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2002 J. Phys.: Condens. Matter 14 L467

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LETTER TO THE EDITOR

Misidentification of nitrogen–vacancy absorption in diamond

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Received 1 March 2002

Published 14 June 2002

Online at stacks.iop.org/JPhysCM/14/L467

Abstract

The annealing of electron-irradiated type IaB diamond at 1600 °C substantially reduces the concentration of H4 centres, and increases the concentration of H3 centres. In addition, defects are created producing absorption in zero-phonon lines near 536 and 575 nm. Occasionally these same absorption lines are seen at considerable strength in natural brown type Ia diamonds. The interpretation of the annealing behaviour proposes that the H4 centre (four nitrogen atoms and two vacancies) is dissociating to produce smaller defects. The H3 centre, for example, contains two nitrogen atoms and a vacancy, and it has been assumed that the absorption line close to 575 nm is the zero-phonon transition at the neutral nitrogen–vacancy centre. In this work we show that the line, and the line seen for natural brown diamonds, is an independent transition at an unknown defect centre.

There has been renewed interest in the study of the optical properties of defects in diamond following the announcements by General Electric, NovaDiamond and others that the colour of natural brown diamonds can be enhanced by processing at high pressure and high temperature (HPHT)—see, for example, Fisher and Spits (2000), Collins *et al* (2000). The interpretations of the phenomena observed have been based partly on earlier high-temperature annealing studies of diamonds that have been subjected to radiation damage. These data have been obtained on a small number of specimens, and, for that reason, we have repeated some of the investigations to check whether the conclusions reached are true in general, or are specimen dependent. A full account of the work is being prepared for publication, and in this letter we draw attention to an important finding for an electron-irradiated type IaB diamond that has been annealed to 1600 °C.

The various nitrogen-related defects in diamond have been discussed in many previous publications and the details are briefly summarized here. Nitrogen can occur in three dominant forms in diamond—single substitutional nitrogen, the A aggregate, which comprises a nearest-neighbour pair of substitutional nitrogen atoms, and the B aggregate which consists of four

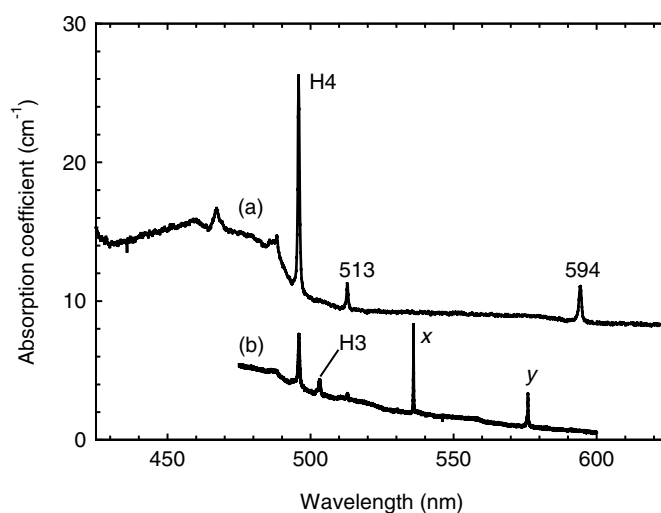


Figure 1. Absorption spectra of an electron-irradiated type IaB diamond following annealing at (a) 900 °C and (b) 1600 °C for 1 h. The spectra were measured at 77 K and have been displaced vertically for clarity.

substitutional nitrogen atoms surrounding a vacancy. Diamonds in which these centres are the major impurity are known respectively as type Ib, type IaA and type IaB. Radiation damage produces vacancies and interstitials, and, following annealing at ≈ 800 °C, the vacancies become mobile and may be trapped at the various forms of nitrogen to form N–V centres in type Ib diamond, H3 centres in type IaA diamond and H4 centres in type IaB diamond.

The negative and neutral charge states of N–V give rise to vibronic absorption/luminescence bands with zero-phonon lines (ZPL) at 637 and 575 nm, respectively. The H3 and H4 centres have vibronic bands with ZPLs at 503 and 496 nm, respectively. Other, minor, nitrogen-related defects are produced by radiation damage and annealing to 800 °C, the most notable of which produces a ZPL in the absorption spectrum at ≈ 594 nm.

