On the existence of positively charged single-substitutional nitrogen in diamond

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Abstract. Infra-red (IR) absorption results on irradiated and annealed synthetic diamond are presented which confirm an earlier proposal that a component found in the defect-induced one-phonon region of some diamonds arises from positively charged single-substitutional nitrogen (N^+). The concentration ratio of N^+ to neutral substitutional nitrogen (N^0) centres may be changed by shining light of various energies onto the examined samples. By correlating changes in absorption of the IR component associated with N^0 centres with changes in the N^+ component, and using a previously determined relation between the concentration of N^0 centres and peak absorption coefficient at 1130 cm^{-1}, the relationship between peak absorption at 1332 cm^{-1} and concentration of N^+ centres has been derived, namely 1 cm^{-1} of absorption is produced by (5.5 ± 1) ppm N^+ centres. Other defects may also give rise to absorption at 1332 cm^{-1}, but the N^+ component is uniquely identified by further peaks at 1046 and 950 cm^{-1}.

The significance of this component is demonstrated by the fact that some samples can contain in excess of 80 ppm N^+ centres, and this must consequently be accounted for when assaying the total nitrogen concentration in such samples.

Using the above relationship useful parameters relating the concentration of neutral vacancies, negative vacancies and negatively charged nitrogen–vacancy centres to their respective zero-phonon line integrated absorptions have been derived.

1. Introduction

Nitrogen is the most common atomic impurity found in natural and, unless steps are taken to deliberately exclude it, high-pressure synthetic diamond. Indeed diamond is classified in terms of the shape of its infra-red spectrum in the defect-induced one-phonon region ($\sim$500–1500 cm^{-1}) which results from vibrations at different atomic arrangements of nitrogen. Three different structural forms of nitrogen have been acknowledged as giving rise to different infra-red absorption features. The absorption spectrum shown in figure 1(a) arises from single-substitutional nitrogen atoms (commonly termed C-form nitrogen) and diamonds exhibiting this type of spectrum are classified as type Ib. The vast majority of synthetic diamonds are of this type. The concentration of nitrogen in C-form centres may be determined from the strength of absorption of the peak at 1130 cm^{-1}, namely (25 ± 2) atomic ppm per cm^{-1} of absorption at 1130 cm^{-1} [1]. The sharp peak at 1344 cm^{-1} is due to a localized vibrational mode at the C-centre and in this study the strength of this peak is used to determine the concentration of N^0 centres. The spectrum (b) in figure 1 arises from adjacent-substitutional pairs of nitrogen atoms (commonly termed the A-aggregate) and

