Positron lifetime spectroscopy with optical excitation: a case study of natural diamond

J-M Mäki, T Kuittinen, E Korhonen and F Tuomisto
Department of Applied Physics, Aalto University, 00076 Aalto, Finland
E-mail: jussi-matti.maki@aalto.fi

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Abstract. In this paper, we report positron lifetime results obtained under high-power steady-state and transient optical excitation. We present a model for analysing the results. The method has been applied to vacancy clusters in natural diamond, for which we self-consistently analyse optoelectronic constants such as optical absorption cross-section and hole recombination cross-section. The temperature dependences of transient and steady-state measurements are studied, suggesting the possibility of analysing the positron trapping to extended defects and vacancy clusters in semiconductors.

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1 Author to whom any correspondence should be addressed.
1. Introduction

Positron annihilation spectroscopy is a method sensitive to neutral and negatively charged open volume defects. The decreased electron density in a vacancy manifests itself as an increase of positron lifetime and the narrowing of the 511 keV photo-peak in the annihilation gamma spectrum, compared to a defect-free crystal [1, 2]. Positron lifetime spectroscopy provides information on the atomic structure, the charge state and often the concentration of the vacancies. Positron annihilation spectroscopy has been efficiently used to identify and quantify opto-electronically important vacancy-related defects in, for example, the III-nitrides [3–6] and ZnO [7–10].

As the positron trapping to defects is charge state sensitive and the charge state can be manipulated optically or thermally, the ionization levels related to vacancies can be studied. Optical positron spectroscopy has been successfully used in studying the optical transitions in for example semi-insulating GaAs [11, 12] and SiC [13], among others. Positron spectroscopy combined with sub-band-gap illumination effectively probes the density of states related to defects in semiconductor material in a similar manner as optical deep-level transient spectroscopy or electronic paramagnetic resonance combined with illumination. The only requirement is that the charge state of the vacancy can be manipulated using optical excitation with the vacancy being populated/depopulated to a concentration that can be detected using positron annihilation spectroscopy (>10^{15} \text{cm}^{-3}).

In order to obtain more information about the optical processes related to vacancies, we have developed a method for probing positron lifetime during illumination-induced charge-transfer processes [14]. The decay of the illumination effect provides information about the recombination dynamics of the system, providing an unambiguous identification of the defect in question at the same time. The method has been applied to natural diamond, in which we self-consistently analyse optoelectronic constants related to vacancy clusters, such as optical absorption cross-section and hole recombination cross-section. Furthermore, the method allows us to study the positron trapping to extended defects (dislocations and vacancy clusters) in semiconductors.

Some of the basic positron lifetime parameters in natural diamond have been determined in earlier studies. A typical positron lifetime spectrum of brown type IIa natural diamond can be decomposed into two components $\tau_1 = 115$–$132 $ps and $\tau_2 = 420 \pm 20 $ ps when measured in the dark at 20–300 K [15]. The reported lifetime for annihilations in the diamond lattice, i.e. the bulk lifetime, is $\tau_B = 100$–$110 $ ps [16], whereas monovacancy-type defects result in a lifetime of 140–150 ps [17]. Thus the component $\tau_1$ is a superposition of positrons annihilating in the diamond lattice and some defect (or defects) with open volume comparable to the monovacancy, possibly related to dislocations. The second lifetime component $\tau_2$ corresponds to vacancy clusters of several tens of atoms missing (40–60 missing atoms if the vacancy cluster is of a spherical shape [15]). Illumination of monochromatic sub-band-gap light on a brown natural type IIa diamond results in a much increased average positron lifetime due to negative charging of the 400 ps vacancy clusters. Positron annihilation measurements have provided conclusive evidence that the vacancy clusters cause brown coloration in natural type IIa diamond [15, 18]. A schematic representation of the continuum of the states caused by the vacancy clusters is shown in panel (a) of figure 1.