Figure 1 shows the absorption spectrum of a type IaB diamond after annealing for 1 h at (a) 900 °C and (b) 1600 °C. The diamond contained ≈ 400 ppm of nitrogen, virtually all in the form of B aggregates. The dominant features after annealing at 900 °C are the H4 vibronic band, a ZPL at 513 nm and the 594 nm ZPL. The latter line anneals out at 1000 °C and, as it anneals, an absorption line known as H1c, with a ZPL at 1936 nm, grows in intensity, as found previously (Woods and Collins 1986). After the anneal at 1600 °C (figure 1(b)), the intensity of the H4 band has decreased substantially, some H3 absorption has been produced and two absorption lines, *x* and *y*, with nominal wavelengths 536 and 575 nm, have appeared. Occasionally these latter lines are seen together in the absorption spectra of natural brown diamonds, particularly those that exhibit pink luminescence when excited with long-wavelength ultraviolet (LWUV) radiation at ≈ 365 nm (Collins 1982a). In figure 2 the absorption spectrum of a natural brown diamond is compared with that of the high-temperature-annealed type IaB diamond. The two sharp lines and the H3 ZPL are common to both spectra. This brown diamond also contained ≈ 400 ppm of nitrogen, virtually all in the form of B aggregates.

These results confirm those obtained by Collins (1982b). In that work it was concluded that, at high temperatures, the H4 centre (four nitrogen atoms plus two vacancies) dissociates to form H3 centres (two nitrogen atoms plus one vacancy) and other products. The finding that H3 is more stable than H4 explained why natural diamonds rarely exhibit H4 absorption,

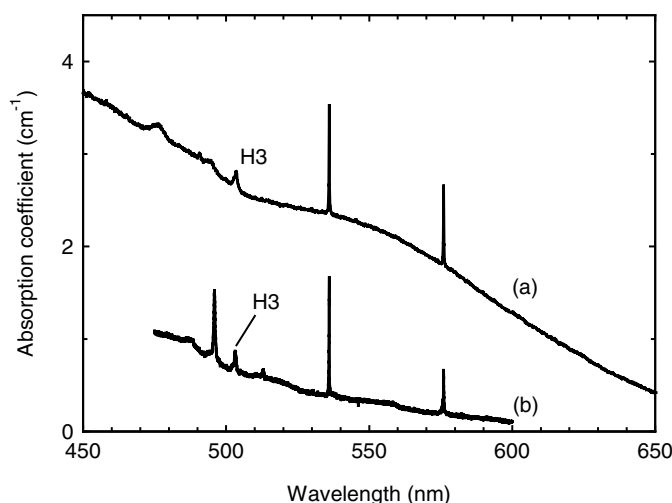


Figure 2. Absorption spectra of (a) an untreated natural brown diamond, redrawn from Collins (1982a), and (b) the electron-irradiated type IaB diamond used in the present investigation, following an anneal at 1600 °C for 1 h. To assist comparison, the absorption coefficients in (b) have been reduced by a factor of 5. The spectra were measured at 77 K and have been displaced vertically for clarity.

even when most of the nitrogen is in the form of B aggregates, whereas H3 absorption is not uncommon in natural brown diamonds. Collins (1982b) also detected some absorption at 637 nm, due to the zero-phonon transition at $(N-V)^-$, in the high-temperature-annealed diamond, and assumed that line γ (shown here in figure 1(b)) was the familiar 575 nm line that is now known to be the zero-phonon transition at $(N-V)^0$. Very weak absorption at 637 nm was also observed in the type IaB diamond used in the present investigation, first appearing after an anneal at 1500 °C.

It seems entirely plausible that N–V centres will form when H4 dissociates. However, careful measurement of line γ shows that it is a structured line with the major component at 575.97 nm (figure 3(a)) and is quite unrelated to the $(N-V)^0$ ZPL at 575.00 nm (figure 3(c)). The natural diamond used to record the spectrum of figure 2(a) is no longer available, but six specimens exhibiting pink luminescence under LWUV excitation, and said to show weak absorption at 575 nm, have been examined. Data for the most strongly absorbing specimen are shown in figure 3(b), and it is clear that the absorption feature is not the $(N-V)^0$ ZPL, but is the same as that observed in the high-temperature-annealed type IaB diamond. This was true for all six specimens.

In figure 4 we compare the cathodoluminescence (CL) spectrum from the natural brown diamond with the absorption spectrum from the high-temperature-annealed type IaB diamond. $(N-V)^0$ centres are very efficiently excited using CL, but, in fact, we observe that the only emission in this region originates from the 576 nm feature.

