$] $\geqslant$ 650 ppm the area of the ZPL varies erratically with [N$_A$]. However, for the same specimens, there is a good linear correlation (CC = 0.89) between the
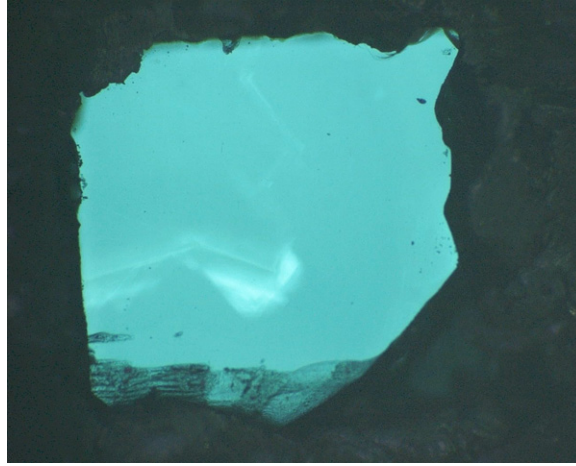
Figure 1. A micrograph of an electron-irradiated type IaA specimen. The lightly coloured region has a smaller concentration of vacancies and nitrogen. Sample dimensions are $\sim$1 $\times$ 1 $\times$ 0.5 mm^3.

(This figure is in colour only in the electronic version)
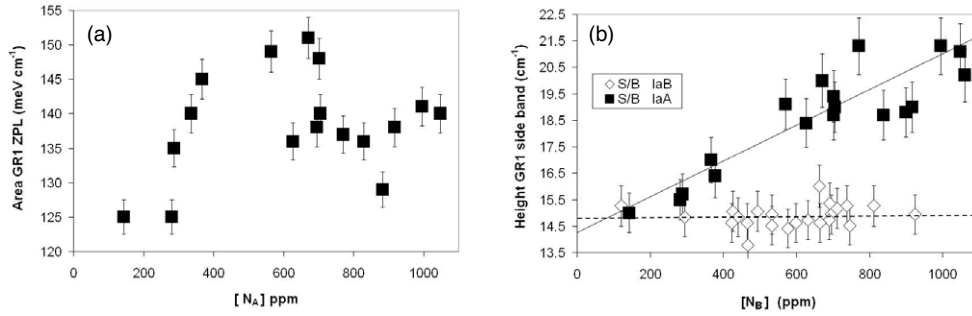
Figure 2. (a) The relationship between the area of the GR1 ZPL and [N_A] in the type IaA diamonds. (b) The relationship between the height of the GR1 vibronic side band at 2 eV and [N_A] in the type IaA diamonds (CC = 0.89), and the lack of correlation with [N_B] in type IaB diamonds.

height of the GR1 absorption side band at 2 eV and [N_A], as shown in figure 2(b). In the light of this observation, which will be discussed in more detail in section 4, we assume that the absorption at 2 eV gives a better measure of the [V^0] than does the area of the GR1 ZPL. This leads to the following relationship:

$$H = (6 \pm 1) \times 10^{-18} [V^0] \tag{1}$$

where H is the height of the GR1 vibronic side band at 2 eV in cm^{-1}, and [V^0] is the concentration of neutral vacancies in cm^{-3}. This formula has been used to calculate [V^0] throughout this paper.

To determine the height of the vibronic side band, two types of base line were subtracted: either (1) a straight line joining the two extremes (at $\sim$2.4 and $\sim$1.55 eV) of the band; or (2) a second-order polynomial, coinciding with the spectral shape on both sides of the band, using six points on the high-energy side between 2.69 and 2.48 eV, and six points on the low-energy side between 1.54 and 1.4 eV. The second procedure gave an average increase of 6% in the height and a marginally better correlation with [N_A] (CC = 0.89 instead of 0.85). These differences
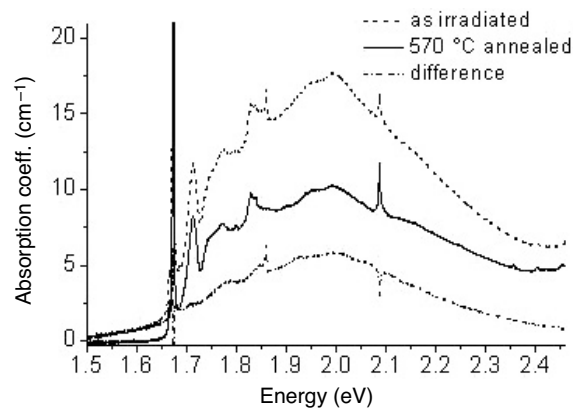
Figure 3. From top to bottom: the spectra of a type IaA specimen before and after annealing at 570 °C for 1 h and the difference spectrum revealing the S-band and some other, minor sharp peaks.

are within the experimental accuracy of this quantity. Nevertheless, all the data presented in this paper have been obtained by subtracting polynomial baselines.