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diamonds which exhibit this type of spectrum are classified as type IaA. The concentration of nitrogen in A-centres may be determined from the strength of absorption of the peak at 1282 cm^{-1}, namely (16.5 ± 1) atomic ppm per cm^{-1} of absorption at 1282 cm^{-1} [1]. Type Ib synthetic diamonds can be converted to type IaA by high temperature annealing, in which C-centres become mobile and aggregate to form A-centres. Spectrum (c) of figure 1 arises from a higher aggregation state of nitrogen, believed to consist of four nitrogen atoms surrounding a vacancy, commonly called the B-aggregate. Again, the concentration of nitrogen in B-centres may be determined from the absorption coefficient of the plateau at 1282 cm^{-1}, namely (79.4 ± 8) atomic ppm per cm^{-1} absorption at 1282 cm^{-1} [2]. For diamonds which exhibit a combination of nitrogen forms, the concentration in each form is typically determined by computer minimization of multiples of the component spectra to the experimental spectrum. The above relationships are then applied in order to determine the nitrogen concentration associated with each component.
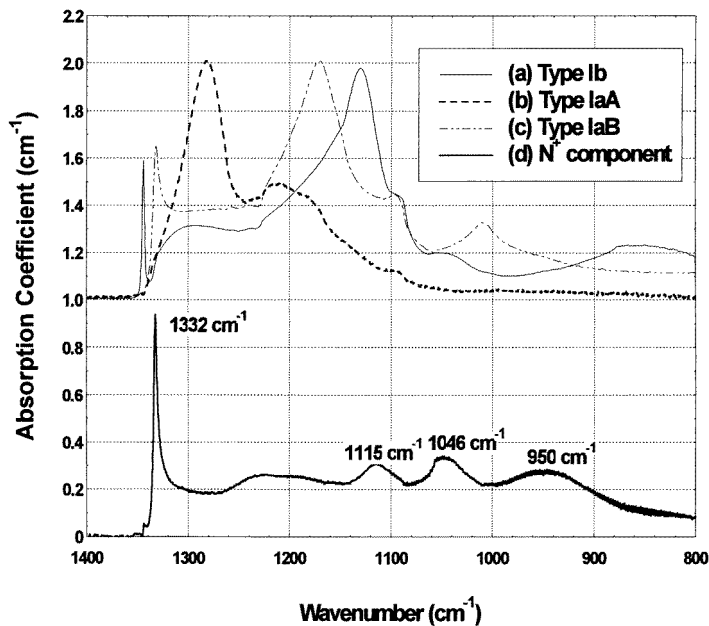
Figure 1. Infra-red absorption spectra in the defect-induced one-phonon region of diamond due to (a) single-substitutional nitrogen, (b) adjacent-substitutional pairs of nitrogen atoms, (c) four tetrahedrally co-ordinated nitrogen atoms surrounding a vacancy and (d) positively charged single-substitutional nitrogen.

In this article we provide firm experimental confirmation of an earlier proposal [3] that the infra-red spectrum shown in figure 1(d) (the so-called X-component of [3]) arises from another form of nitrogen, namely positively charged single-substitutional nitrogen (N$^+$).

Before discussion of the experiments which were carried out to confirm the above proposal, phenomenological support for the association of the X-component with N$^+$ is briefly outlined.

It was observed that the X-component is common to electron-irradiated diamond, boron-doped diamond and diamond grown using a nickel containing solvent–catalyst [3]. It was therefore proposed that it arises at a defect which is common to these different types of diamond. Single-substitutional nitrogen acts as a donor in diamond, nickel and vacancy

centres are found in a negative charge state and compensation of the boron acceptor occurs when single substitutional nitrogen is present. If C-form nitrogen is the dominant species to donate electrons to the boron, vacancy or nickel centres, then for each electron donated one nitrogen centre must exist in a positive-charge state. This, then, would be the defect common to all the above types of diamond and was consequently postulated as giving rise to the X-component. It is possible to conceive of some nitrogen or self-interstitial related defect being formed in nickel-containing, boron-containing and electron-irradiated diamond which gives rise to the X-component. However it would require some rather convoluted arguments to explain its annealing behaviour and the charge-transfer effects which are reported here. The simplest explanation for the X-component, and one which is in complete harmony with previously published work on vacancy charge states, is that it is produced by the N$^+$ defect. Such an identification also helps to explain anomalies in the annealing behaviour of nitrogen- and nickel-containing diamond where it had been shown that nickel–nitrogen complexes form and yet there was no apparent decrease in the total C- and A-form nitrogen concentration as an annealing sequence proceeded, even though it was estimated that up to about 60 ppm of nitrogen should have become 'lost' in the form of nickel–nitrogen complexes. The X-component also decreased during an annealing sequence and, by assuming that this component is due to another form of nitrogen, the apparent anomaly could be reconciled.

It has been shown that vacancies, introduced into the diamond lattice by electron irradiation, can exist in two charge states; neutral (V^0), giving rise to GR1 absorption, and negative (V^-), giving rise to ND1 absorption. Most irradiated diamond contains an equilibrium concentration of the two, the ratio being dictated by the position of the Fermi energy. In diamond containing greater than a few ppm C-centres the vacancy is dominantly in its negative charge state due to donation of electrons from C-form nitrogen to the vacancies. By shining light of various energies onto the sample the equilibrium ratios of neutral to negative vacancies can be changed [4]. Based on the above proposal this should also result in a change in the concentration ratio of neutral to positive nitrogen. Observation of such changes, as monitored by changes in the C- and X-components in the present work, provides firm support for the proposal.