In this paper, we present positron lifetime results obtained in combination with high-power steady-state and transient 400 nm (near-UV) optical illumination. The illumination is
Figure 1. Panel (a) shows the band structure of the diamond containing vacancy clusters. The vacancy clusters induced a continuum of states starting from 2.0 eV. In darkness the charge state of the vacancy clusters is neutral and the positron-trapping coefficient is $\mu^0$; above 2.0 eV, at least part of the clusters are in negative charge and the trapping coefficient is $\mu^-$. In panel (b), a representation of the transient illumination experiment is shown. The light pulse and the measurement intervals after the pulse are indicated. The cycle is repeated in order to obtain sufficient annihilation statistics per spectrum. The average positron lifetime shown is measured at 45 K.

provided by high-power LEDs of 400 nm (3.1 eV), providing a flux of $2 \times 10^{16} \text{cm}^{-2} \text{s}^{-1}$. In the transient measurements, the positron lifetime spectrum was collected in consecutive time slots of 1–10 s, enabling us to study the positron lifetime as a function of time following a light pulse. The measurement method has been applied to slightly brown type IIa (low impurity content) diamond. The diamond sample in question shows colossal positron lifetime effect under illumination due to an easily separable 400 ps light-sensitive lifetime component, thus enabling us to concentrate on the optical effect. More subtle effects, such as the ones caused by monovacancies, can be studied as well, as long as the defects show optical activity [11–13, 19–20].

2. Method

2.1. Photoexcitation of vacancy clusters in diamond

A simple two-state model can be used to study the time-dependent illumination effect [14]

$$\frac{d[V^-]}{dt} = \sigma_{abs}\phi[V^0] - g[V^-],$$

(1)

where $[V^0]$ and $[V^-]$ are the concentrations of vacancy clusters in neutral and negative charge states, respectively, $\sigma_{abs}$ is the optical absorption cross-section of the vacancy cluster, $g$ is the transition rate back to the ground state and $\phi$ is the photon flux. The model assumes that
electrons are excited from the valence band to the clusters, leaving behind a hole and giving rise to photoconductivity [14].

The total vacancy cluster concentration is constant ([\(V_{\text{dark}}^0\]) = \([V^-] + [V^0]\)); hence during steady-state illumination the fraction of negative cluster can be written as

\[
\frac{[V^-]}{[V_{\text{dark}}^0]} = \frac{\phi}{\phi + g_s/\sigma_{\text{abs}}},
\]

where the absorption cross-section \(\sigma_{\text{abs}} = 150 \times 10^{-18} \text{ cm}^2\) [14] and \(g_s\) is the steady-state transition rate under illumination. The transition rate \(g\) in equation (1) is assumed to be

\[
g = \langle v_p \rangle \sigma_p p,
\]

where \(\langle v_p \rangle\) is the thermal velocity of holes, \(\sigma_p\) is the recombination cross-section and \(p\) is the free hole concentration.

The value of the steady-state transition rate \(g\) can be estimated by studying the decay of the photoexcitation effect after switching off the illumination. By assuming that the free holes originate predominantly from the photoexcitation, i.e. \(p = [V^-]\), the time derivative given by equation (1) can be combined with equation (3) to give

\[
\frac{d[V^-]}{dt} = -\langle v_p \rangle \sigma_p [V^-]^2.
\]

This can be solved to give the concentration of negative clusters after switching off the illumination

\[
[V^-](t) = \frac{[V_s^-]}{\sigma_p \langle v_p \rangle [V_s^-]t + 1},
\]

where \(V_s\) is the concentration of negative clusters in steady state and hence the transition rate in steady state is \(g_s = \sigma_p \langle v_p \rangle [V_s^-]\). The resulting transition rate as a function time is of hyperbolic form. With high photon fluxes the illumination effect is in saturation and the transition rate can be written as

\[
g_s = \langle v_p \rangle \sigma_p [V_{\text{dark}}^0].
\]

