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2001 J. Phys.: Condens. Matter 13 6015

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Trapping of vacancies by defects in diamond

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Received 9 February 2001

Abstract

Optical absorption measurements were performed on irradiated diamonds containing different concentrations of nitrogen defects. Analysis of the results suggests that the single substitutional nitrogen centres trap vacancies about eight times more efficiently than the substitutional nitrogen pairs. In irradiated diamond crystals with a low impurity content, as well as in synthetic diamond films, an undocumented IR spectrum is observed and ascribed to intrinsic defects.

Nitrogen is a dominant impurity in diamond. In synthetic diamonds it is mostly present as single substitutional atoms (N_S or C centres), but the vast majority of natural stones contains nitrogen predominantly in the form of A and B centres, which are believed to be an N_S-N_S pair and a complex of four substitutional nitrogen atoms around a lattice vacancy, respectively (Davies 1999). Laboratory annealing at temperatures above 1500 °C results in the conversion of the C nitrogen first to the A and then to the B form. The conversion rate is much higher in samples containing larger concentrations of vacancies (Collins 1980) or/and transition elements, like Ni and Co (Kiflawi *et al* 1997). During annealing the A, B and C centres effectively trap vacancies forming $2N_S-V$, $4N_S-2V$ and N_S-V centres, respectively. Their $[2N_S-V]^0$ and $[4N_S-2V]^0$ charge states have been associated with the absorption systems with zero-phonon lines (ZPLs) at 2.463 eV (H3 centre) and 2.498 eV (H4 centre), respectively; the 1.945 eV absorption system was assigned to the $[N_S-V]^-$ complex (Davies 1999).

In order to understand the nitrogen aggregation process it is important to know the relative rates of a vacancy capture by the A, B and C centres. This question was addressed in papers by Collins (1980) and Lawson *et al* (1992). In those studies the diamonds, where the concentration of nitrogen in the A, B and C forms was known from IR absorption, were electron irradiated and annealed at temperatures high enough for vacancies became mobile. From the relative strengths of the H3, H4 and 1.945 eV absorption lines it was deduced that the C nitrogen traps vacancies a factor of about 20 more efficiently than the A and 80 times faster than the B centres. In the analysis it was assumed that the absorption at the 2.463 eV, 2.498 eV and 1.945 eV ZPLs is proportional to the concentrations of the $2N_S-V$, $4N_S-2V$ and N_S-V centres, respectively. However, later studies revealed the existence of charge states other than $[2N_S-V]^0$ and $[N_S-V]^-$: ZPLs at 1.257 eV and 2.156 eV were associated with the $[2N_S-V]^-$ and $[N_S-V]^0$ centres

(Mita *et al* 1990, Iakoubovskii *et al* 2000), respectively. As they were not taken into account in the previous studies (Davies 2000) there is a clear need for the reconsideration of the obtained results, and therefore, the present work reports corrections to the relative vacancy capture rates by the C and A centres.

The monocrystalline diamond samples used in this study were grown by the high-pressure high-temperature (HPHT) technique. The first sample, mentioned hereafter as Ib/IaA, contained 60 ppm of the C centres, as deduced from the 1130 cm^{-1} IR absorption peak, and <0.5 ppm of other nitrogen defects. It was annealed in H_2 plasma at 1850°C for 30 min using the set-up designed for chemical vapour deposition (CVD) of diamond (Iakoubovskii *et al* 2000). As a result, 10 ppm of C centres was converted to the A form. The relatively low conversion rate for a low-pressure annealing (Kiflawi *et al* 1997) is probably due to the very small concentration of vacancies and transition metal atoms in the sample (well below 0.1 ppm), as deduced from the strength of the corresponding photoluminescence signals. The second sample, referred to as Ib, contained 10 ppm of the C centres. In the third (IIa) crystal the nitrogen content was below 1 ppm. All samples were irradiated by a dose of 10^{18} (MeV neutrons) cm^{-2} at the Research Reactor of Moscow Engineering Physics Institute. Subsequent annealing treatments were performed in the temperature range $300\text{--}1200^\circ\text{C}$ and a vacuum of 10^{-6} Torr.

Polycrystalline diamond films were grown by the microwave-assisted CVD technique, as described elsewhere (Iakoubovskii *et al* 2000, Iakoubovskii and Adriaenssens 2000). Some samples were grown on Si, which was removed by etching in HF:HNO_3 1:1 mixture after the deposition. Other samples were grown on natural IIa diamonds in a Si-free reactor. IR absorption was measured with a commercial Fourier-transform IR spectrometer at 300 K. Visible absorption spectra were recorded with a home-built spectrometer at 77 K. The concentrations of the vacancy-related defect centres were determined by integration of the corresponding ZPLs using the calibrations of Davies (1999). The oscillator strength of the H2 centre was assumed to be equal to that of the H3 ZPL, relying on the result of Mita *et al* (1990) that additional illumination produces equal increase in the $[\text{2N}_S\text{-V}]^-$ and decrease in the $[\text{2N}_S\text{-V}]^0$ absorption signals.

