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## LETTER TO THE EDITOR

## The production of vacancies in type Ib diamond

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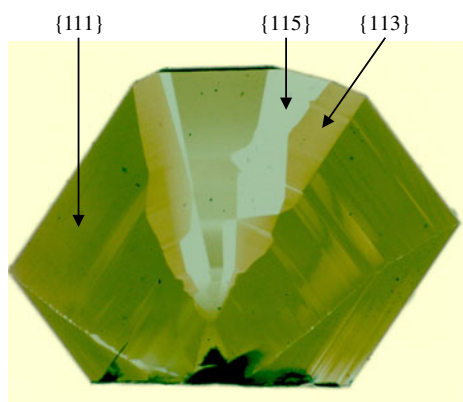
### Abstract

Optical absorption measurements on different growth sectors of a polished slice of electron-irradiated type Ib synthetic diamond show that the vacancy concentration is almost four times higher in the high-nitrogen  $\{111\}$  sectors than in the low-nitrogen  $\{115\}$  sectors. Evidence is presented to show that the self-interstitials are trapped by nitrogen, thereby reducing the amount of correlated recombination with vacancies which occurs in the absence of nitrogen.

Radiation damage is used extensively in the fundamental study of point defects in diamond. Such studies also have technological significance while diamond is being evaluated as a radiation-hard detector material. Irradiation with high-energy electrons (2–3 MeV) principally produces vacancies and self-interstitials, and in many cases it is important to quantify the amount of damage that has occurred.

Considerable progress has been made in recent years in establishing calibration factors between the concentrations of point defects in diamond and the strengths of optical absorption bands produced by these defects (Davies 1999). These investigations have also produced evidence that the concentration of vacancies observed, following electron irradiation, is influenced by other defects present in the diamond. For example, in type IaA diamond (those that contain nitrogen mainly in the form of A aggregates, where an A aggregate is a nearest-neighbour pair of substitutional nitrogen atoms), it appears that approximately 40% of the vacancies are within 0.7 nm of an A aggregate. In a typical diamond these regions comprise no more than 3% of the total volume, and it has been proposed that the strain field associated with the A aggregate reduces the amount of correlated recombination that occurs between the vacancies and the self-interstitials (Davies 1999).

In the present study we have investigated how the concentration of vacancies, observed after irradiation, is affected by the presence of single substitutional nitrogen, using diamonds grown by high-pressure, high-temperature (HPHT) synthesis. Synthetic diamonds typically have a cubo-octahedral morphology, in which the dominant faces are  $\{100\}$  and  $\{111\}$ . Between the cubic and octahedral faces there are frequently small higher-index facets such as  $\{113\}$  and  $\{115\}$ . In addition,  $\{110\}$  facets may separate adjacent octahedral faces. When a thin  $\{110\}$  slice is cut from the centre of a synthetic diamond, the different types of growth sector can be observed radiating out towards the corresponding facet.

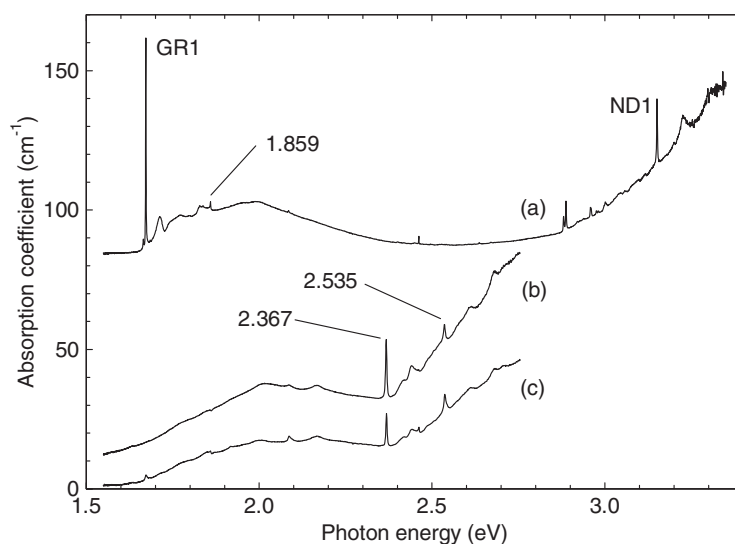


**Figure 1.** A photograph of the  $\{110\}$  slice of synthetic diamond used in this investigation, following irradiation with  $2 \times 10^{18} \text{ cm}^{-2}$  electrons of energy 3 MeV. The specimen is 4.4 mm across and 0.5 mm thick. The seed face is at the bottom, and the three growth sectors where absorption measurements were carried out are identified.