To eliminate the possibility that the lack of correlation observed in figure 2(a) might be due to inhomogeneity in the $[N_A]$, we topographically measured the IR absorption of all the type IaA samples, using a 0.15×0.15 mm^2 aperture. We then compared the average IR absorption of the topographic measurements of each sample with the original value obtained by measuring the whole sample and excluded the three samples where the differences were above 10%. This has no significant effect on the results.

By contrast, no correlation was found between the height of the side band and $[N_B]$ for the 23 type IaB diamonds examined (figure 2(b)). Note that, as one would naturally expect, the $[V^0]$ values are similar in type IaA and type IaB diamonds at small nitrogen concentrations. From a study of the type IaA/B diamonds, a two-step correlation procedure showed a dependence of the absorption at 2 eV, hence $[V^0]$, on $[N_A]$ but not on $[N_B]$. This is consistent with the results obtained on the 'pure' type IaA and type IaB diamonds.

3.1.2. The S absorption band. Figure 3 shows the spectra of a type IaA specimen before and after annealing at 570 °C for 1 h. Subtraction of these two spectra reveals the existence, in the unannealed diamonds, of a featureless broad band with a maximum at 2 eV. We will refer to this band as the S-band and to the total absorption at 2 eV associated with the GR1 centre as the GR1 vibronic side band.

The existence of a featureless unidentified broad band at 2 eV has been reported previously (O'Donnell and Davies 1981, Collins 1981). The annealing of this band and its relation to vacancies and interstitials will be addressed in section 3.4; preliminary results have been presented earlier (Iakoubovskii *et al* 2003). This band may be attributed to vacancies located in the strain fields of nearby interstitials, of impurities such as the different nitrogen centres, and structural defects such as dislocations. This assumption will be substantiated further in this paper.

3.1.3. The width of the GR1 ZPL. The width Γ_{GR1} of the GR1 ZPL, as a function of nitrogen concentration, increases linearly for type IaA and type IaB diamonds, as seen in figure 4. Figure 4 also shows that Γ_{GR1} of high-quality synthetic HPHT and CVD type IIa diamonds varies between 1.1 and 1.7 meV. For the one *natural* type IIa diamond studied, $\Gamma_{GR1} = 5.6$ meV
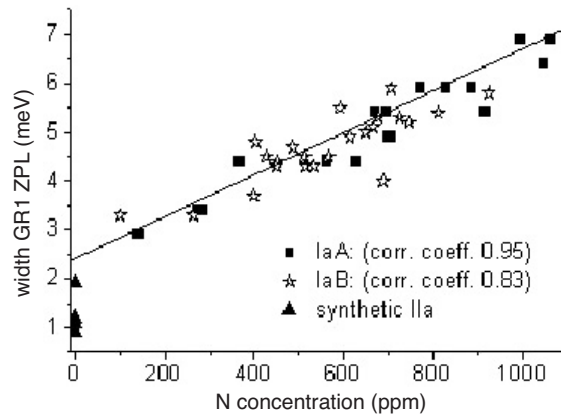
Figure 4. The relationship between the width (full width at half maximum, FWHM) of the GR1 ZPL and the N concentration: type IaA (squares), type IaB (stars) and type IIa (triangles).
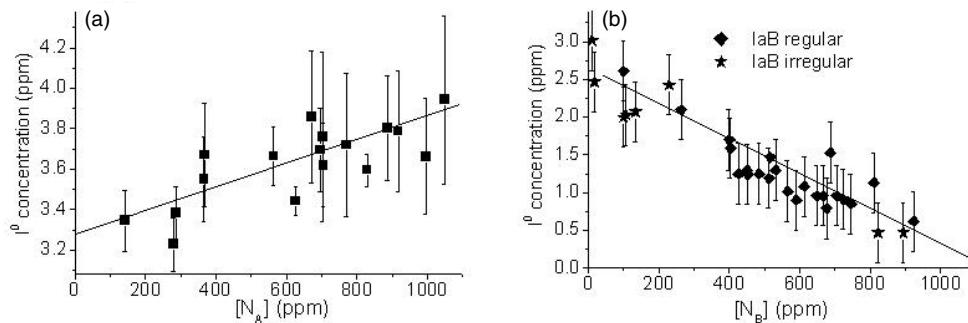
Figure 5. Relationship between the concentration of interstitials and the concentration of nitrogen in (a) type IaA and (b) type IaB diamonds. Stars represent irregular diamonds (free from platelets).