In their study of natural brown, nominally type IIa, diamonds (i.e. those specimens with a very low nitrogen concentration) that had been colour enhanced by HPHT annealing, Fisher and Spits (2000) drew attention to the fact that photoluminescence spectra at around 575 nm consisted of two lines at 574.8 and 575.8 nm in 8 of the 16 diamonds that they examined. Among the untreated specimens, colourless diamonds did not show any luminescence at 575.8 nm, but pale brown stones usually had both lines present. They also suggested that the luminescence

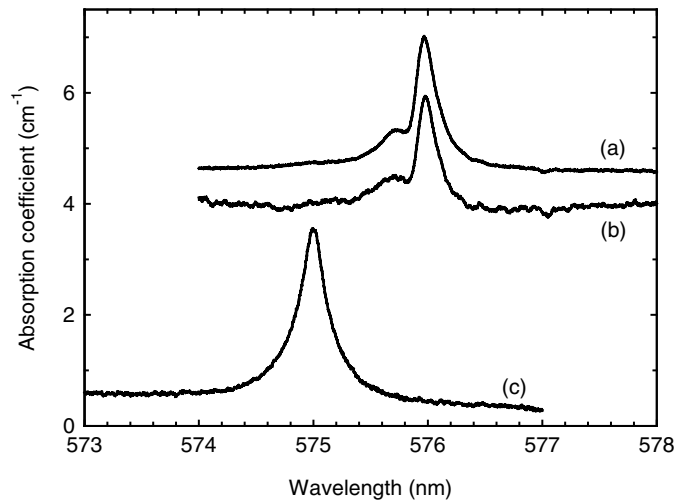


Figure 3. Absorption spectra near 575 nm for (a) the electron-irradiated type IaB diamond, following an anneal at 1600 °C for 1 h, (b) an untreated natural brown type IaB diamond and (c) a low-nitrogen region in an electron-irradiated synthetic type Ib diamond, after annealing at 800 °C for 1 h. To assist comparison, the absorption coefficients in (b) have been increased by a factor of 7. The spectra were measured at 77 K and have been displaced vertically for clarity.

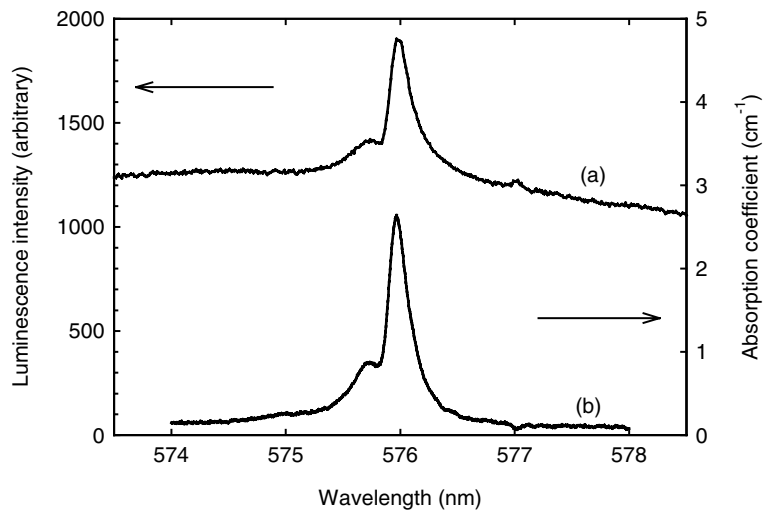


Figure 4. (a) The cathodoluminescence spectrum for the untreated natural brown type IaB diamond compared with (b) the absorption spectrum for the electron-irradiated type IaB diamond, following an anneal at 1600 °C for 1 h.

line observed at a nominal wavelength of 575 nm by Jorge *et al* (1983) could be the 575.8 nm line. The measurements that we report in this letter show that this is almost certainly the case. The slight differences between the wavelengths quoted by Fisher and Spits and those given in the present study are probably instrumental. Here we give the wavelengths in air, calibrated with respect to the mercury yellow line at 576.96 nm, and believe that the uncertainties do not exceed ± 0.05 nm.

The defects responsible for the absorption lines at 536 and 576 nm are not known. Anderson (1962) first noted that diamonds showing 575 nm luminescence may also display an emission line at 536 nm, and Fisher and Spits (2000) report observing both of these lines in the luminescence spectra of some natural brown diamonds and some colour-enhanced specimens. However, Smith *et al* (2000) found that, after HPHT processing, the 536 nm luminescence disappeared in the specimens that they investigated.

The HPHT annealing of natural brown diamonds releases vacancies, which then form nitrogen–vacancy complexes (Collins *et al* 2000). In nature, similar processes occur at lower temperatures (perhaps 1200 °C) over very extended time periods ($\sim 10^9$ years). The 575.97 nm transition is observed in absorption and luminescence in natural brown diamonds containing the B form of nitrogen, and in type IaB diamond which has been subjected to irradiation damage and annealed at 1600 °C. A radiation damage product and the B form of nitrogen therefore appear to be essential prerequisites. The nature of the defect is unknown, but the present investigation has demonstrated that the feature is unrelated to the zero-phonon transition at $(N-V)^0$.

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