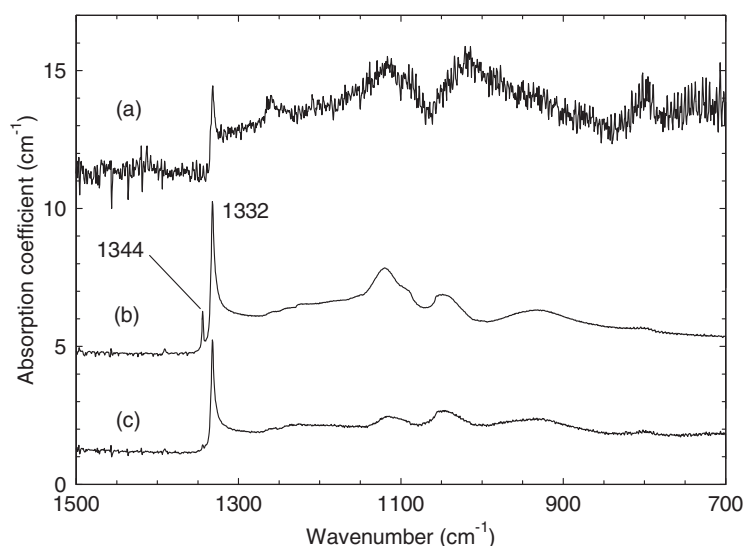
Single substitutional nitrogen is normally the dominant impurity in HPHT synthetic diamond, and is taken up at different concentrations in the different growth sectors (Burns *et al* 1990). This form of nitrogen is an electrical donor with an ionization energy of 1.7 eV, and absorption associated with donor-to-conduction-band transitions gives the diamond a characteristic yellow colour. Concentrations 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  $1130 \text{ cm}^{-1}$  (Woods *et al* 1990) or the sharp peak at  $1344 \text{ cm}^{-1}$  (Lawson *et al* 1998) associated with a localized vibrational mode. In the specimen used here, the nitrogen concentrations were approximately 75 ppm in the  $\{111\}$  sectors, 25 ppm in the  $\{113\}$  sectors and  $\leq 2$  ppm in the  $\{115\}$  sectors. At these concentrations, in a slice 0.5 mm thick, the growth sectors appeared yellowish, pale yellow and colourless, respectively.

Following radiation damage by  $2 \times 10^{18} \text{ cm}^{-2}$  electrons, with an energy of 3 MeV, the growth sectors are strikingly delineated, as shown in figure 1. The  $\{111\}$  sectors have a drab green colour, the  $\{115\}$  sectors are blue, and the  $\{113\}$  sectors are yellow/brown. Growth-banding, associated with varying nitrogen concentrations in the different regions, is also clearly evident. Three reasonably homogeneous regions—one of each type—have been selected for study. Absorption spectra have been measured from 370 to 800 nm (3.35 to 1.55 eV) with the diamond at 77 K, and from 4000 to  $400 \text{ cm}^{-1}$  with the diamond at room temperature. The results are shown in figures 2 and 3, respectively, and important features have been identified in each figure.

In the low-nitrogen  $\{115\}$  sector (figure 2(a)) the GR1 vibronic band with a zero-phonon line (ZPL) at 1.673 eV, and part of the ND1 band with a ZPL at 3.150 eV, are clearly visible. The GR1 centre and the ND1 centre are attributed to the neutral and negative charge states of the vacancy, respectively (Davies 1977). At low nitrogen concentrations most of the vacancies are in the neutral charge state and the GR1 absorption dominates. The weak absorption line at 1.859 eV is due to a localized vibrational mode associated with the self-interstitial in a split  $\langle 001 \rangle$  configuration (Hunt *et al* 2000). The concentrations of self-interstitials, and neutral and negative vacancies, can be determined from the areas of the corresponding absorption lines.



