Optical transitions at the substitutional nitrogen centre in diamond

LETTER TO THE EDITOR

Optical transitions at the substitutional nitrogen centre in diamond

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Abstract.   Optical transitions at the single substitutional nitrogen centre (P1) in synthetic diamond are discussed. It is shown that the 4.6 eV absorption band is not due to P1, but due to some other centre, tentatively suggested as a nitrogen–boron complex. The 4.5 eV photocurrent threshold is assigned to the transition from the valence band to the ground state of the P1 centre.

It is widely accepted that nitrogen is a dominant impurity in diamond. While in natural diamond, due to the very long synthesis time, it is present dominantly in the aggregated state, in synthetic diamond nitrogen mainly forms the single substitutional (the so-called P1) centre. This centre is a donor with thermal and optical ionization thresholds at 1.7 eV and 2.2 eV, respectively (Walker 1979, Rosa *et al* 1999), the difference in ionization energies being attributed to a pseudo-Jahn–Teller effect (Lannoo 1982). The P1 centre has a characteristic IR spectrum (see figure 1(a)), with a sharp peak at 1344 cm^{-1} and a band at 1130 cm^{-1}, absorption of 1 cm^{-1} at 1130 cm^{-1} corresponds to 25 ppm of P1 centres (Walker 1979). Diamonds containing nitrogen mainly as the P1 centres (Ib type) show a broad absorption band centred at 4.6 eV accompanied by some sharp zero-phonon lines (ZPLs). This feature was found to consist of vibronic bands due to trigonal centres with ZPLs at 4.059 and 4.567 eV (Nazare and Neves 1987). Linear correlation between the concentration of P1 centres and the intensity of absorption at 4.6 eV was also observed (Nazare and Neves 1987). It was deduced that the same amount of P1 centres produces absorption at 4.6 eV 45 times larger than at 1130 cm^{-1}, which suggested the use of UV absorption as a convenient tool for determination of P1 centre concentration. Photocurrent spectra, instead, reveal a threshold at 4.5 eV (Rohrer *et al* 1996, van Enckevort and Versteegen 1992), which is currently unassigned.

    For the moment, there exist no plausible model for the 4.6 eV band. On the basis of stress results, this band was assigned to transitions between the ground state of P1 centres and the valence band (Koppitz *et al* 1986). This was questioned by Nazare and Neves (1987), because such transitions should have not any narrow lines. In addition, the ground state of a centre with a ZPL at 4.567 eV should be at least 4.6 eV from the conduction band (CB), which does not fit the P1 centre. Moreover, the phonon modes of the 4.05 eV and 4.567 centres, 60 and 120 meV, or 968 and 484 cm^{-1} (Nazare and Neves 1987), do not correspond at all to the modes observed in the IR spectrum from the P1 centre.

    In this letter we report on the optical and electrical characterization of the P1 centre in synthetic diamond. It is shown that the 4.6 eV absorption band is not due to P1, but due to some
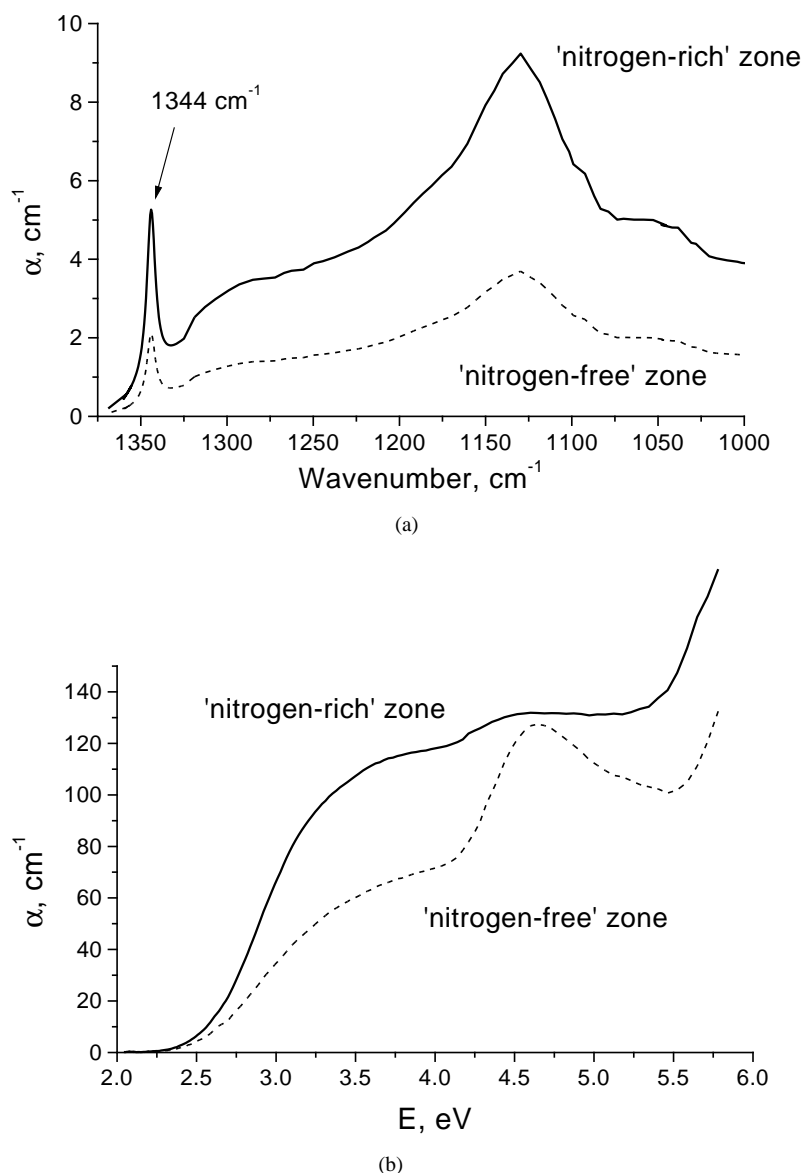
Figure 1. IR (a) and UV–visible (b) absorption spectra from different zones of HPHT diamond.