(not shown in figure 4). A cathodoluminescence topograph of the latter specimen shows a large concentration of dislocations, similar to a topograph described as a 'tatami' pattern (Henley *et al* 1977). We assume that the large concentration of dislocations contributes to the broadening of the ZPL.

The concentration of negative vacancies in the type IaA diamonds was found to vary between 1.6 and 2.5 ppm, which constitutes $\sim$17% of $[V^0]$. There is a moderately fair correlation (CC = 0.61) between $[V^-]$ and $[N_A]$. As with the neutral vacancies (figure 2), a better correlation (CC = 0.87) is obtained for $[N_A] \leqslant 650$ ppm. The concentration of negative vacancies also increases with increasing $[N_B]$ in type IaB diamonds.

3.2. Relationship of the presence of N and the characteristic absorption due to interstitials

3.2.1. Single carbon self-interstitial I^0. The self-interstitial is known to produce the electron paramagnetic resonance (EPR) system labelled as R2. This centre also produces characteristic optical absorption in the visible region of the spectrum with sharp lines at 1.859 and 1.685 eV (Walker 1977, Hunt *et al* 2000, Smith *et al* 2004). The area of the peak at 1.859 eV, associated with a local vibrational mode, gives a measure of $[I^0]$ (Hunt *et al* 2000). We find that this concentration *increases* linearly (CC $\sim$ 0.72) with $[N_A]$ in type IaA diamonds (figure 5(a)), and *decreases* linearly (CC = -0.86) with $[N_B]$ in type IaB diamonds (figure 5(b)).

Our initial measurements were carried out using regular type IaB diamonds, and we speculated that the negative gradient in figure 5(b) might be caused by platelets in these diamonds trapping some interstitials. Specimens with a higher $[N_B]$ have a higher platelet concentration which, it was considered, might trap more interstitials. However, subsequent results from the platelet-free irregular diamonds refuted this assumption (star shapes in figure 5(b)). It is to be noted that the values for the irregular diamonds shown in figure 5(b) are multiplied by a factor of six to fit on the same scale. This is because of the lower dose and lower energy of the electrons used to irradiate the irregular samples, compared with the dose and electron energy used for the regular specimens (see section 2).

In the case of type IaA/B regular diamonds, a regression model using the assumed relationship

$$[I^0] = [I^0(0)] + \alpha[N_A] + \beta[N_B]$$

gives $[I^0(0)] = 2.23 \pm 0.2$; $\alpha = (6 \pm 2) \times 10^{-4}$ and $\beta = (-3 \pm 1) \times 10^{-3}$.

Here $[I^0(0)]$ is the concentration of interstitials in samples with zero N content. The gradients of figures 5(a) and (b) are $(5.5 \pm 1.2) \times 10^{-4}$ and $-(2.3 \pm 0.2) \times 10^{-3}$, respectively, in good agreement with the values of α and β. There is a negligible probability of obtaining this result from random values. In both cases the gradients have been calculated using unweighted least squares fits.

3.2.2. The 3H centre. The 3H centre (ZPL 2.463 eV), observed in all types of diamond after electron irradiation, is believed to involve the self-interstitial, and the structure I^0–C–I^0 has been proposed (Twitchen *et al* 2001). Uniaxial stress measurements (Smith 2004) have confirmed that the symmetry is C_{2v}, as required by this proposal, but the atomic configuration could not be determined from these measurements. As in the case of the self-interstitial, a similar relationship was found between the integrated intensity of the 3H peak and the N concentration; in type IaA samples the intensity of the 3H ZPL increased linearly with $[N_A]$ (CC = 0.965) and in regular type IaB diamonds the intensity *decreased* linearly with $[N_B]$ (CC = -0.85). The areas of the 3H peaks in the type IaA diamonds are typically an order of magnitude higher than in the type IaB specimens.

### 3.3. Summary of the results presented so far

By examining a large number of samples, we have established the existence of correlations between $[V^0]$, $[V^-]$, $[I^0]$, [3H], Γ_{GR1} and $[N_A]$ in type IaA diamonds, and $[N_B]$ in type IaB diamonds. The results are summarized in table 2.

3.4. The effect of annealing on the concentrations of vacancies and interstitials

Two types of annealing experiments were conducted: isochronal annealing at various temperatures for a duration of 1 h each, and isothermal annealing at fixed temperatures of 390 °C for type Ia diamonds and 420 °C for type IIa diamonds, for periods of between 10 min and 25 h. The changes in $[V^0]$, $[V^-]$, $[I^0]$, and in the shapes of the ZPLs, were monitored.