**Figure 2.** Optical absorption spectra in the visible and near-ultraviolet regions, recorded with the diamond at 77 K, for three different growth sectors: (a) {115}, (b) {111} and (c) {113}. The spectra have been adjusted vertically to avoid curves intersecting.



**Figure 3.** Optical absorption spectra in the defect-induced one-phonon region, recorded with the diamond at room temperature, for three different growth sectors: (a) {115} multiplied by 10, (b) {111} and (c) {113}. The spectra have been adjusted vertically to avoid curves intersecting.

At high nitrogen concentrations ( $\sim 75$  ppm) the spectrum in the visible region is dramatically different (figure 2(b)). 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 2.367 and 2.535 eV, are present which were not detectable in the low-nitrogen sector, and the steeply rising absorption precludes measurements at energies above approximately 2.8 eV. The spectrum in figure 2(c), from the growth sector with  $\sim 25$  ppm of nitrogen, is similar,

**Table 1.** Concentrations of neutral nitrogen ( $N^0$ ), positive nitrogen ( $N^+$ ), neutral vacancies ( $V^0$ ) and negative vacancies ( $V^-$ ) in three 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	$29 \pm 5.3$	$29 \pm 5$
{113}	$5.5 \pm 0.5$	$22 \pm 3.8$	—	$1.3 \pm 0.5$	$22 \pm 3.8$	$23 \pm 4$
{115}	0	$1.7 \pm 0.5$	$0.8 \pm 0.1$	$6.9 \pm 1.8$	$\sim 1.1$	$8 \pm 2$

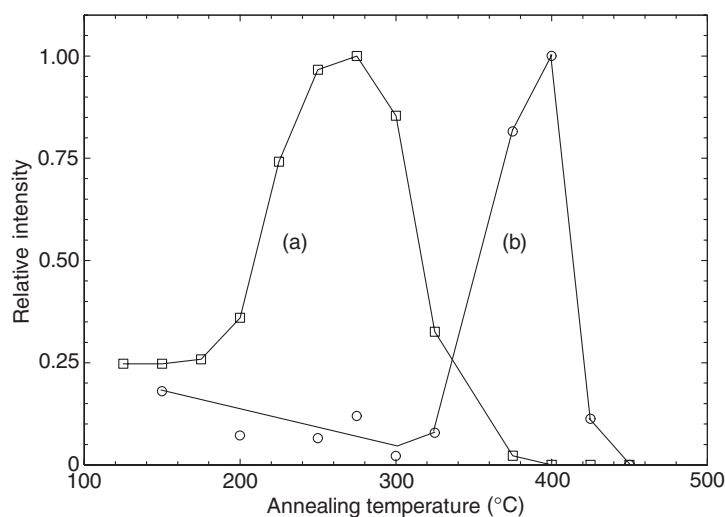
although the intensities of the broad absorption bands, and the 2.367 eV line, are rather lower. In addition, a weak GR1 ZPL is just visible, but the width of the line is approximately 12 times greater than in the low-nitrogen growth sector. Although not visible on the scale used to plot figure 2, weak absorption at 1.859 eV, produced by the self-interstitial, is present in both the {111} and {113} growth sectors.

Spectra in the defect-induced one-phonon region are shown in figure 3. Nitrogen in the positive charge state ( $N^+$ ) produces a characteristic absorption band with a sharp spike at 1332  $\text{cm}^{-1}$  (Lawson *et al* 1998). Provided that 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  $\text{cm}^{-1}$  (Lawson *et al* 1998, Twitchen *et al* 1999). 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  $N^0$ , in (b) the concentrations of  $N^0$  and  $N^+$  are similar, and in (c) most of the nitrogen is ionized, but it is nevertheless possible to detect approximately 6 ppm of  $N^0$ . At these low residual concentrations of  $N^0$ , some GR1 absorption (due to  $V^0$ ) can be observed (figure 2(c)) because the charge transfer process depends to some extent on the proximity of the nitrogen to the vacancy (Collins 2002).