other centre, tentatively suggested as an N–B complex. The 4.5 eV photocurrent threshold is assigned to transitions from the valence band (VB) to the ground state of the P1 centre.

Crystals of Ib high-pressure high-temperature (HPHT) diamond were purchased from Drukker International. Optical absorption measurements show that they contain predominantly P1 centres with no other defects detectable. Photoluminescence (PL) measurements reveal minute amounts of nitrogen–vacancy (N–V) and N–V–N centres that can be attributed to the high sensitivity of this technique. Optical window quality diamond films were grown by the microwave-assisted chemical vapour deposition (CVD) technique at the IMO, Diepenbeek, Belgium (Rosa *et al* 1999). They were grown on Si substrates, which were then removed

by chemical etching in HNO_3:HF mixture. Typical growth parameters were as follows: microwave power 5 kW, substrate temperature 800 °C, gas mixture 1:99 CH_4:H_2 flowing with a rate of 300 cm^3 min^{-1}. Control over nitrogen doping of CVD samples was performed by changing the ambient pressure in the growth chamber before the deposition. Resulting samples were free-standing thick (0.5–1 mm) polycrystalline films, with large (>10 μm), randomly oriented grains. Absorption and photoconductivity measurements have been performed at room conditions using a standard one-beam absorption spectrometer. In order to minimize elastic light scattering in CVD films in absorption measurements, samples were placed on top of a detector.

Representative absorption spectra from Ib-type HPHT diamond in the IR and UV–visible range are shown in figures 1(a) and (b). Such IR spectra are standard for Ib diamond, and thus the absorption at 1130 cm^{-1} was utilized for determination of the P1 centre concentration. Nitrogen-induced IR absorption in CVD films was too low to be detected. The concentration of the P1 centres in CVD films was measured (Rosa *et al* 1999) by electron spin resonance (ESR). UV–visible spectra from Ib diamond show a well known threshold at 2.2 eV and a broad band at 4.6 eV. While a linear correlation between absorption at 2.7 eV due to the 2.2 eV threshold, and at 1130 cm^{-1} was observed, in agreement with results of Sobolev *et al* (1969), no correlation was found between absorption bands at 4.6 eV and at 1130 cm^{-1}. A characteristic example is shown in figures 1(a) and (b): absorption in a dark yellow zone of a HPHT crystal shows a much weaker 4.6 eV band than the spectrum from a light yellow one, while the absorption strengths in the ranges 2.0–4.0 eV and 1360–1000 cm^{-1} change proportionally in those sample areas. Similar anticorrelations can be seen in results of Collins *et al* (1990), while in the works of Vandevelde *et al* (1998) and Rohrer *et al* (1996) the 4.6 eV band was not detected in HPHT diamond crystals. The mentioned light and dark yellow zones are certainly different growth sectors of the crystal, most probably cubic and octahedral, respectively, according to visual examination. Absorption (see figure 1) and PL measurements revealed much lower content of nitrogen and nitrogen-related complexes (N–V, N–V–N) in the light zones relative to the dark ones. Therefore, these parts of a sample will be further referred to as 'nitrogen-free' and 'nitrogen-rich'.

Figure 2 shows absorption spectra in two CVD films, A and B, and their difference. Those films were grown at the same conditions; they have similar thickness and morphology; however, due to the different ambient pressure in the growth chamber film A has 10 ppm of P1 centres, while in film B nitrogen contamination was undetectable by ESR and PL. The spectrum from the P1 centre in film A is obscured by light scattering and some background absorption, but, after subtraction of spectrum B from spectrum A, background bands are removed, and a spectrum appears that is identical to the one from a light-coloured zone of the HPHT crystal (see figure 1(b)).

