Lattice relaxation at V^-, NV^-, and NVN^- defects in diamond investigated by positron annihilation

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Abstract
Experimental positron lifetime data for three vacancy-related defects in synthetic type Ib
diamonds with well known structures are uniquely suitable for comparison with theoretical
investigations of lattice relaxation.

Lattice relaxation around a defect is an important part of its characteristics and has been calculated using many different schemes which resulted in many different relaxations. Experiments should narrow down theoretical models, but only a few methods are sensitive to lattice relaxation. Magnetic resonance methods and optical absorption (in particular in the case of diamond) have been used to demonstrate relaxation caused by externally applied stress. Positron annihilation is a more general technique in the sense that the positron lifetime depends on the average electron density locally at the defect, and hence essentially detects 'breathing mode' relaxation.

Gilgien *et al* [1] showed that in calculating positron annihilation characteristics in GaAs the positron lifetime is much influenced by the *outward* lattice relaxation that a positron causes when trapped by a vacancy. Later theoretical works [2, 3] expanded Gilgien *et al*'s self-consistent approach to Si, Ge, GaN, and four metals. In the most investigated cases of Si and GaAs the theoretical models yield bulk lifetimes that are 10–20 ps smaller than experimental values [4, 5]. In GaAs Gilgien *et al* [1] calculate the positron lifetime for V_{As}^- to be 254–261 ps, whereas Makkonen and Puska [3] predict no trapping: trapping by V_{Ga}, however, occurs with a binding energy of 0.39–0.46 eV, giving a positron lifetime of 234–237 ps [3]. Experimental values for vacancies are close to 260 ps [4] with a positron binding energy of 0.3 eV [6]. In the case of Si the theoretical positron lifetime for the monovacancy of 260 ps [3] agrees well with experiment, but the binding energy is *negative*, in contrast to experiment [7].

The discords between theory and experiment may in part arise from the fact that the defect types suggested by experimental positron data were not verified by independent methods, with the only arguable exception being the divacancy

in silicon [8]. Contrasting semiconductors, diamond is an ideal choice for independent defect identification since optical zero-phonon absorption lines arising from well known vacancy-type defects can be correlated with positron results on the very same samples [9].

The samples were synthetic high-pressure high-temperature single crystalline type Ib diamonds with a concentration of 80–100 ppm substitutional nitrogen calculated from the calibration by Kiflawi *et al* [10]. The samples were irradiated at 80 K with a 12 MeV scanning proton beam to a fluence of 2.5×10^{16} cm^{-2} accumulated during 8 h; after irradiation the samples were returned to room temperature. The protons penetrated the 0.35 mm thick samples.

Results from positron measurements are based on a total of at least 7×10^7 counts, which makes possible a very accurate determination of positron lifetimes and their intensities. The lifetime spectrometer had a full-width at half-maximum of 200 ps, and the time calibration was 6.44 ps per channel. The 0.8 μm thick Al-encapsulated positron source had a strength of 15 μCi. Two-term least squares fits [11] were adequate (χ^2 values of 1.1 ± 0.1) for the unirradiated samples as well as for the variously annealed irradiated samples. In the former case the dominant lifetime component, with an intensity of 96.5%, had the bulk value as 99 ± 1 ps, and the other lifetime component, with an intensity of 3.5%, had a value of 345 ± 20 ps; this lifetime may arise from the positron source, but could also be a contribution from grown-in vacancy clusters. For the irradiated samples the dominant ($>98\%$) lifetime component had values between 132 and 148 ps and a weak ($<2\%$) component which randomly scattered between 300 and 360 ps. This lifetime component is necessary to obtain statistically good fits, and may in part be related to the positron

