The Fermi level in diamond

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Abstract

Diamond is a wide-band-gap material with large donor and acceptor ionization energies. In principle, at room temperature and below, the Fermi energy is pinned close to the donor or acceptor level, depending on which is present in the higher concentration. In semiconductors with shallow donors and acceptors the equilibrium charge states of defects are determined by the position of the Fermi level. However, in an insulating material like diamond we show that the calculated position of the Fermi level does not necessarily predict the correct charge state of a defect, and propose instead that the charge state is influenced by the proximity of the defect to a donor (or acceptor). Qualitatively this accounts for the dependence of the charge state on the concentration of isolated substitutional nitrogen and also explains why many optical centres can be present in two different charge states in the same diamond.

1. Introduction

A number of defects which give rise to optical absorption in diamond, for example the vacancy (Davies 1977), the nitrogen–vacancy centre (Mita 1996) and the nitrogen–vacancy–nitrogen centre (Mita *et al* 1990), can exist in more than one charge state. In previous publications this behaviour has been attributed to the change in position of the Fermi level with the concentration of single substitutional nitrogen, which behaves as a deep donor. In fact, as we show below, the Fermi energy is almost independent of the concentration of single nitrogen, provided this is the dominant defect. To account for the range of phenomena observed we therefore propose that the charge state of a defect is influenced by its proximity to a nitrogen-related donor.

Unless steps are taken to reduce its concentration, single substitutional nitrogen is the dominant impurity in diamond grown by high-pressure, high-temperature (HPHT) synthesis. Electrical conductivity measurements and Seebeck measurements demonstrated that the nitrogen behaves as a donor with an ionization energy of 1.7 eV (Vermeulen and Farrer 1975).

The A aggregate of nitrogen, comprising a nearest-neighbour pair of substitutional nitrogen atoms (Davies 1976), is the dominant impurity in most natural diamonds. Photo-Hall measurements show that the A aggregate behaves as a very deep donor with an ionization energy of 4 eV (Denham *et al* 1977).

When diamond containing single nitrogen is subjected to HPHT annealing, the nitrogen aggregates to form A centres (Chrenko *et al* 1977, Brozel *et al* 1978, Evans and Qi 1982) according to

$$N + N \rightleftharpoons A. \tag{1}$$

At the lower temperatures and much longer times experienced by diamonds in nature the reverse reaction is negligible, and the process generally goes almost to completion (Evans 1992), but at the temperatures used in the laboratory (1700–2100 °C) the reverse reaction is significant (Brozel *et al* 1978).

Radiation damage produces vacancies and interstitials, and the vacancy is stable at temperatures below approximately 500 °C. In diamond containing single substitutional nitrogen most of the vacancies are in the negative charge state, producing the ND1 absorption band with a zero-phonon line (ZPL) at 3.150 eV, whereas in diamonds with a very low concentration of single nitrogen, or diamonds containing predominantly the A form of nitrogen, most of the vacancies are in the neutral charge state, producing the GR1 absorption band with a ZPL at 1.673 eV (Davies 1977).

Annealing an irradiated diamond to approximately 800 °C for 1 h causes virtually all the vacancies to become mobile and subsequently trapped. In diamonds containing single substitutional nitrogen the vacancies are trapped to form N–V centres. For high concentrations of nitrogen (>100 ppm) most of these centres are in the negative charge state, giving rise to an absorption band with a ZPL at 1.945 eV, but for low nitrogen concentrations an appreciable fraction is present as $(N–V)^0$ centres, producing an absorption band with a ZPL at 2.156 eV. For example, for a diamond containing 9 ± 1 ppm of nitrogen, and irradiated to produce approximately 6 ppm of vacancies, Lawson *et al* (1998) found that, after annealing, 40% of the N–V centres were in the neutral charge state.

When the nitrogen is present as A aggregates, capture of the vacancies produces N–V–N centres (also known as H3 centres) which give rise to an absorption band with a ZPL at 2.463 eV (Davies 1972). In a series of HPHT annealing measurements, on irradiated diamonds containing nitrogen present initially in only the single form, Mita *et al* (1990) observed that the concentration of (N–V) centres was substantially reduced and a significant concentration of H3 centres was formed. (H3 centres are produced as a result of the vacancy-enhanced aggregation of nitrogen (Collins 1980).) More importantly, after annealing, the diamonds also contained an appreciable concentration of H2 centres which produce an absorption band with a ZPL at 1.257 eV.