The optical absorption spectrum in the range 1.25–2.6 eV is shown for the sample Ib/IaA in figure 1. The sample was annealed at 650°C for 16 h after the irradiation. This annealing was expected to result in the complete removal of the isolated vacancies; however, a ZPL at 1.673 eV due to the V^0 centres is still seen in the spectrum. Also present are ZPLs at 1.257 eV ($[\text{2N}_S\text{-V}]^-$), 1.77 eV, 1.945 eV ($[\text{N}_S\text{-V}]^-$) and 2.085 eV with the associated vibronic bands. The 1.77 eV and 2.085 eV lines originate from some interstitial-related defects (Nisida *et al* 1989) and will not be discussed here. The presence of the 2.463 eV ($[\text{2N}_S\text{-V}]^0$) line was revealed after the background subtraction, as shown by the inset in figure 1. Integration yielded the concentrations of 0.07, 0.16, 7.9 and 0.12 ppm for the $[\text{2N}_S\text{-V}]^-$, V^0 , $[\text{N}_S\text{-V}]^-$ and $[\text{2N}_S\text{-V}]^0$ centres, respectively. The 2.156 eV line was undetectable in this sample, probably because only a small part (10 out of 50 ppm) of the N_S centres was converted to the $\text{N}_S\text{-V}$ complexes. Consequently, the Fermi level before and after the irradiation and annealing is determined by the N_S^0 donors, which pin the Fermi level at the position 1.7 eV below the conduction band, thus determining the preponderance of $[\text{N}_S\text{-V}]^-$ over $[\text{N}_S\text{-V}]^0$ centres (Iakoubovskii and Adriaenssens 2000). Meanwhile, in the sample Ib with the lower N_S content (10 ppm) the 2.156 eV absorption line was clearly seen after the same irradiation and annealing treatment.

From the deduced concentrations of the $2\text{N}_S\text{-V}$ and $\text{N}_S\text{-V}$ centres, taking into account the initial concentrations of the A (10 ppm) and C (50 ppm) centres, we conclude that the single nitrogen centres capture vacancies 8 ± 3 times more efficiently than the nitrogen pairs. The

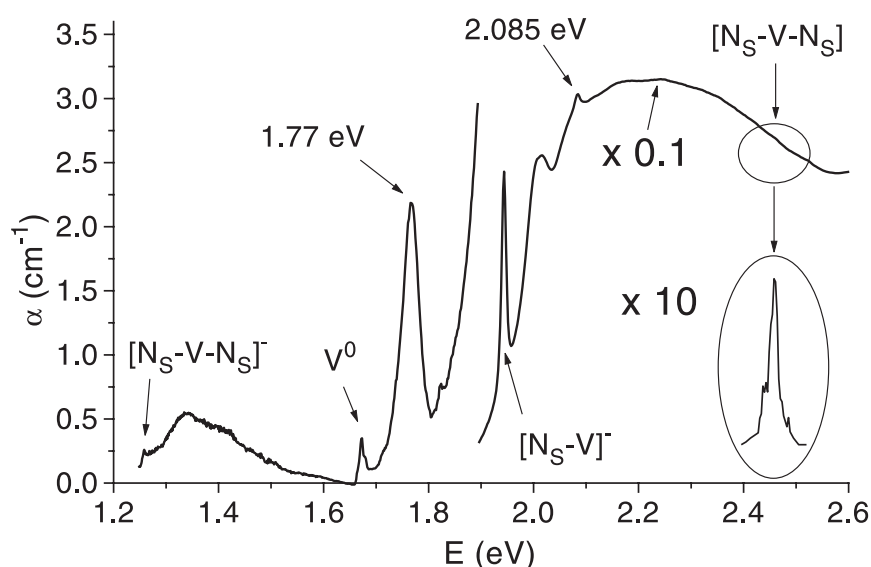


Figure 1. Optical absorption spectrum (77 K) from the sample Ib/IaA, neutron irradiated and annealed at 650 °C for 16 h. The inset shows the magnification of the spectrum around the 2.463 eV line with the background subtracted.

error originates from the uncertainties in the calibration coefficients (Davies 1999) and in the determination of the baseline under the absorption peaks.

The defect size decreases in the row of B, A and C nitrogen centres, and one might expect the decrease in the rate of vacancy trapping by those defects. Instead, an increase in the trapping rate is observed experimentally. It correlates with the strain induced in the lattice by nitrogen, which is also increased in the row of B, A and C defects (Lang 1994). Therefore, the mentioned variation in the trapping rate probably reflects the tendency to relieve the strain around the nitrogen centres in diamond via the capture of a vacancy.