Table 1 shows the concentrations of nitrogen and vacancies in the three different growth sectors, calculated from the original spectra used to prepare figures 2 and 3 using the calibration data from Davies (1999), Lawson *et al* (1998) and Twitchen *et al* (1999). The uncertainties shown take into account the uncertainties in the calibration data and the uncertainties associated with deconvoluting spectra and measuring peak areas and/or peak intensities. We obtain the remarkable finding that the total concentration of vacancies in the growth sector containing 75 ppm of nitrogen is almost four times higher than in the low-nitrogen sector. This factor is rather lower (about three) for the growth sector with 25 ppm of nitrogen.

To understand this phenomenon we again consider the differences in the spectra shown in figure 2. Collins and Rafique (1979) first drew attention to the absorption peaks at 2.367 and 2.535 eV in irradiated type Ib diamond. They showed that the 2.367 eV peak annealed out after heating the diamond to 250 °C, and that the decrease in intensity of this peak was accompanied by an increase in the intensity of the 2.535 eV peak. This peak annealed out, in turn, after heating the diamond to 400 °C. Because of the low temperatures at which these processes occurred, Collins and Rafique attributed the optical centres to complexes involving isolated nitrogen and carbon interstitials.

In the present investigation we have carried out detailed isochronal annealing studies of the absorption spectra from a {111} growth sector of another polished slice of type Ib synthetic diamond. Figure 4 shows the relative intensities of the 2.535 eV line and the 1.859 eV line as a function of annealing temperature. The 2.535 eV line first increases in intensity between 175 and 275 °C, as the 2.367 eV line anneals out, and then itself anneals out between 275



**Figure 4.** Annealing curves for (a) the 2.535 eV line and (b) the 1.859 eV line. The diamond was heated for 1 h at each point.

and 400 °C. During the annealing of the 2.535 eV line, the 1.859 eV line increases and reaches a maximum at 400 °C. We attribute the growth in the 1.859 eV line to the release of self-interstitials as the 2.535 eV nitrogen–interstitial complex anneals out.

The annealing out of the 1.859 eV line, which in this diamond occurs between 400 and 450 °C, is observed in all diamond types over a similar temperature range, and is accompanied by a partial loss of vacancies (Allers *et al* 1998). For the diamond used here, there was a progressive loss of  $N^+$  absorption for annealing temperatures between 275 and 400 °C, equivalent to a reduction in the concentration of  $V^-$  by approximately 30%. This suggests that, when the annealing of the 2.535 eV centre releases interstitials, some annihilate vacancies immediately while others move on to a split  $\langle 001 \rangle$  site (thereby producing absorption at 1.859 eV) and are subsequently released at a slightly higher annealing temperature.

The results presented here lead us to the following conclusion: during electron irradiation of diamond containing a low concentration of isolated substitutional nitrogen, most of the vacancies undergo a correlated recombination with the self-interstitials. However, in diamonds that contain significant concentrations of isolated substitutional nitrogen, the self-interstitials are preferentially trapped to form nitrogen–interstitial complexes; consequently, a higher concentration of vacancies remains in the diamond. Our present results indicate that 25 and 75 ppm of nitrogen result in enhancements of the vacancy concentration by factors of  $\sim 3$  and  $\sim 3.6$ , respectively. Measurements on other specimens, containing approximately 300 ppm of nitrogen, show that the enhancement factor may be as high as 5.

Finally we note that, in a thin slice of low-nitrogen (2 ppm) diamond,  $2 \times 10^{18} \text{ cm}^{-2}$  3 MeV electrons produce  $\sim 8$  ppm ( $1.4 \times 10^{18} \text{ cm}^{-3}$ ) of vacancies. The vacancy production rate per electron of  $\sim 0.7 \text{ cm}^{-1}$  is comparable to the value of  $0.6 \text{ cm}^{-1}$  obtained with 2 MeV electrons in a type Ib diamond containing 9 ppm of nitrogen (Lawson *et al* 1998).

Very recent work by Yakubovskii *et al* (2003) indicates that the calibration factor proposed by Davies (1999) under-estimates the  $V^0$  concentration by a factor of two. If confirmed, that result nevertheless leaves unchanged the conclusions presented here, although the numerical values will be different.

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