Mita *et al* also observed photochromic effects in which the intensity of the H3 absorption could be increased, and that of H2 decreased, and vice versa, by irradiating the diamond with light of the appropriate wavelengths. These observations led them to propose that the H2 centre was a negative charge state of the H3 centre, and was favoured in their diamonds because the Fermi level was shifted well towards the conduction band, due to the presence of single substitutional nitrogen. Lawson *et al* (1992) subsequently carried out uniaxial stress measurements on the H2 and H3 zero-phonon lines and showed that the symmetries of the centres were the same and the shift rates of the ZPLs with applied stress were very similar, giving substantial support to the proposal by Mita *et al*.

Small concentrations of vacancy-related optical centres can occur naturally in diamond, and the relative concentrations of the 1.945 and 2.156 eV centres in gem diamonds have recently acquired considerable commercial significance (Fisher and Spits 2000), following the disclosure that brown type IIa diamonds can be colour-enhanced, by HPHT annealing, to produce almost colourless specimens. Type IIa diamonds contain insufficient nitrogen to detect easily by infrared absorption spectroscopy, but may, nevertheless contain several ppm of nitrogen, almost all of which is in an aggregated form. Photoluminescence (PL) spectra from

untreated colourless type IIa diamonds, excited at 514 nm, frequently exhibit the 2.156 eV ZPL. In the majority of cases the 1.945 eV ZPL is either absent or present at a lower intensity than the 2.156 eV line. However, in specimens which have been subjected to HPHT processing, some of the aggregated nitrogen dissociates to form single nitrogen donors (equation (1)), and in most cases the 1.945 eV ZPL, associated with (N–V)⁻, then dominates in the PL spectra. PL spectroscopy is now an important technique in the assessment of gem diamonds, and stones which exhibit dominant luminescence at 1.945 eV are referred for further scrutiny (Lawson 2001).

Nickel forms a large number of optical centres in HPHT synthetic diamond. In diamonds with a high concentration of single nitrogen (typically 250 ppm) two vibronic bands with ZPLs at 1.883 and 2.51 eV are dominant. In diamonds grown with a low concentration of nitrogen (approximately 5 ppm) these absorption bands are very weak and the spectra are dominated by a vibronic band with a zero-phonon doublet at 1.40 eV and a broad underlying absorption band with a maximum near 1.4 eV (Collins *et al* 1990a). At intermediate nitrogen concentrations all of the absorption systems are clearly visible.

The concentration of the 2.51 eV centre correlates moderately well (Collins *et al* 1998) with an EPR system, known as W8, that has been attributed to negatively charged substitutional nickel (Isoya *et al* 1990). The changes in the optical absorption spectra with nitrogen concentration, described above, were attributed by Collins *et al* (1990a) to the change in position of the Fermi level, giving rise to centres in different charge states.
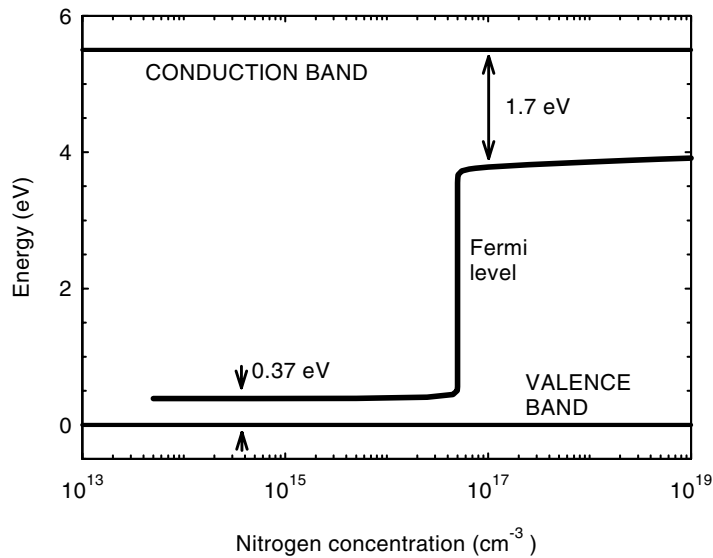
2. Position of the Fermi level

In all of the examples cited the authors have presumably visualized the Fermi level varying with the nitrogen (donor) concentration in the way illustrated for silicon and germanium in standard semiconductor texts (see, for example, figure 4.3 in Smith (1961)). However, the situation is very different in diamond; the donors and acceptors in silicon and germanium are fully ionized at room temperature whereas the nitrogen donors in diamond are hardly ionized at all. To calculate the position of the Fermi level we must therefore, in principle, use the formulae which apply in the carrier freeze-out region.