Finally, the effect of switching on the illumination can also be studied in order to verify that the value of \(g\) is independent of illumination flux. Equation (1) is then written as

\[
\frac{d[V^-]}{dt} = \sigma_{\text{abs}} \phi ([V_{\text{dark}}^0] - [V^-]) - \langle v_p \rangle \sigma_p [V^-]^2.
\]

The equation can also be solved analytically

\[
[V^-](t) = 2[V_{\text{dark}}^0] - \frac{2[V_{\text{dark}}^0]C}{C + \sqrt{\phi \sigma_{\text{abs}} \tanh (\frac{1}{2}C \sqrt{\phi \sigma_{\text{abs}}} t)}},
\]

where \(C = \sqrt{\phi \sigma_{\text{abs}} + 4[V_{\text{dark}}^0] \sigma_p v_p}\) and the solution can be fitted to the experimental data.

2.2. Data analysis

Positrons annihilate in a defect-free crystal with a decay constant typical of the lattice. The positron can get trapped at negative or neutral vacancies. If trapping takes place, the positron
lifetime increases due to the reduced electron density at the vacancy. The positron lifetime spectrum is

\[ N(t) = -\frac{dn(t)}{dt} = \sum_{i}^{k+1} \frac{I_i}{\tau_i} \exp\left(-\frac{t}{\tau_i}\right), \tag{9} \]

where \( k + 1 \) different lifetime components \( \tau_i \) contribute to the spectrum with intensity \( I_i \). The lifetime component is the inverse of the corresponding decay constant, \( \tau_i = \lambda_i^{-1} \). The lifetime components correspond to slopes in the annihilation spectrum when plotted on a semi-logarithmic scale. The lifetime spectrum is analysed as a sum of exponential decay components convoluted with the Gaussian timing resolution of the experimental setup. The positron in the state \( t \) annihilates with the lifetime \( \tau_i \) and intensity \( I_i \). The spectrum can be decomposed into 1–3 components corresponding to annihilations in a delocalized state in the lattice or localized state at vacancies, given that they differ at least by a factor of \( \tau_i/\tau_j > 1.3–1.5 \). The increase of the average lifetime

\[ \tau_{\text{ave}} = \sum I_i / \tau_i \] \tag{10} 

above the lifetime in the lattice (called the bulk lifetime) indicates that neutral or negative vacancy defects are present.

The transition rate of a thermalized positron into a vacancy in the lattice (called the trapping rate) is defined as

\[ \kappa_D = \mu_D c_D, \tag{11} \]

where \( c_D \) is the defect concentration and \( \mu_D \) is the trapping coefficient. The value of the trapping coefficient depends on the physical size and the charge state of the vacancy and on the measurement temperature. Two distinct phases are present in the trapping: diffusion to the defect and the quantum mechanical transition from the free Bloch state to the localized state in the vacancy. In case small vacancies (e.g. monovacancies) are present in the sample in high concentrations, the diffusion to the defect is fast and the trapping depends on the transition rate to the bound state, whereas with small concentration of large defects (vacancy clusters or voids) the diffusion rate limits the trapping coefficient. This is also very often the case with dislocations. In this case, the trapping coefficient can be written as [21]

\[ \frac{1}{\mu_D} = \frac{1}{\mu_{\text{diff}}} + \frac{1}{\mu_{\text{trans}}}. \tag{12} \]

In the temperature range 30–500 K, the diffusion of positrons is limited by scattering off longitudinal acoustic phonons, resulting in a temperature dependence \( T^{-1/2} \) [1].

It should be noted that the trapping coefficient \( \mu_D \) is very sensitive to the charge state of the vacancy when the trapping is transition limited. At low temperatures \( \mu_D \) for a negative vacancy can be an order of magnitude higher compared to a neutral one, whereas the differences between different negative charge states are much smaller [2]. The changes in \( \mu_D \) are easily observed in the average lifetime and in the intensity of the component in question.