In this article we concentrate on changes which are produced in well characterized electron-irradiated diamond. Changes have also been reported recently in natural diamond where the nature of the acceptor was unknown, and where different light excitation energies are required to convert N$^+$ to N^0 [5]. [5] examined changes in the electron-spin-resonance signals of neutral nitrogen on light excitation and correlated them with changes in the X-component in the IR (unfortunately, because the N$^+$ centre is ESR inactive no direct structural or electronic information could be obtained by such measurements). It reached the same conclusions as reached in this article and derived a relationship between the N$^+$ concentration and peak intensity at 1332 cm^{-1} of (7.0 ± 0.5) ppm per cm^{-1}.

2. Experiment

The success of the experiments presented here depended largely upon careful selection of well characterized samples. As outlined in the introduction, defects produced in electron-irradiated type Ib diamond are well understood. However, in order to observe significant changes in the absorption of N^0 centres it was necessary to select samples for which the concentration of vacancies produced by electron irradiation was comparable to the concentration of N^0 centres, but for which the concentration of N^0 centres was sufficient to produce measurable absorption at 1344 cm^{-1}. In addition, the irradiation dose could not be

so high as to introduce di-vacancies or general lattice disorder which would complicate the analysis. The selected sample was grown using a cobalt-containing solvent–catalyst with Ti as a nitrogen getter. Infra-red measurements, taken prior to irradiation through a 1 mm thick polished slice, revealed that the sample contained (9 ± 1) ppm N^0 centres and no other forms of nitrogen. A sample grown from a nickel-containing solvent catalyst would have had the added complications of nickel acting as an acceptor, and experiments had shown that the N^+ to N^0 conversion was not induced by light excitation in such samples.

The sample was irradiated at room temperature with a dose of 2×10^{18} cm^{-2} 1.9 MeV electrons, which is estimated to produce a vacancy concentration of 1×10^{18} cm^{-3} (6 ppm), based on the assumption that ten electrons produce one vacancy [6] and that the 1.9 MeV electrons can penetrate ~ 2 mm of diamond.

IR measurements were performed at room temperature on a Nicolet Magna IR 750 FTIR spectrometer using a 1.5 mm diameter aperture to sample through the centre of the cross-section and employing one wavenumber resolution. The sample could be bathed with light of various photon energies during collection of the infra-red spectrum by passing filtered light from a 150 W Xe arc-lamp through a quartz fibre whose open end was held close to the sample within the FTIR sample chamber. Filtering was achieved using a selection of long-wave-pass sharp-cut Schott glass filters which have 50% transmission at their specified cut wavelength and 5 and 0.2% transmission at 10 and 15 nm shorter wavelength respectively. The nitrogen concentration was uniform over the region examined. The relationship between the N^0 concentration (in parts per million) and the strength of absorption at 1344 cm^{-1} (in cm^{-1}) has been determined from the relationship between the N^0 concentration and peak absorption at 1130 cm^{-1} given in the introduction and the relation μ_{1344} (cm^{-1}) $= 0.572\mu_{1130}$ (cm^{-1}) (unpublished data determined for measurement at 1 cm^{-1} resolution), namely