Results shown in figure 1 suggest that the 4.6 eV band is not due to the P1 centre, but due to some other defect. This defect is not observed by ESR. It does not show ionization thresholds either to the conduction or to the valence band, and is therefore probably not a donor or acceptor, but rather a neutral defect. It shows some correlation with nitrogen and is present in CVD diamond. It is widely accepted that due to the low growth temperatures CVD diamond does not contain nitrogen complexes. Therefore, the centre responsible for the 4.6 eV band must involve one nitrogen atom. This centre has C_{3v} symmetry (Nazare and Neves 1987), leaving two possible structures: one nitrogen atom surrounded by three vacancies or impurities (N–X–X–X), or an N–X complex. The first structure is rather improbable in CVD diamond. Optical transitions at the nitrogen–vacancy (N–V) defect are well known and were not observed in any of the samples studied here. Thus, X must be some impurity. The most likely candidate is boron, since it easily incorporates in diamond and can form three bonds
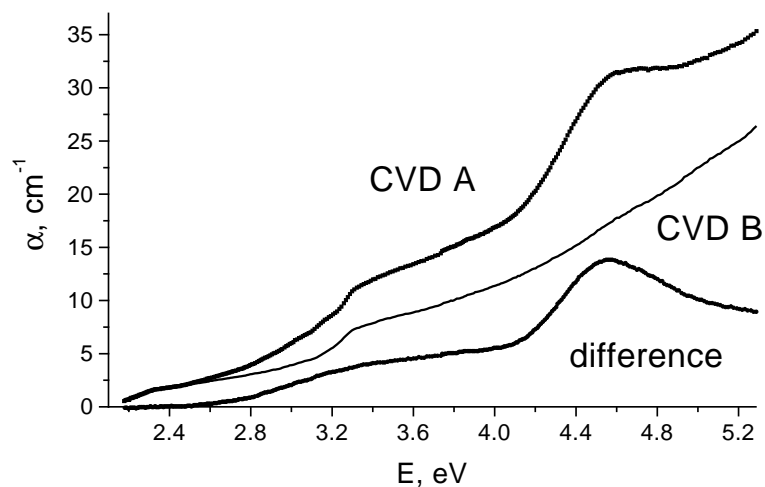
Figure 2. Absorption spectra from two similar CVD films, A and B, differing only in nitrogen content, and the differential spectrum.
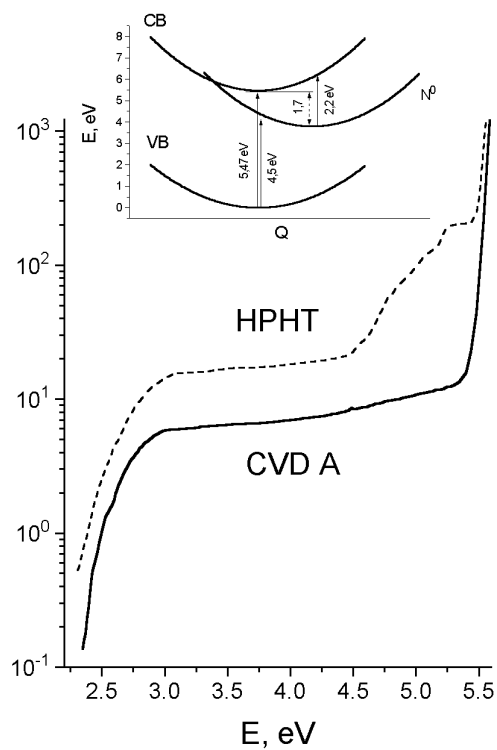

Figure 3. Normalized photoconductivity spectra in HPHT and nitrogen-doped CVD diamond. The inset shows the proposed model for observed thresholds.

with neighbouring carbon atoms, maintaining the C_{3v} symmetry. Nevertheless, although the suggested N–B model for the 4.6 eV band is plausible and satisfies all above criteria, it should be considered as tentative.

Typical photoconductivity spectra from HPHT diamond and nitrogen-doped CVD film are shown in figure 3. The spectrum from HPHT diamond shows strong (note a semilogarithmic

scale) thresholds at 2.3 eV and 4.5 eV; the latter is not seen in CVD film. The 4.5 eV threshold was observed in all HPHT crystals studied, both in the nitrogen-free and nitrogen-rich zones, mentioned earlier. The photocurrent threshold at 2.3 eV is also observed in absorption and is assigned to the ionization of the P1 centre (Walker 1979, Rosa *et al* 1999), while the second one is absolutely absent in absorption spectra, measured on the same sample. Since photocurrent value depends not only on absorption coefficient, but also on the lifetime of the carrier, the most plausible explanation for the 4.5 eV threshold is a weak absorption transition creating long-lived carriers. Since the 2.3 eV threshold is ascribed to the excitation of electrons, the 4.5 eV one should be then assigned to the excitation of holes, which may have a large relaxation time in HPHT diamond. The absence of this 4.5 eV threshold in polycrystalline CVD films may be due to abundant structural defects, acting as efficient hole traps. Indeed, a relaxation time of about 1 ns for hole photoconductivity in CVD diamond was reported (Nebel *et al* 1998). We observe a good correlation between the appearance of the 4.5 eV photoconductivity threshold and the increase in P1 content, in accordance with results of Rohrer *et al* (1996) and van Enckevort W J and Versteegen (1992). This threshold can be naturally explained by the transition from the valence band to the unoccupied P1 centre, as shown by the inset in figure 3.

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