3.4.1. Isochronal annealing. The following specimens were annealed: three type IaA, two type IaB, one type IIa HPHT and one type IIa CVD. In all cases, isochronal annealing shows that neutral vacancies anneal in two stages; there is an initial reduction in the strength of the GR1 absorption at 390–410 °C followed by sharp decrease beyond 700 °C. The part of the GR1
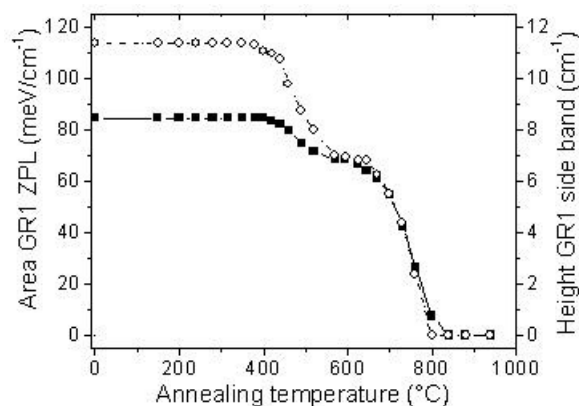
Figure 6. Isochronal annealing of an HPHT synthetic type IIa diamond. Circles show the height of the GR1 sideband, and squares show the area of the ZPL.

**Table 2.** Summary of the observed correlations.

Type	Correlated quantities	Linear correlation coefficient
IaA	$[V^0]^a$ versus $[N_A]$	0.9
	$[V^-]$ versus $[N_A]$	0.6^b
	Γ_{GR1} versus $[N_A]$	0.95
	$[I^0]$ versus $[N_A]$	0.72
	$[3H]$ versus $[N_A]$	0.97
IaB	$[V^0]^a$ versus $[N_B]$	No correlation
	$[V^-]$ versus $[N_B]$	0.66^b
	Γ_{GR1} versus $[N_B]$	0.83
	$[I^0]$ versus $[N_B]$	-0.86
	$[3H]$ versus $[N_B]$	-0.85

[a] $[V^0]$ is obtained using equation (1).
[b] Much better correlation exists for $[N] \leqslant 650$ ppm.

vibronic band that starts annealing at the first stage is the broad band labelled earlier as the S-band (figure 3). Figure 6 shows the annealing behaviour of a type IIa HPHT synthetic diamond. In this case, after the first annealing stage, the area of the GR1 ZPL is reduced by 20% and the intensity of the GR1 vibronic side band at 2 eV is reduced by 40%. Similar behaviour was observed for the other annealed samples, i.e. a higher reduction in the strength of the vibronic band compared with the reduction of the area of the ZPL. The results are summarized in table 3. Table 3 also includes the results of two type IaB samples annealed for 1 h at 570 °C.

3.4.2. Isothermal annealing.   Five type IaA and two type IaB diamonds were isothermally annealed at 390 °C. Annealing was found to cause a narrowing of the GR1 ZPL. The narrowing is mainly on the high-energy side, as shown for a type IaA diamond in figure 7(b). A more substantial narrowing was observed for the natural type IIa diamond after annealing at 570 °C for 1 h, as shown in figure 7(c). We propose that the vacancies which anneal first are located in a strain field, and we refer to these as 'strained vacancies'. To study this phenomenon more carefully, we decomposed the GR1 ZPL into its various components. Davies (1974) observed that the GR1 ZPL in type IaA diamonds can be decomposed into two components and what he termed a high-energy tail. We analysed the ZPL using 'PeakFit' spectral fitting routines. The
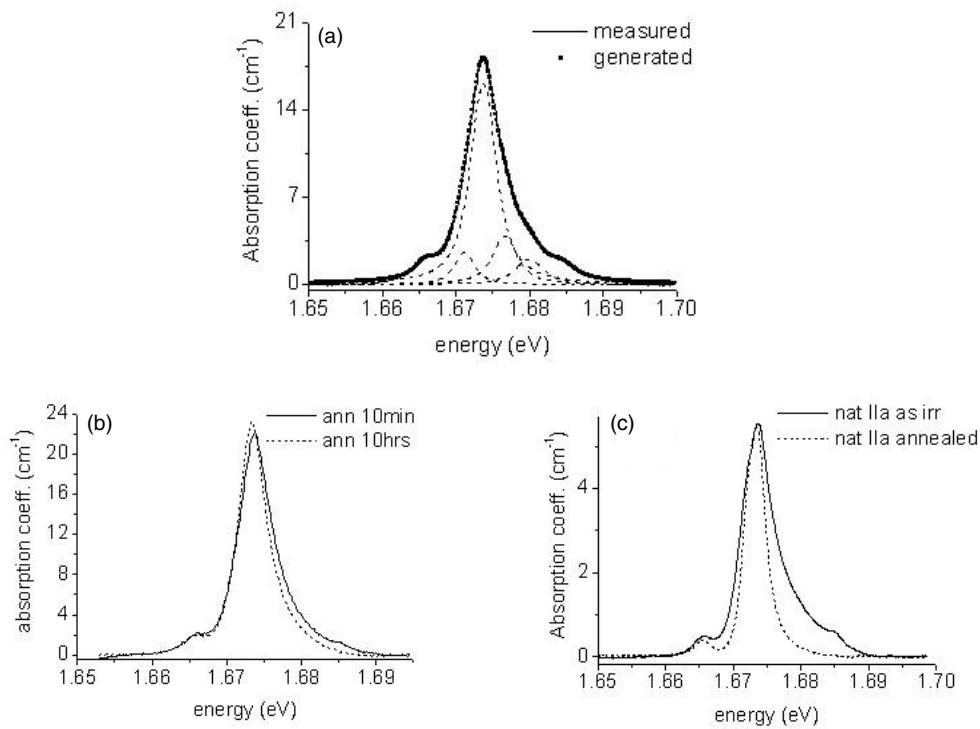
Figure 7. (a) The components of the GR1 ZPL main peak in a type IaA sample before annealing (1.671, 1.674, 1.677 and 1.680 eV). The low-energy peak of the GR1 doublet and the 1.685 eV interstitial peak are not shown. (b) The GR1 ZPL of a type IaA diamond before and after annealing, showing that the narrowing is on the high-energy side. (c) Narrowing of the GR1 ZPL of a natural type IIa diamond after annealing at 570 °C for 1 h.