$$N^0 \text{ (ppm)} = 37.5\mu_{1344} \text{ (cm}^{-1}) \tag{1}$$

3. Results

3.1. Effect of irradiation damage and annealing

Figure 2 shows the defect-induced one-phonon region of the synthetic type Ib sample used in this study (a) before irradiation, (b) after irradiation and (c) after a 900 °C 4 h anneal. A large decrease in the C-component can be observed following irradiation and the appearance of a component which has a sharp peak at 1332 cm^{-1} and additional broader peaks at 950, 1046 and 1115 cm^{-1}. Subtraction of the C-component from this spectrum yields the spectrum shown in (d) of figure 1. This spectrum is identical to that shown in [3], except for the addition of the peak at 1115 cm^{-1}. The spectrum shown in [3] was obtained from a nickel-containing diamond and it is therefore assumed that the 1115 cm^{-1} peak is characteristic of another irradiation damage product and not related to the N^+ component. This is supported by the fact that it appears to have annealed out following the 900 °C anneal (figure 2(c)). Using equation (1), the second column of table 1 was constructed showing the concentration of N^0 centres before and after irradiation and annealing. As expected from our model, the concentration of neutral nitrogen decreases on irradiation due to the conversion of some of the N^0 centres to N^+ centres in the creation of negatively charged vacancies. On annealing of the sample to produce nitrogen–vacancy (N–V) centres, the N^0 concentration is further decreased. The concentrations of N^+ centres shown in column 3 of table 1 are derived from an examination of the photochromic behaviour of the N^+ and N^0 components, as detailed in the next section.
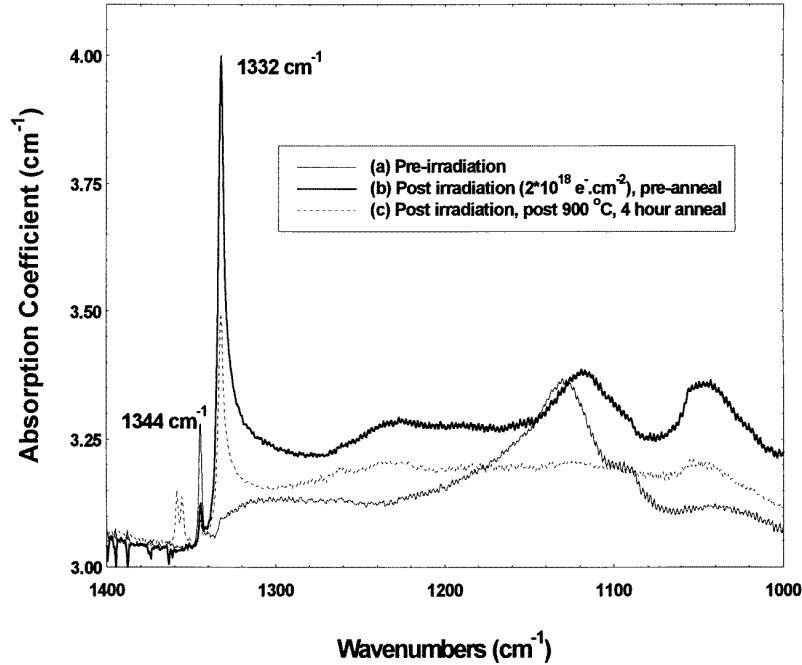
Figure 2. Defect-induced one-phonon absorption of a synthetic type Ib diamond (a) before irradiation, (b) after irradiation with 1.9 MeV electrons and (c) after a 4 h anneal at 900 °C.

Table 1. Changes in the N^0 and N^+ concentrations after irradiation and annealing.

Treatment	[N^0] (ppm)	[N^+] (ppm)	Total (ppm)
Pre-irradiation	9.0	0.0	9.0
Post-irradiation	3.3	5.2	8.5
Post-irradiation + 900 °C anneal	1.6	2.6	4.2