The presence of negative vacancies can be observed by carrying out measurements as a function of temperature. For a neutral vacancy the trapping is temperature independent whereas for a negative vacancy the trapping coefficient varies as \( T^{-1/2} \) [2] when the positron trapping is transition limited and the transition to the vacancy is direct. The transition can also be a multiple stage process, where the positron is first bound to a shallow Rydberg-like precursor.
state introduced by the Coulombic attraction by the vacancy with a rate $\kappa_R$ and from there the positron is trapped to the ground state of the vacancy with a rate $\eta_R$. In this case, the trapping coefficient can be written as \[ \mu_V(T) = \mu_R \left( 1 + \frac{\mu_R}{\eta_R N_{\text{at}}} \left( \frac{m_e k_B T}{2\pi\hbar} \right)^{3/2} e^{-E_b/k_B T} \right)^{-1}, \] (13)

where $\mu_R = \mu_R^0 T^{-1/2}$ is the positron trapping coefficient from the delocalized state to the Rydberg state, $m_e$ is the effective mass of the positron, $E_b$ is the binding energy of the positron to the Rydberg state and $N_{\text{at}}$ is the atomic density of lattice ($N_{\text{at}} = 1.77 \times 10^{23} \text{ cm}^{-3}$ for diamond). The practical importance of the trapping to the shallow states comes from the fact that at high enough temperatures, positrons can escape from the Rydberg state, resulting in a temperature dependence $\mu \propto T^{-1}$ in a certain temperature range defined by the binding energy, i.e. stronger than for direct trapping to the negative vacancy. Such a behaviour has been reported, for example, in the case of GaAs [24] and Si [25].

Positron annihilation spectroscopy can be used to study the optically active vacancy defects because external illumination can be used to manipulate the charge state of the defects. The intrinsic charge carrier concentration has to be low enough so that the charge state of vacancies is not screened. The change of the charge state is observed as a change of the trapping rate to the defect in question. When measurement is made as a function of photon energy, information about the density of states related to the vacancies is obtained. This can be compared, for example, to the absorption coefficient.

The trapping rate can be directly obtained from the experimental data in some special cases, of which the easiest is when there is only one trapping defect present. In the case of natural diamond, a two-component fit can be done and the shortest lifetime component is a mixture of bulk and lifetime components corresponding to open volume in dislocations or monovacancies and the longest component is 400 ps, i.e. the longest lifetime component is well separated but the two shortest components are mixed. The trapping rates can then be written as \[ \kappa_1 = \frac{\tau_{1,\text{exp}} (\lambda_B - I_{2,\text{exp}} \lambda_{D2}) - I_{1,\text{exp}}}{\tau_{D1} - \tau_{1,\text{exp}}}, \] (14)

\[ \kappa_2 = \frac{I_{2,\text{exp}}}{I_{1,\text{exp}}} (\lambda_B - \lambda_{D2} + \kappa_1), \] (15)

where the decay constant is $\lambda = \tau^{-1}$ and the subscript exp denotes the experimental fit for the component and B, D1 and D2 denote the values for the defect-free bulk, the small defect and the large defect, respectively. In case the positron trapping is very rapid ($\kappa_{1,2} \geq 100 \lambda_B \gg \lambda_B - \lambda_{D1,2}$), all positrons annihilate in defects, i.e. positron trapping is in saturation and the sensitivity to defect concentrations is lost. However, the ratio of the trapping rates can still be estimated as the ratio of experimental intensities \[ \frac{\kappa_1}{\kappa_2} = \frac{I_1}{I_2}. \] (16)

As will be shown later, the positron trapping approaches saturation under photoexcitation and at low temperatures, but there are still some positrons annihilating in the lattice, meaning that equation (16) is not strictly correct. The defects corresponding to the shorter lifetime do not show any optical activity and $\kappa_1$ can be considered to be constant, while the relative trapping
rate $\kappa_2$ can be calculated directly as a fraction of intensities when measuring at low temperature during illumination.