Table 3. Summary of the isochronal annealing results. The uncertainties in all the measured quantities are approximately ±5%.

Specimen	Type	[N] (ppm)	Reduction (%)	
			Area GR1 ZPL	Abs. coeff. at 2 eV
CVD02	IIa	<0.1	12	29
HPHT-K	IIa	<0.1	20	40
Natural-A	IIa[a]	<0.1	41	63
vnA14	IaA	143	18	40
vn23	IaA	264	10	24
vn25	IaA	1023	10	33
vnA4	IaA	1063	27	52
vnB23	IaB[a]	264	NDC[b]	28
vnB6	IaB	427	NDC[b]	24
vnB22	IaB	532	NDC[b]	10
vnB5	IaB[a]	924	NDC[b]	31

[a] The results for these samples were obtained after annealing at 570 °C for 1 h.
[b] No detectable change.

analysis was carried out over the range 1.640–1.694 eV. After subtraction of a cubic baseline, the spectra were decomposed into a suitable number of Voigt or Gaussian functions, using the
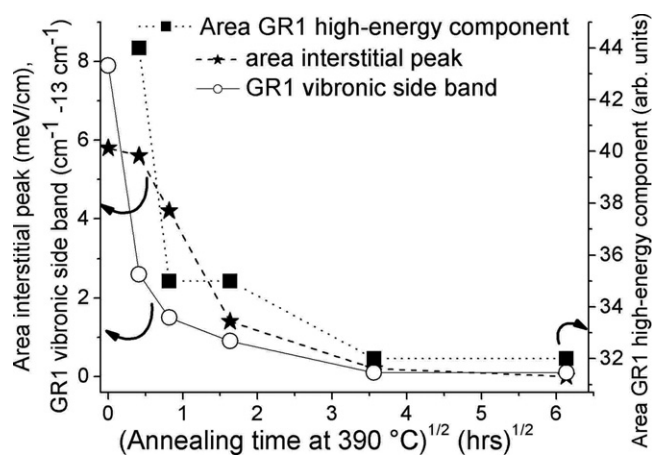
Figure 8. The changes, as a consequence of isothermal annealing at 390 °C, of the high-energy component of the GR1 ZPL, the GR1 side band (curve is offset by 13 cm^{-1}) and the interstitial peak at 1.859 eV, measured in a type IaA diamond with nitrogen concentration of 1023 ppm. A nonlinear (square root) time axis has been used to show more clearly the data near the beginning of the annealing sequences.

minimum number of peaks required to obtain an acceptable fit. Apart from the peaks at 1.671 and 1.673 eV, observed by Davies, we found that the 'high-energy tail' can be represented by two small broad peaks at 1.677 and 1.680 eV (figure 7(a)).

The isothermal annealing of the type IaA specimens caused the elimination with time of the 1.859 eV interstitial peak, the annealing of the S-band and the narrowing of the GR1 ZPL, as described above. The changes in the intensity of the S-band were obtained by measuring the reduction of the height of the GR1 side band at 2 eV. By comparing the changes, produced by the isothermal annealing, in the height of the S-band, the integrated intensity of the 1.859 eV peak and the intensity of the high-energy GR1 ZPL components (obtained by spectral subtraction), we obtained the results shown in figure 8.