3.2. Photochromic behaviour of the GR1, ND1, N^0 and N^+ centres

Figure 3 is a difference absorption spectrum derived by recording the transmission of the sample with no external excitation as a background spectrum and the spectrum of the sample with the full excitation of a Xe lamp illuminating it as the sample spectrum. It was then converted into absorption coefficient units. It is clear that a decrease in the 1332 cm^{-1} component has been accompanied by an increase in the 1344 cm^{-1} component. Application of relation (1) to the change in absorption coefficient of the 1344 cm^{-1} component gives the increase in the N^0 concentration due to the light excitation. By carrying out these measurements for a number of excitation energies, as described in section 2, it is found that there is a direct correlation between increases in the 1344 cm^{-1} component and decreases in the 1332 cm^{-1} component, as shown in figure 4. The point in the top right-hand corner of figure 4 represents the *increase* in 1332 cm^{-1} absorption and *decrease* in 1344 cm^{-1} absorption due to the electron irradiation (i.e. it has been reflected from the negative quadrant into the positive quadrant of the graph). This point was not included in the linear regression fit represented by the solid line because the electron irradiation also produces nitrogen
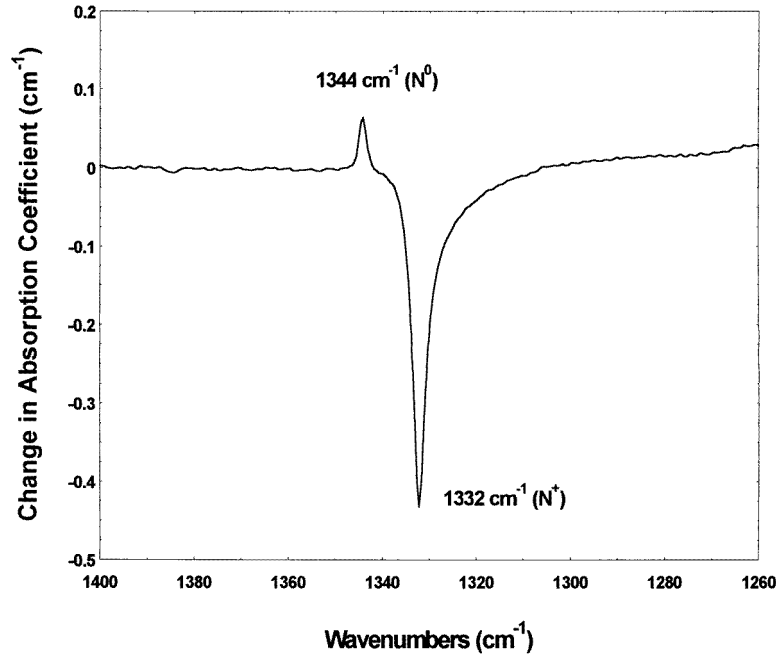
Figure 3. Difference absorption spectrum showing the increase in the neutral nitrogen absorption and corresponding decrease in positive nitrogen absorption for excitation with light from a Xe lamp.

interstitials which would be expected to give rise to a larger decrease in N^0 centres than increase in N^+ centres, as illustrated in figure 4. The vertical displacement of this point from the regression fit represents a decrease of 0.5 ppm, which in fact corresponds to the decrease in total nitrogen concentration after irradiation, as shown in column 4 of table 1. This, then, could represent the nitrogen interstitial concentration. By using the correlation shown in figure 4 to support the proposal that the increase in the N^0 concentration equates to a decrease in the N^+ concentration and using relation (1), the following relationship between peak absorption at 1332 cm^{-1} and concentration of N^+ centres (in ppm) is derived for measurement at 1 cm^{-1} resolution:

$$N^+ \text{ (ppm)} = (5.5 \pm 1)\mu_{1332} \text{ (cm}^{-1}) \tag{2}$$

It should be remembered that other point defects may also give rise to absorption at 1332 cm^{-1} due to the high density of phonon states in this region. The above relationship only applies if the components at 1046 and 950 cm^{-1} are also clearly observable.

The N^+ concentrations shown in column 3 of table 1 were derived using (2).

From table 1 it is seen that the total nitrogen concentration (in N^0 and N^+ forms), derived using equation (2), remains constant, to within 5%, after the irradiation.