Boron forms an acceptor in diamond with an ionization energy of 0.37 eV. Some extremely rare natural diamonds exist in which boron is the major impurity at a concentration of typically 5×10^{16} cm⁻³, and such specimens are semiconducting at room temperature (Collins and Williams 1971). If, during the production of HPHT synthetic diamond, a sufficient concentration of nitrogen getters is added to the growth capsule to reduce the nitrogen concentration in the diamonds to less than $\sim 10^{16}$ cm⁻³, the resulting specimens are usually slightly semiconducting because of the accidental presence of boron. Cathodoluminescence measurements on a typical specimen indicated that the uncompensated boron concentration was $\sim 3 \times 10^{16}$ cm⁻³ (Collins *et al* 1990b).

For the purposes of illustration we will assume that all diamonds for which nitrogen is the major impurity also contain some boron, and so can be treated as partially compensated semiconductors. We will consider a diamond with a boron concentration of 5×10^{16} cm⁻³ and calculate how the Fermi level changes with the concentration of single substitutional nitrogen. In the carrier freeze-out region the position of the Fermi level E_F is (Smith 1961)

$$E_F = (E_g - E_D) + k_B T \ln\left(\frac{N_d - N_a}{2N_a}\right) \qquad \text{for } N_d > N_a \qquad (2)$$

Figure 1. Position of the Fermi level as a function of nitrogen donor concentration for a diamond containing 5×10^{16} cm^{-3} boron acceptors, calculated from equations (2) and (3).

and

$$E_{\mathrm{F}} = E_{\mathrm{A}} - k_{\mathrm{B}}T \ln\left(\frac{N_{\mathrm{a}} - N_{\mathrm{d}}}{2N_{\mathrm{d}}}\right) \qquad \text{for } N_{\mathrm{a}} > N_{\mathrm{d}} \tag{3}$$

where E_{g} is the energy gap, E_{D} and E_{A} are the donor and acceptor ionization energies, N_{d} and N_{a} are the donor and acceptor concentrations, k_{B} is Boltzmann's constant and T is temperature. (The equations differ slightly from those in Smith, since we have adopted the more usual convention that energies are measured with respect to zero at the top of the valence band.)

The results are shown in figure 1 which shows clearly that the position of the Fermi level changes only slightly for nitrogen concentrations between 10^{17} and 10^{19} cm^{-3} (0.6–60 ppm). It is unlikely that this small variation can be responsible for the changes in the charge states of the optical centres described above. The position of the Fermi level switches when the nitrogen and boron concentrations are equal, being pinned close to the boron acceptor level below this concentration, and close to the nitrogen donor level above this concentration.

A further phenomenon which has not been addressed previously is that all of the optical centres under consideration can exist in more than one charge state in the same specimen. An elementary interpretation of the Fermi level is that all electron states below this level are filled, and vice versa. This appears not to be the case in diamond, and this may be because, even when it contains nitrogen donors, it is still an insulating crystal. (The probability of ionizing the 1.7 eV donor at and below room temperature is negligible.) We therefore propose that the charge state of a defect depends on its proximity to a nitrogen donor. Centres near a donor will be in the negative charge state, whereas those that are less close will be in the neutral charge state.