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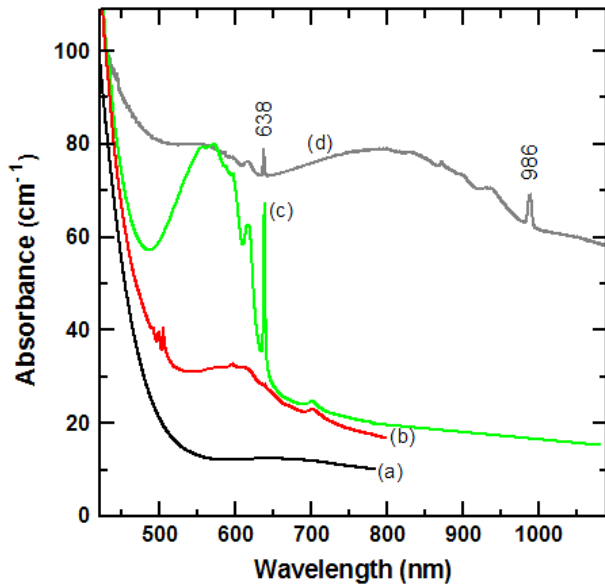
Figure 1. Optical absorption spectra at 80 K for type Ib diamond: (a) unirradiated, (b) as irradiated, (c) irradiated and annealed at 830 °C, and (d) further annealed to 1585 °C. Spectrum (d) is displaced vertically for the sake of clarity.

(This figure is in colour only in the electronic version)

source, but has little effect on the main lifetime component. Annealing of the samples was done in flowing He ambient at normal pressure.

Figure 1 shows optical absorption spectra for one of the samples subjected to three stages of treatments. Absorption due to the irradiation-produced negatively charged monovacancy, V^-, with a zero-phonon line at 394 nm [12], is obscured by the absorption from substitutional nitrogen (curve (a) in figure 1). The zero-phonon line at 638 nm and its vibrational sideband at shorter wavelengths is due to NV^- formed by migration of V^- to substitutional nitrogen, and the line at 986 nm is due to NVN^- (labelled the H2 centre). For the sake of completeness, it is noted that absorption from neutral vacancies (at 741 nm), or from neutral divacancies (at 488 nm), was too weak for observation.

Figure 2 shows in panel (a) the absorption of NV^- at 638 nm as a function of annealing temperature (1/2 h per annealing step), and in panel (b) the (Gaussian) full-width at half-maximum. The kinetics for the formation of NV^- between 600 and 800 °C yields an activation energy of 2.7 ± 0.2 eV (assuming a first order process), in good agreement with the result obtained by Davies *et al* of 2.3 ± 0.3 eV [13]. Above 1400 °C absorption due to NV^- decreases and the absorption from NVN^- appears, but the kinetics of formation is not as simple as in the case of NV^- because of the simultaneous agglomeration of nitrogen atoms.
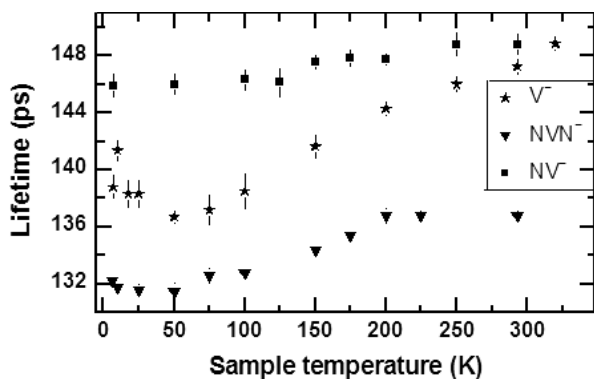
Positron lifetime results for the irradiated samples identical to those used for the optical measurements are shown in panel (c) of figure 2. As V^- forms NV^- the positron lifetime decreases by 2–4 ps, and after NVN^- was formed the lifetime decreased by ~10 ps. Nearly all of the latter decrease, however, occurs *before* the optical absorption from NV^- decreases (note, for example, the data points at 1400 °C),
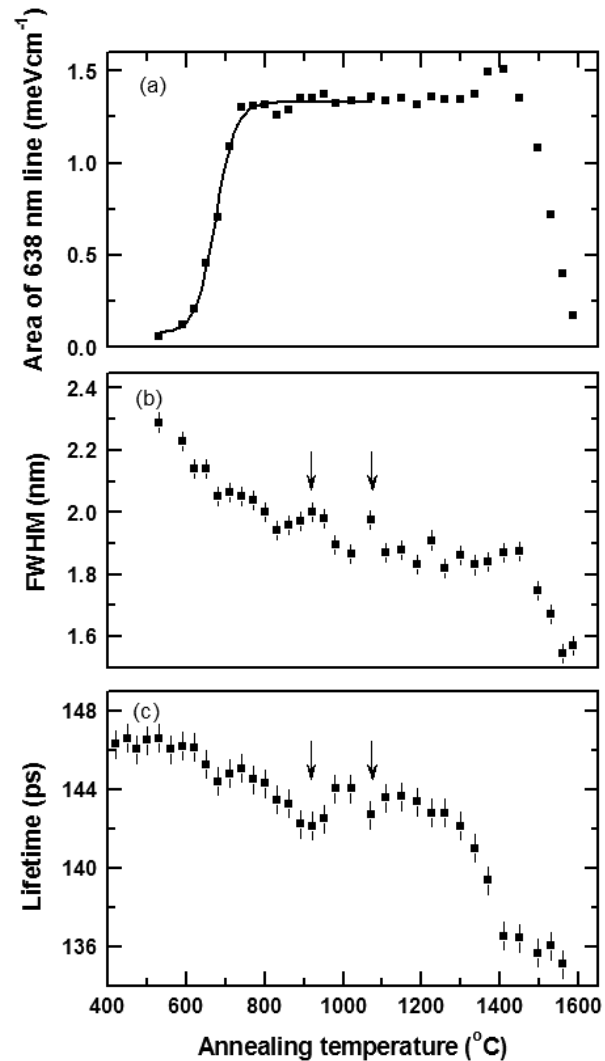
Figure 2. (a) Integrated absorption of the 638 nm line for the NV^- defect as a function of isochronal annealing. The curve fitted to the data is a sigmoidal fit. (b) Full-width at half-maximum of the 638 nm absorption line. (c) Radiation-produced positron lifetime measured at room temperature on the same sample as used for the optical data. Arrows indicate local extrema.