This figure shows that the intensities of the S-band and the 1.859 eV I^0 peak are reduced to zero, and the intensity of the GR1 ZPL high-energy component reached a minimum, after annealing for 13 h with no further changes with annealing time. No additional changes were observed after further annealings for 2 h at 430 °C and 2 h at 450 °C. The results shown in figure 8 are for a specimen with [N] = 1023 ppm; similar results were obtained for three more specimens with nitrogen concentrations of 264, 288 and 995 ppm.

Comparisons of the concentrations of annealed vacancies $\Delta[V]$ and interstitials $[I^0]$, as a consequence of isothermal annealing at 390 °C for type IaA diamond, and isochronal annealing up to 600 °C for type IIa diamond, are given in table 4. As stated in section 3.1.1, the concentrations of neutral vacancies were calculated from the height of the GR1 side band.

This table shows that, for the type IIa and low-nitrogen type IaA diamonds, $-\Delta[V]$ and $[I^0]$ are almost equal to within experimental error while, for the specimens with high N concentration, $|\Delta[V]| > [I^0]$. As expected, we did not detect absorption due to the H3 (N–V–N) centre, which might have accounted for the extra annealed vacancies. The formation of this centre requires the mobility of the vacancies, which happens at higher annealing temperatures.

From an examination of two synthetic type IIa diamonds, Hunt *et al* (2000) found $\Delta[V]/[I^0]$ to be 0.44 in one sample and 0.40 in the other. Using the recent conversion factor (Iakoubovskii *et al* 2003) for calculating $[V^0]$ would have doubled $[V^0]$, making their results similar to those in table 4.

Table 4. Summary of changes in the concentrations of vacancies and interstitials induced by isothermal annealing at 390 °C for type IaA diamonds, and isochronal annealing up to 600 °C for type IIa diamonds. In both cases this results in the interstitials being completely annealed out. Uncertainties shown are *relative* uncertainties, resulting from the errors in measurement and peak integration. The total uncertainties should also include the uncertainties in the calibration factors and are ~25%.

Specimen	Type	[N] (ppm) ±5%	$\Delta[V^0]$ (ppm) ±5%	$\Delta[V^-]$ (ppm) ±5%	$\Delta[V]$ (ppm) ±6%	$[I^0]^a$ (ppm) ±5%	Ratio $|\Delta[V]/[I^0]|$ ±8%
			Type IaA				
vn23	IaA	264	−4.8	+0.5	−4.3	3.6	1.19
vnA18	IaA	288	−3.7	+0.2	−3.5	3.4	1.03
vnA14	IaA	143	−4.3	+0.5	−3.8	3.4	1.12
vn25	IaA	1023	−5.5	0.0	−5.5	3.8	1.45
vnA5	IaA	995	−5.9	+0.1	−5.8	3.6	1.60
			Type IIa				
CVD02	IIa	<0.1	−2.4	b	−2.4	2.1	1.14
HPHT-K	IIa	<0.1	−1.7	b	−1.7	2.3	0.74

[a] The numbers in this column are the total concentrations of the interstitials represented by the area of the 1.859 eV peak. The total number of annealed interstitials might be higher.
[b] The total concentration of negative vacancies in these samples is ⩽0.07 ppm.

Isothermal annealing of type IaB diamonds shows a correspondence between the reduction of the GR1 vibronic side band and the annealing of the interstitial peak, but we *did not* find a similar relationship between the reductions of the GR1 side band and its ZPL. In fact, within experimental error, we did not observe any change in the GR1 ZPL, in this type of diamond, as a consequence of such annealing. As in the type IaA diamonds, there is a reduction in the height of the vibronic side band after annealing at 390 °C for 10 h; no further reduction was observed after annealing for further 25 h at this temperature.

4. Estimating the concentration of neutral vacancies

As stated in section 2, it has been customary to determine $[V^0]$ from the area *A* of the GR1 ZPL. There are problems in following this procedure caused by the formation of the S-band by the strained vacancies, and the difficulty of assessing the contribution of these strained vacancies to the area of the ZPL. We need to distinguish between two effects:

(1) The effect of the strain field caused by impurities such as A-centres in type IaA diamonds and structural defects (dislocations) in natural type IIa diamonds. In these cases the contribution is in the form of added high-energy components to the ZPL which, together with the interstitial peak at 1.859 eV, anneal out at 390/420 °C, as seen in figure 8.

(2) The effect of interstitials in the vicinity of vacancies, forming vacancy–interstitial pairs. In this case there is a distribution of ZPLs at different wavelengths, depending on the distances between the constituents. It is to be noted that this is true only for relatively distant pairs (Briddon 2006). Hence the total contribution can be grossly underestimated in the process of subtracting the baseline in order to measure the area of the ZPL. This problem will be more severe in the case of substantially broadened ZPLs in samples with high nitrogen concentration, as in figure 2(a).