In the case of the vacancy, the oscillator strength of the negative vacancy is four times that of the neutral vacancy and for both centres the zero-phonon line (ZPL) forms the same fraction of the total vibronic absorption band strength, namely 0.041 [7]. Following irradiation of the sample used in this study, the integrated absorptions of the ND1 and GR1 zero-phonon lines were measured as 359 and 33 meV cm^{-1} respectively. This, then, corresponds to a negative vacancy concentration 2.7 times that of the neutral vacancy
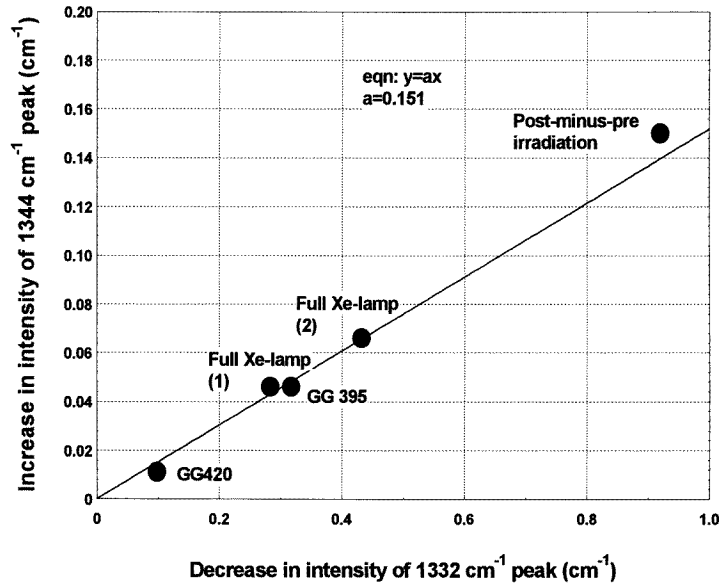
Figure 4. Plot of the decrease in the 1332 cm^{-1} peak intensity and correlated increase in 1344 cm^{-1} peak intensity for different excitation conditions (GG420 and GG395 correspond to the cut-in wavelengths of the long-wavelength pass sharp-cut Schott filters).

concentration, under the light excitation conditions experienced during the measurement. From our model we would expect a maximum negative vacancy concentration equal to the positive nitrogen concentration, which from table 1 corresponds to 5.2 ppm (this represents an upper limit because the nitrogen may also compensate other, unknown, irradiation damage products—although in the sample chosen this is thought to be an unlikely scenario). This, then, would give a V^0 concentration of $\sim$2 ppm and a maximum total vacancy concentration of 7 ppm. As outlined in section 2, based on previous results the irradiation dose used would be expected to yield a total vacancy concentration of $\sim$6 ppm [6]. In view of the approximations used in [6] and the fact that there may have been a different equilibrium during the GR1 and ND1 absorption measurements compared to the N^0, N$^+$ measurements, this is a pleasing result. From our results a room temperature electron dose of 2×10^{18} e$^-$ cm^{-2} produces a vacancy concentration of 7 ppm (1.2×10^{18} cm^{-3}) which yields a vacancy production rate of 0.6 cm^{-1}. This is an order of magnitude greater than that obtained using detailed balance arguments on irradiated type IIa diamond [7], and is thought to be a more direct and accurate measurement of this parameter. The parameter is, however, affected by the recombination rate of vacancies with self-interstitials produced during the irradiation and this is dependent upon the irradiation energy, irradiation temperature and possibly also on the diamond type. The parameter relating the integrated absorption in the ND1 ZPL (measured at 80 K) to the concentration of V$^-$ centres may be derived as

$$f_{ND1} \text{ (meV cm}^2) = A_{ND1}/[\text{V}^-] = 359/9.2 \times 10^{17} = 3.9 \times 10^{-16} \text{ meV cm}^2$$

where A_{ND1} is the integrated absorption of the ND1 ZPL (meV cm^{-1}) and [V$^-$] is the concentration of negative–vacancy centres (cm^{-3}). Similarly, from [7], $f_{ND1}/f_{GR1} = 4$, yielding