The average positron lifetime can be written as a sum with trapping rates

$$
\tau_{\text{ave}} = \frac{1 + \kappa_1 \tau_1 + \kappa_2 \tau_2}{\lambda_B + \kappa_1 + \kappa_2},
$$

(17)

where $\kappa_1$ is the trapping rate to the dislocations/monovacancies and $\tau_1$ is the corresponding positron lifetime. $\kappa_2$ and $\tau_2$ are the trapping rate and positron lifetime for the vacancy cluster. The total trapping rate $\kappa_2$ to the vacancy clusters in diamond during steady-state illumination can be written as the sum of the trapping rates to neutral and negative clusters

$$
\kappa_2 = \left(1 - \frac{[V^-]}{[V^0_{\text{dark}}]} \right) \kappa^0 + \frac{[V^-]}{[V^0_{\text{dark}}]} \kappa^-,
$$

(18)

where $[V^-]/[V^0_{\text{dark}}]$ is the fraction of clusters in negative charge state, and $\kappa^0$ and $\kappa^-$ are the trapping rates to cluster in neutral and negative charge states, respectively. Here it is assumed that $[V^0_{\text{dark}}]$ is the total concentration of vacancy clusters, i.e. all the clusters are neutral and only then convert to negative when illuminated (the illumination does not make any positively charged vacancy clusters negative even if they were present). From this, the fraction can be written as

$$
\frac{[V^-]}{[V^0_{\text{dark}}]} = \frac{(\kappa_2 - \kappa^0)}{(\kappa^- - \kappa^0)}.
$$

(19)

The experimental value of $\kappa_2$ is given by equation (15). If it is assumed that the defect corresponding to $\kappa_1$ is not optically active, equation (15) is a function of only $I_2/I_1$ and the fraction of negative clusters can be finally simply written as

$$
\frac{[V^-]}{[V^0_{\text{dark}}]} = \frac{I_2/I_1 - (I_2/I_1)^0}{(I_2/I_1)^- - (I_2/I_1)^0}.
$$

(20)

2.3. Experimental details

Measuring the positron lifetime is based on detecting the time difference between the radiation emitted during $\beta^+$ decay of the $^{22}$Na source and the radiation emitted after annihilation of the positron [1, 21]. Before annihilation the implanted positrons rapidly lose their kinetic energy. After the thermalization the positrons may get trapped at vacancy, causing an increase in the positron lifetime. The attractiveness of the vacancy depends on the charge state, with negative vacancies causing a bigger effect on the positron lifetime than a similar concentration of neutral vacancies. Positive vacancies do not trap positrons when the concentration of the defects is of the order usually encountered in semiconductors ($\lesssim 10^{20} \text{cm}^{-3}$). The positron experiments were performed in a cryostat cooled by a closed-cycle He cryocooler capable of achieving temperatures between 30 and 600 K. The positron lifetime was recorded using conventional instrumentation [1].

For the optical illumination, we used high-power UV LEDs LZ1-10 by LedEngin Inc. The near-UV LED had nominal radiant flux of 700 mW ($\pm 5\%$) at 400 nm (3.1 eV), corresponding to photon flux of $\phi = 2.4 \times 10^{16} \text{cm}^{-2} \text{s}^{-1}$ on the sample with our measurement geometry. The photon flux emitted by the LEDs was not monitored during the measurement, but special care has been taken to estimate the flux at the sample based on the rotationally symmetric LED radiation pattern. Further, the LEDs were not moved between the steady-state and
Transient measurements in order to ensure that the flux was constant on the sample between measurements. The LEDs were controlled by a MOSFET transistor. The LEDs were used in either steady-state or transient illumination mode. During the transient measurements the collection of positron lifetime spectra was started after the illumination had been switched off and the spectra were collected in 1–10 s time slots, and the timing stamp of each spectrum was defined as the centre of the time slot. A representation of the measurement and the decay of positron lifetime is shown in panel (b) of figure 1. As short as 1 s time slots were used. In principle, a pulse generator can be used to rapidly switch the LED on and off with frequencies even in the microsecond range. This is necessary when the transition rate back to the ground state is higher than in the data presented in the following sections.