3. Dependence on nitrogen concentration

We can gain some insight into this situation by means of a simple model. Suppose we take a simple cubic lattice, with a certain concentration of nitrogen atoms placed randomly at
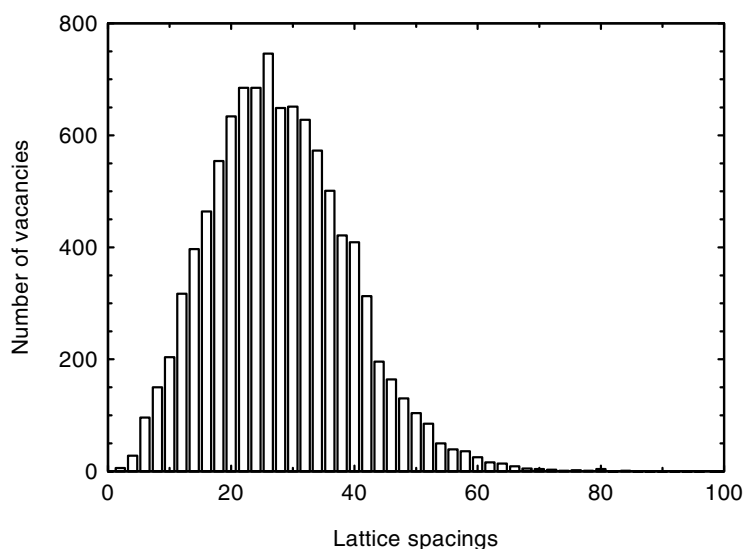
Figure 2. Distribution of the distances between a vacancy and a single substitutional nitrogen atom
for 10 000 vacancies placed at random in a simple cubic lattice containing 10 ppm of nitrogen.
Distances are expressed as a multiple of the lattice spacing.

the lattice points, and introduce a vacancy at a random lattice position. It is straightforward
to calculate the distance from the vacancy to the nearest nitrogen atom. By repeating this
calculation a large number of times we can generate a distribution showing the distances
from the vacancies to the nearest nitrogen atom. Figure 2 shows a histogram generated for
a nitrogen concentration of 10 ppm. This demonstrates that the most probable separation
between a vacancy and the nearest nitrogen atom is 26 lattice spacings, and that approximately
5% have separations between 2 and 10 lattice spacings. (Because N–V centres are not observed
immediately after irradiation we assume that, in an actual diamond, there is an energy barrier
which prevents the formation of a vacancy immediately adjacent to a nitrogen atom. That
restriction has not been included in the simple model here.)

If the calculation is repeated for a nitrogen concentration of 250 ppm we find the most
probable separation between the vacancy and the nitrogen atom is 9 lattice spacings, and almost
60% have separations between 2 and 10 lattice spacings.

Suppose now that a vacancy within 10 lattice spacings of a nitrogen atom acquires a
negative charge and the remaining vacancies are neutral. In the specimen with 250 ppm
of nitrogen more than half the vacancies would be in the negative charge state whereas
in the specimen with 10 ppm of nitrogen approximately 95% of the vacancies would be
neutral. Qualitatively this is exactly what is observed with vacancies produced in a series
of diamonds having different concentrations of single substitutional nitrogen. Furthermore, a
similar behaviour is seen with the ratios of (N–V–N)$^-$:(N–V–N)^0 centres and (N–V)$^-$:(N–V)^0
centres.

4. Other donors and acceptors

To generate figure 1 we considered a diamond containing nitrogen donors and boron acceptors.
Recently it has been shown unambiguously that phosphorus donors can be incorporated into
diamond grown by chemical vapour deposition (Koizumi *et al* 1997, 2000). Furthermore, any

defect to which an electron can be transferred is technically an acceptor, and any defect that can release an electron is technically a donor. We consider such centres in more detail below.

4.1. Phosphorus

The driving force for investigating a range of dopants in diamond is the need to find shallow donors and acceptors in order to fabricate p–n junction devices. Phosphorus can be incorporated into epitaxial layers of CVD diamond at concentrations up to 2.5×10^{19} cm^{-3}. The donor ionization energy determined from Hall effect measurements is ∼600 meV, and this agrees well with optical absorption and photoconductivity thresholds in the infrared spectral region (Koizumi *et al* 2000). For diamond layers in which phosphorus is the dominant defect, and assuming that there are some compensating acceptors, the Fermi level will be pinned at approximately 0.6 eV below the conduction band (equation (2)), and at room temperature the thermal activation of donors will be negligible. To the author's knowledge no radiation damage studies on P-doped diamond have been reported. However, we would expect that the charge-compensation phenomena reported above for nitrogen would be very similar in P-doped diamond, and that, in heavily doped material, vacancies would be present predominantly as V$^-$, and the majority of P–V centres, if they form, would be in the negative charge state.

4.2. The vacancy

In section 1 we have noted that the GR1 and ND1 absorption lines have been attributed, respectively, to V^0 and V$^-$. The early theoretical work of Coulson and Kearsley (1957) calculated stable energy levels by the LCAO method for a vacancy in diamond with three, four or five electrons. In pure diamond they showed (not surprisingly) that the most stable configuration was a vacancy with four electrons (i.e. V^0).