A clear example of case 2 was reported by Collins (1982), who observed that the GR1 absorption spectrum, after irradiating a type Ia diamond at low temperature ($< -25\,°C$) with 2 MeV electrons, consists of a broad band with barely detectable features near 1.673 and 1.859 eV. On annealing at $450\,°C$ there was an overall reduction in absorption and a dramatic sharpening of the lines in the spectrum. Similar results were observed by Clark *et al* (1956a). They measured the GR1 absorption spectra of type Ia diamonds irradiated by 0.6 MeV electrons, gamma rays and neutrons. They found that the principal lines, after irradiation by γ-rays and neutrons, were much broader than those produced by electron irradiation. After annealing, they found that there was a substantial reduction of the total absorption for both gamma- and neutron-irradiated diamond, and the GR1 ZPL became sharper (Clark *et al* 1956b). This suggests that irradiation of type Ia diamonds, by γ-rays from ^{60}Co (Clark *et al* 1956b) or 2 MeV electrons at low temperature (Collins 1982), produces predominantly the broad S-band. However, when high-energy (2–3 MeV) electrons are used, with the specimen nominally at room temperature, the extra excitation and higher temperature might result in a partial 'annealing'. The resulting spectrum is consequently dominated by a well-resolved GR1 spectrum, superimposed on the broad S-band.

The concentration of neutral vacancies can, in principle, be determined from the integrated intensity of the GR1 ZPL. However, in light of the above, it might be difficult to determine the area of the ill-defined GR1 ZPL. The alternative is to measure the absorption coefficient at the maximum of the side band near 2.0 eV; the effective area of the ZPL may then be inferred from the ratio of the height of the vibronic side band and the area of the ZPL, using high-quality type IIa diamonds (either HPHT or single-crystal CVD). The GR1 ZPL in these types of diamonds is very well defined. The average ratio, from five as-irradiated specimens, was 8.2 ± 0.6 meV cm^{-2}. However, the data shown in table 3, and the results of Collins (1982), indicate that we will get a higher proper value if we measure the ratios after annealing the specimens at 420–450 $°C$, which causes the annealing out of the strained vacancies and the 1.859 eV interstitial peak, i.e. the recombination of most or all of the vacancy–interstitial pairs. Using the GR1 absorption spectra of three annealed type IIa diamonds, we obtained an average ratio of 10.2 ± 0.9 meV cm^{-2}. The area A of the ZPL can then be inferred from the height H of the vibronic side band, using the ratio $A(\text{meV cm}^{-1})/H(\text{cm}^{-1}) = 10.2 \pm 0.9$. It is to be noted that, once A is inferred by this method, the existing relationship between A and V^0 can be used to determine [V^0]. That relationship was obtained using several cycles of charge transfer by the photochromic effect, transforming V^0 to V$^-$, measuring the *changes* in the area of the GR1 ZPL (and so there was no need to measure the *total area*) and the changes in the concentration of V$^-$, as determined by an accurate and independent EPR technique (Iakoubovskii *et al* 2003). The concentration, [V^0], can consequently be estimated from the maximum (H) at $\sim$2 eV of the GR1 vibronic side band from equation (1):

$$H = (6 \pm 1) \times 10^{-18}[\text{V}^0]$$

where H is the absorption coefficient in cm^{-1}, obtained after subtracting a second-order polynomial baseline, and [V^0] is the neutral vacancy concentration in cm^{-3}.

The relationship between the areas of the ND1 ZPLs ([V$^-$]) and [N$_A$] in type IaA diamonds is similar to the relationship between the areas of the GR1 ZPLs and [N$_A$]; in both cases there is a better correlation for samples with [N$_A$] $\leqslant$ 650 ppm (table 2). This implies that similar considerations need to be applied to the effect of the strained negative vacancies on the ND1 ZPL. No such calculation was undertaken. Besides, it is not yet possible to relate the area of the ND1 peak to a more reliable source of information. The same argument can be presented regarding the area of the 1.859 eV interstitial peak; indeed, Hunt *et al* (2000)

attributed the width of the EPR line of single carbon interstitials to possible interaction with close-by vacancies in vacancy–interstitial pairs.

5. Discussion

5.1. The relationship between the concentration of nitrogen and the concentration of vacancies and interstitials in type Ia diamonds

There are two significant differences between the behaviour of type IaA and type IaB diamonds regarding the relationships between the concentrations of vacancies and interstitials and the concentrations of nitrogen; in type IaA diamonds, $[V^0]$ increases with $[N_A]$, while there is no such correlation for type IaB diamonds. Also, the concentrations of self-interstitials and 3H centres increase with $[N_A]$ in the type IaA diamonds and decrease with $[N_B]$ in the type IaB diamonds.