A positron lifetime spectrum was obtained for each 1–10 s time slot corresponding to the time after illumination. Each spectrum had at least 200 000 counts, thus for a typical 300 s measurement cycle a total of 60 million counts had to be obtained, meaning that for a count rate of 100 counts s$^{-1}$ the whole measurement took 1 week. The lifetime spectra were analysed by fitting (nonlinear least-squares approach) a sum of exponentials (equation (9)) convoluted with the 250 ps (full-width at half-maximum (FWHM)) Gaussian resolution function of the experimental setup.

3. The transient photoexcitation effect

The decay of the photoexcitation effect has been studied as a function of temperature, illumination flux and the measurement slot length. The positron lifetime spectrum as a function of time after a light pulse is shown in figure 2. Based on the positron lifetime spectrum it is clear that there are two positron lifetime components present, of which the 400 ps component is optically active. The intensity of long-lifetime (400 ps) annihilations decays, as is evident from the spectra after a light pulse.

The average positron lifetime is shown in figure 3(a) during and after the light pulse of 3.1 eV and flux of $2 \times 10^{16}$ cm$^{-2}$ s$^{-1}$. After the illumination is switched on, the average lifetime increases to its final value rapidly, in less than 1 s. After 10 s (at $t = 0$) the illumination is switched off, and the average positron lifetime starts decaying slowly and non-exponentially. The onset of the decay effect has been plotted in more detail in figure 3(b) with the fraction of negative vacancy clusters and the average positron lifetime shown. The fraction of negative vacancy clusters has been estimated using equation (20). The onset is rapid and measurement slots as short as 0.5 s are too long to show much detail when illuminating with flux of $2 \times 10^{16}$ cm$^{-2}$ s$^{-1}$. The curve at $t < 0$ s is the analytical solution of equation (7), with the parameters used being obtained from the decay measurements (described in detail below). The fit matches the experimental points well, verifying that illumination does not affect the decay rate of the photoexcitation effect.

Most of the positron photoexcitation decay measurements were carried out with 10 s time slots in order to obtain sufficient annihilation statistics per spectrum and have the time in the dark long enough so that most of the excitation effect has disappeared. The fraction of negative clusters estimated using equation (20), obtained using either 3 or 10 s measurement time slots, are shown in figure 3(d). Additionally, 1 s slots were tested (not shown for clarity). All these resulted in similar data, providing evidence that measuring the positron lifetime in 10 s slots is viable in the case of UV wavelength illumination. Selecting the slot as long as 10 s decreases the measurement times considerably compared to the slot of 1–3 s. The illumination times were
Figure 2. Positron annihilation spectra as a function of time after light pulse. The decay of the intensity as a function of time is shown on the lower right-hand side. The decay of the intensity is also clearly illustrated in the spectrum on the right upper corner, as the intensity decays and the longer lifetime component is constant 400 ps after illumination.

also varied (not shown), with both 3 and 10 s illumination yielding similar results, in line with the rapid onset of the photoexcitation effect.