indicating that positrons are sensitive to the second nitrogen atom before it is being detected by optical absorption. It is noteworthy that in the 800–1200 °C range, where only NV^- is present, the positron lifetime and FWHM are not constant. Particularly large FWHM values, as indicated by short vertical arrows in figure 2(b), correlate with particular small lifetime values, which suggests that more than one configuration of the NV^- defect exists.

It is clear from figure 1 that NV^- persists after annealing at 1585 °C; in fact 13% of the concentration at lower temperatures remains. Adjusting for this unresolvable contribution, the proper lifetime for the NVN^- complex is 2 ps lower than shown by the experimental data in figures 2 and 3. It is also clear (cf figure 1) that as-irradiated samples contain NV^- after *proton* irradiation in contrast to electron irradiation, but the effect on the positron lifetime for V^- is estimated to be less than 0.3 ps and hence of minor significance.

Figure 3. Positron lifetimes as a function of temperature for the samples whose optical absorption spectra are shown in figure 1. The legend indicates the *dominant* defect in the three cases of annealing, i.e. V⁻ (as irradiated), NV⁻ after annealing at 830 °C, and NVN⁻ after annealing at 1585 °C. Note that due to the 13% admixture from NV⁻ the lifetime for NVN⁻ is calculated to be lower by 2 ps than shown in the figure.

The temperature dependences shown in figure 3 greatly exceed that expected from thermal expansion [14], which is an increase of 0.2 ps between 7 and 300 K. Several calculations [15–19] *without* the positron yield a 10–12% outward relaxation for the three defects. In the absence of positron-induced relaxation, the lifetimes for the three defects at least at 7 K should have been very much the same, and this not being the case suggests positron-induced relaxation, which may also be responsible for the temperature dependences shown in figure 3. The relaxation in diamond contrasts the commonly calculated inward relaxation in semiconductors such as Si [19], and qualitatively explains the exceptionally large percentage increase in lifetime from the bulk lifetime (48%) for the monovacancy in diamond [9] compared to 24% in the case of silicon [7].

Illumination of a sample was done with the purpose of investigating lattice relaxation for the excited state of NV⁻. The sample was annealed at 950 °C and illuminated at room temperature by monochromatic light with a band width of 10 nm. The positron lifetime for different wavelengths between 610 and 700 nm, including 638 nm, showed no effect.

In conclusion, V⁻, NV⁻, and NVN⁻ constitute a set of well known defects in diamond which are appropriate for theoretical studies of lattice relaxation.

Acknowledgments

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