The dependence of the width of the GR1 ZPL on $[N_A]$ in type IaA diamonds is similar to the dependence on $[N_B]$ in type IaB diamonds (figure 4). This is an unexpected result; for a given nitrogen concentration, the number of B-centres is half the number of A-centres and, furthermore, intuition suggests that the strain associated with a B-centre is lower than that produced by an A-centre. The GR1 vibronic side band in both types of diamonds decreases after annealing at 390 °C, and the decrease in both cases is correlated with the disappearance of the single interstitials. On the other hand, there is no observed change in the GR1 ZPL in type IaB diamonds, while in type IaA diamonds the width of the ZPL and its area are reduced as a consequence of this annealing process (table 3).

The reasons for the similar dependences of the width of the ZPL on nitrogen concentration, and the very different annealing behaviours, for type IaA and type IaB diamonds are not currently understood.

5.2. Annealing

We have established that a fraction of the vacancies created by electron irradiation anneals out at 390–420 °C. At the same time, the S-band and the self-interstitials anneal out, and the high-energy component of the GR1 ZPL reaches a minimum intensity (figure 8). The spectrum for a natural type IIa diamond shown in figure 7(c) might suggest that the broadening of the ZPL can also be introduced by structural defects (dislocations).

The fact that the S-band was also observed in HPHT and CVD type IIa diamonds can be due to the effect of the presence of some defects in these crystals trapping vacancy–interstitial pairs. The CVD single crystals were found to contain dislocations in the direction of growth (Martineau *et al* 2006). It is also possible that such pairs are formed even without the presence of strain fields caused by other impurities or defects.

The observed reduction in the width of the GR1 ZPL for type Ia diamonds described by Davies *et al* (1992), and its attribution to the annealing of vacancies in close vicinity to A-centres, does not describe the complete situation. When type Ia diamonds are annealed at 600 °C the decay of the GR1 ZPL exhibits both fast and slow components (Davies *et al* 1992, Lawson *et al* 1992). Lawson *et al* (1992) ruled out the recombination of vacancies and interstitials accounting for the fast process, because the fast decay of GR1 absorption was correlated with a fast growth of H3 absorption. In the present annealing measurements at ∼390 °C, no H3 or H4 centres were formed, but nevertheless a significant narrowing of the GR1 ZPL was observed. This narrowing could be attributed to the recombination of interstitials with 'nearby' vacancies.

At the end of the annealing process the optical absorption features due to self-interstitials disappear, and the number of annealed interstitials is comparable with the number of annealed vacancies (table 4). This suggests that most single interstitials, produced by electron irradiation at room temperature, are part of vacancy–interstitial pairs. Furthermore, EPR and optical investigations of single interstitials in type IIa (Hunt *et al* 2000) and type Ib (Iakoubovskii *et al* 2005) diamonds indicate that vacancy–interstitial pairs are formed in these types of diamond. Therefore, it is possible that the presence of interstitials in diamonds at temperatures of up to 390–420 °C is due to their having been trapped in this way, i.e. no 'free' interstitials can survive up to such temperatures.

6. Conclusions

- The concentrations of vacancies [V] and interstitials [I^0] in type IaA electron-irradiated diamond increase linearly with the concentration of nitrogen [N_A].
- This increase of [V] and [I^0] with [N_A] is probably caused by the trapping of vacancies and interstitials in the strain field of nitrogen, preventing them from recombining.
- In type IaB diamonds no such relation has been found between [V] and B nitrogen [N_B]; on the other hand, [I^0] *decreases* linearly with [N_B].
- In both types of diamonds the width of the GR1 ZPL increases, to the same extent, with the nitrogen concentration.
- We suggest that for vacancies formed in a strain field, most of the resulting interstitials stay near the vacancies, forming vacancy–interstitial pairs. The pairs do not recombine, because of the barrier caused by the strain field surrounding them as well as the intrinsic strain field caused by the proximity of interstitials and vacancies.
- Annealing at temperatures of around 390–420 °C causes the interstitials to move and recombine with nearby vacancies. The stability of interstitials up to these temperatures may be due to their being present as vacancy–interstitial pairs.
- The presence of the strained vacancies causes the measurement of the area of the GR1 ZPL, and hence the evaluation of the concentration of neutral vacancies, to become unreliable.
- A new formula is proposed based on the height of the GR1 side band:

$$H = (6 \pm 1) \times 10^{-18} [V^0]$$

where H is measured in cm^{-1}, after subtracting a second-order polynomial baseline, and [V^0] is in cm^{-3}.

Acknowledgments

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