$$f_{GR1} \text{ (meV cm}^2) = 9.8 \times 10^{-17} \text{ meV cm}^2.$$

Following the 900 °C anneal there is a decrease in the total nitrogen concentration of 4.3 ppm due to the formation of nitrogen–vacancy centres. Both $(N–V)^0$ and $(N–V)^-$ centres are formed, giving rise to the 575 and 637 nm absorption bands respectively [8]. Assuming that all of the vacancies migrate to and are trapped at the nitrogen centres, this result gives an initial vacancy concentration of 4.3 ppm, which is 3 ppm below that derived from the strength of the N^+ component. This result may imply that a significant fraction of the vacancies are not trapped at nitrogen centres during the anneal (in this case ∼40%) but either recombine with self-interstitials or form other defects (such as di-vacancies). Another, less favoured, possibility is that the assumption regarding the absence of other irradiation damage products which nitrogen may compensate on irradiation is incorrect. The fact that 2.6 ppm of N^+ remains after the 900 °C anneal is consistent with there being 2.6 ppm of $(N–V)^-$ centres—and consequently 1.7 ppm of $(N–V)^0$ centres. The concentration of $(N–V)^-$ centres may also be calculated independently from the integrated absorption of the 637 nm ZPL (A_{NV}), the value of f_{GR1} given above, and the relation [7]; $f_{NV}/f_{GR1} = 1.15$. A_{NV} was measured as 67 meV cm^{-1}.

$$f_{NV} \text{ (meV cm}^2) = 1.13 \times 10^{-16} \text{ meV cm}^2$$

yielding

$$[N–V]^- = 5.94 \times 10^{17} = 3.4 \text{ ppm.}$$

This is in good agreement with the value derived from the strength of the N^+ component.

The charge transfer process, characterized by the increase in 1344 cm^{-1} absorption and correlated decrease in 1332 cm^{-1} absorption, occurs when photon energies shorter than ∼400 nm are incident upon the sample. This corresponds to the region of ND1 absorption (with ZPL transition at 393.6 nm). If we assume that the first excited state of the ND1 centre lies close to the conduction band so that excitation around this energy (3.149 eV) results in ionization of the centre, an assumption which is supported by photoconductivity measurements [9], then the photochromism results may be explained, with reference to the energy level diagram of figure 5. For excitation at wavelengths shorter than ∼390 nm an electron from the V^- (ND1) centre is released to the conduction band and becomes trapped at the N^+ centre. This results in an increase in the number of V^0 and N^0 centres (characterized by increases in GR1 and 1344 cm^{-1} absorption) and a decrease in the concentration of V^- and N^+ centres (characterized by decreases in ND1 and 1332 cm^{-1} absorption). The increase in N^0 centres and decrease in N^+ centres has already been described. In figure 6 we show the increase in GR1 absorption when light of wavelength shorter than 400 nm bathes the sample, in agreement with earlier work [4]. A decrease in ND1 absorption has also been observed following excitation with the full spectrum of a Xe lamp. We therefore have complete self-consistency for our proposed model in terms of charge transfer between vacancies and nitrogen.

The energy level diagram of figure 5 may also be used to explain the reversible nature of the charge transfer process. Excitation for wavelengths shorter than ∼400 nm results in an increase in the concentration of N^0 centres due to transition 1. This increase may be instantaneously reversed by shining light on the sample for which $400 \leqslant \lambda \text{ (nm)} \leqslant 600$. This corresponds to electron transitions from the N^0 centre being allowed (transition 2 of figure 5), which is essentially the reverse of transition 1.

For the sample examined, 90 minutes in the dark at room temperature also resulted in about a 50% recovery of the charge transfer process. Full recovery was achieved after a one hour 300 °C anneal. These results indicate a possible thermal tunnelling route for charge-equilibrium recovery.