Figure 2 presents IR absorption spectra measured on the sample IIa (curve 1) and two CVD films (curves 2 and 3). The IIa diamond was annealed at 800 °C for 2 h after the irradiation. The two-phonon lattice absorption bands around 2100 cm^{-1} are seen in all curves. Curve 1 also reveals an undocumented spectrum composed of two peaks at 802 and 1262 cm^{-1} and a broader feature around 1050 cm^{-1} . In the irradiated HPHT and natural diamonds these lines could only be observed if the concentration of nitrogen in any form was less than the concentration of vacancies produced by the irradiation. The intensity of the spectrum could be significantly increased by annealing at temperatures where vacancies become mobile (above 500 °C) and it was further unchanged by annealing at 1200 °C for 2 h. The relative intensities of all features in the spectrum were similar in different samples; however, it is not clear whether they originate from one defect or whether several accompanying centres contribute to the spectrum. Its intensity is relatively large, suggesting that the spectrum originates from some as yet unknown intrinsic defects which are a dominant irradiation product in impurity-free diamond.

The spectrum was also observed with a relatively high intensity in many as-grown CVD diamond films, synthesized in the Si-free and Si-containing reactors, suggesting that the same structural defects are present in unirradiated CVD diamond on the level of tens of ppm. A further factor determines the importance of this finding for the studies of CVD diamond: the spectrum contains a peak at 802 cm^{-1} , whose position and width are very similar to those of the

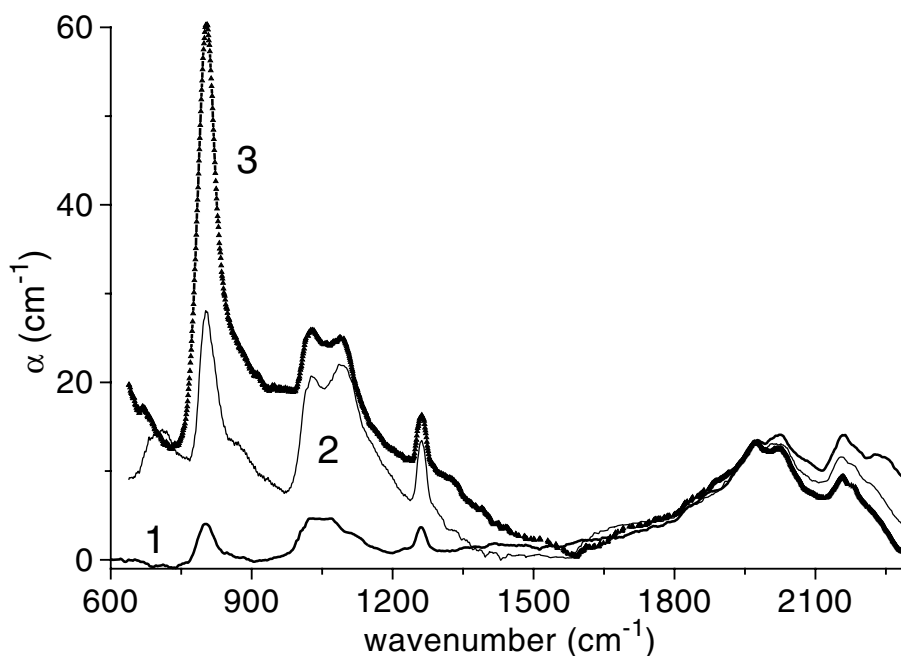


Figure 2. IR absorption spectra measured on the sample IIa (curve 1) and two CVD films (curves 2 and 3). The IIa diamond was annealed at 800 °C for 2 h after the neutron irradiation.

IR absorption peak in cubic and hexagonal SiC. The intensity of this peak is routinely used to estimate the thickness of the interfacial SiC layer between the Si substrate and CVD diamond film (Iakoubovskii and Adriaenssens 2000). The results of figure 2 show that although the SiC absorption may indeed contribute to the 802 cm^{-1} peak (see curve 3), the separation of the contributions from the SiC layer and intrinsic defects is not straightforward. This result also explains our failure to reduce the 802 cm^{-1} peak by polishing the substrate side of CVD film (Iakoubovskii and Adriaenssens 2000).

Acknowledgments

The authors are indebted to N N Dogadkin for reactor irradiation, to M Nesladek and Y K Vohra for provision of CVD samples, to F Meersman for the use of FTIR spectrometer and to the FWO (grant G.0014.96) for financial support.

References

- Collins A T 1980 *J. Phys. C: Solid State Phys.* **13** 2641
 Davies G 1999 *Physica B* **273/274** 15
 ——— 2000 Private communication
 Iakoubovskii K, Adriaenssens G J and Nesladek M 2000a *J. Phys.: Condens. Matter* **12** 189
 Iakoubovskii K and Adriaenssens G J 2000b *Diamond Relat. Mater.* **9** 1349 and references therein
 Iakoubovskii K, Adriaenssens G J and Vohra Y K 2000 *J. Phys.: Condens. Matter* **12** 189
 Kiflawi I, Kanda H, Fisher D and Lawson S C 1997 *Diamond Relat. Mater.* **6** 1643
 Lang A R 1994 *Properties and Growth of Diamond* ed G Davies INSPEC p 106
 Mita Y, Kanehara H, Adachi Y, Nishida Y, Okada M and Kobayashi M 1990 *J. Phys.: Condens. Matter* **2** 8567
 Nisida Y, Mita Y, Mori K, Okuda S, Sato S, Yazu S, Nakagawa M and Okada M 1989 *Mater. Sci. Forum* **38–41** 561