As discussed in section 2, when boron is the major impurity in diamond the Fermi level is pinned at approximately 0.37 eV above the valence band and the material is slightly semiconducting. Optical transitions from the valence band to excited states of the boron acceptor produce absorption bands, at energies just below the ionization threshold, from which the concentration of uncompensated acceptors can be determined (Collins and Williams 1971). When such a diamond is subjected to radiation damage, Dyer and Ferdinando (1966) showed that no GR1 absorption is produced until the boron-related absorption has been destroyed. This suggests strongly that the vacancy is behaving as a donor. Measurements by Collins (1977) showed that very weak GR1 absorption could, in fact, be observed before the boron acceptors were fully compensated. In the context of the present paper we identify the associated GR1 centres as vacancies created too far from a B acceptor for charge compensation to occur. If the majority of the vacancies are indeed behaving as donors we expect to detect optical absorption associated with V$^+$. Recent preliminary work (Newton 2001) has discovered an absorption line in the near-infrared spectral region which appears to have the correct symmetry and annealing behaviour to be identified as a zero-phonon transition at V$^+$.

4.3. Nickel

In diamond grown by HPHT synthesis from a nickel solvent–catalyst, and containing a few hundred ppm of nitrogen, we have noted (section 1) that nickel is present as Ni$_s^-$. A corresponding concentration of nitrogen is compensated by the Ni acceptors and the N$^+$ gives rise to optical absorption at 1332 cm^{-1} (Collins *et al* 1998, Lawson *et al* 1998). When, in a series of diamonds, the nitrogen concentration is progressively reduced until it is less than the

Ni concentration, the Fermi level presumably varies in a similar fashion to that illustrated in figure 1, finally being pinned at the ground state of the Ni_s^-. The energy of this ground state is not currently known, but the absence of electrical conductivity in low-nitrogen diamonds grown from nickel indicates that it is not close to the valence band.

The dominant absorption in low-nitrogen diamonds grown using Ni is the vibronic band with a zero-phonon doublet at 1.40 eV. Measurements by Nazaré *et al* (1991) indicate that it is likely that this transition arises at an interstitial Ni^+.

When diamonds grown using nickel are annealed at HPHT, the nitrogen becomes mobile, and some relaxation around the nickel becomes possible. Initially a neighbouring carbon atom of the Ni_s^- is ejected into an interstitial position, and the Ni_s^- to moves into a semi-divacancy configuration to form the EPR-active defect NE4 (Nadolinny *et al* 1999). In principle, between 1 and 6 nitrogen atoms can be trapped in nearest-neighbour positions around the NE4 core, and five distinct EPR-active defects (NE1, 2, 3, 5, 8), involving two, three or four trapped nitrogen atoms, have been identified. In addition, under these HPHT conditions, single nitrogen donors, with $E_D \sim 1.7$ eV, are uniting to form A aggregates having $E_D \sim 4$ eV. Nadolinny *et al* believe that NE1, NE4 and NE5 are negatively charged, NE2 and NE3 are neutral and NE8 is positively charged. They propose that the equilibrium charge state of these defects is controlled by the position of the Fermi level. However, in diamonds which still have some uncompensated single nitrogen remaining, figure 1 indicates that the Fermi level should not change significantly with HPHT annealing. Following such an annealing the diamonds contain two different nitrogen donors, and a large number of nickel–nitrogen centres, some of which can participate in charge transfer; it seems probable that the mechanism proposed in section 3 will have some influence on the charge state of the defects.

5. Summary

The charge states of many defects in diamonds vary with the concentration of single substitutional nitrogen, with the more negative charge states being favoured at high nitrogen concentrations. However, the calculated position of the Fermi level hardly varies with concentration, as long as nitrogen is the major impurity. Furthermore, many defects can be observed in more than one charge state in the same diamond. We have therefore proposed, because nitrogen-containing diamond is an insulating crystal, that the charge state of a defect depends on its distance from a nitrogen donor. The model explains in a qualitative way why the charge states of defects change with a change in the nitrogen concentration, and accounts for the puzzling, and hitherto unexplained, observation that many optical centres can be present in two different charge states in the same diamond.

Acknowledgment

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