Conduction Band
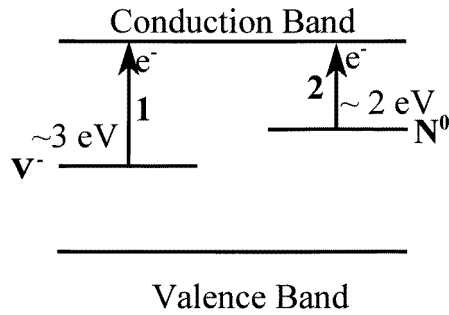
Figure 5. Schematic energy level diagram used to explain the charge transfer processes associated with the photochromic behaviour of the V^0, V^-, N^0 and N^+ species.
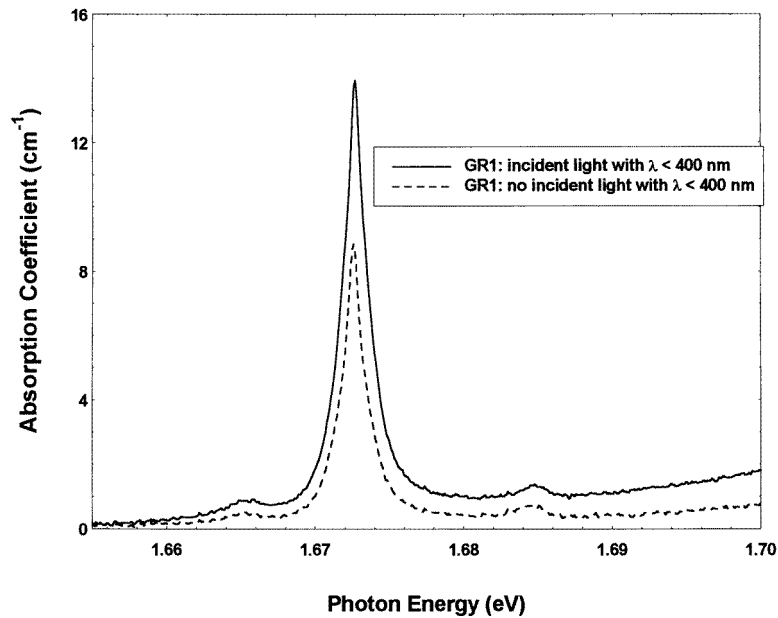
Figure 6. Illustration of the photochromic behaviour of the GR1 zero-phonon line. The solid curve corresponds to that recorded for light with $\lambda < 400$ nm incident on the sample whilst the dashed curve corresponds to that recorded for light with $\lambda > 400$ nm incident on the sample.

4. Summary

The N^+ defect is electron-spin-resonance inactive so that neither the experimental results presented here nor the ESR results presented in [5] are able to provide direct structural and electronic identification of the N^+ defect. However phenomenological observations and measurements on charge transfer between the species V^0, V^-, N^0 and N^+ in a carefully selected sample have provided confirmation of an earlier proposal that a component found in the defect-induced one-lattice-phonon region of diamond arises at positively charged single-substitutional nitrogen (N^+). The relationship between peak absorption at 1332 cm^{-1} and concentration of N^+ centres has been derived for measurement at 1 cm^{-1} resolution, namely 1 cm^{-1} of absorption is produced by (5.5 ± 1) ppm N^+ centres.

The vacancy production rate for room temperature 1.9 MeV e^- irradiation of weak type Ib diamond is determined as 0.6 cm^{-1}.

The following relations between concentrations (cm^{-3}) of GR1, ND1 and 637 nm centres and the integrated absorption of their respective zero-phonon lines (in meV cm^{-1}), for measurement at 80 K, are also determined as follows; $[GR1] = 1.0 \times 10^{16} A_{GR1}$, $[ND1] = 2.6 \times 10^{15} A_{ND1}$, $[N\text{–}V]^- = 8.9 \times 10^{15} A_{637}$.

Acknowledgment

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