The decay rate of the illumination effect as a function of photon flux is shown in figure 3(c) with different photon fluxes in the range \(1 \times 10^{14} - 2 \times 10^{16}\) cm\(^{-2}\) s\(^{-1}\). The measurement has been carried out at 45 K. The fraction of negative clusters as a function of time was estimated using equation (20). The exact time dependence of the decay of the photoexcitation effect has been modelled using equation (5), with the fits shown. The fits correspond to the experimental data very well, especially considering that in the figure the rate \(g_s\) and the vacancy concentration in steady state \([V^-]_s\) are the only parameters fitted ([\(V^-\)] could be obtained from the steady-state measurements, but the parameter has been fitted for practical reasons). The fitted values of \(g_s\) are in the range 0.05–0.06 s\(^{-1}\) for all the three fluxes, i.e. the decay rate \(g_s\) is constant within the measurement accuracy. Similar results were obtained also at 300 K. The steady-state measurements as a function of photon flux [14] suggest that \(g_s\) is constant. This is interesting, as according to equation (5) the decay rate \(g_s\) is a function of the steady-state concentration \([V^-]_s\), i.e. the decay rate should decrease for smaller illumination photon fluxes. In this case, as the flux varies by a factor of 250, \([V^-]_s\) varies roughly by a factor of 3, meaning that the value of \(g_s\) should also vary in a similar manner. A possible explanation for this discrepancy could be that the recombination occurs through a centre with a limited number of states. However, in this case the transition should follow a single exponential which is not observed here. It is clear that the fit to the data based on the model (equation (5)) is very good, suggesting that the model is qualitatively correct. This further suggests that the product of \(\sigma_p[V^-]\) is constant, i.e. the hole-trapping cross-section increases for smaller negative cluster concentration, cancelling the effect of the increasing \([V^-]\). Another possibility is that the hole concentration is not linearly dependent on the negative vacancy concentration with high fluxes as in equation (6).
Figure 3. The average positron lifetime during the illumination experiment measured at 300 K is shown in panel (a). Illumination is switched on at $t = -10$ s, reaching the eventual average lifetime value quickly. After switching the illumination off at $t = 0$, the average lifetime starts to decay. The fraction of negative clusters after switching the illumination on has been shown in panel (b). The fit in the figure is based on equation (7). In panel (c), the flux dependence to the positron data is compared at 45 K. The fluxes have been indicated in the figure. The fluxes are given in units of cm$^{-2}$ s$^{-1}$. The photon flux does not affect the decay rates $g$ within the measurement accuracy when measured at 45 and 300 K, even as the flux varies by a factor of 250. The average lifetime is shown in the inset. In panel (d), the effect of measurement slice length is studied at 45 K. 3 and 10 s slices result in comparable values.

Alternative models explaining the time-dependent decay behaviour of photoexcitation can be considered. Some disordered materials, such as amorphous semiconductors, exhibit time-dependent decay behaviour characterized by a stretched exponential $\exp\left(-\left(t/\tau\right)^\alpha\right)$, $0 < \alpha < 1$ [27, 28]. Such a time-dependent behaviour is usually attributed to a random distribution of traps. The stretched exponential results in a more rapid decay than expected at small values of $t$; otherwise it fits the experimental data well. The decay rates correspond to the values obtained using the model given by equation (5). However, it should be noted that the stretched exponential model has one extra fitting parameter compared to the one we presented.
Figure 4. The decay of the photoexcitation effect measured as a function of temperature. In (a) the decay of average lifetime for selected temperatures is shown. In (b) the fraction of negative clusters and corresponding fits given by equation (5) are shown. Decay rate $g_s$ as a function of temperature is shown in the upper panel of (c) along with a line to guide the eyes. Finally, in the lower panel of (c), the values of the recombination cross-section $\sigma_p$ are shown. The values are estimated using equation (6). $\sigma_p$ follows a temperature dependence $T^{-1}$. Error bars are estimated based on the scatter of the data.

The decay of the photoexcitation effect was measured as a function of temperature in the range 50–300 K in order to obtain information about the behaviour of the recombination cross section associated with the vacancy clusters. The average positron lifetime and the fraction of negative clusters during the decay of the photoexcitation effect are plotted in figures 4(a) and (b). The fraction of negative clusters is estimated using equation (19). Similar estimates were obtained using equation (20) above 200 K, when positron trapping is not in saturation, justifying the use of equation (20). The fit in figure 4(b) is given by equation (5). The decay rate $g$ given by the fit is shown in the upper panel of figure 4(c). Temperature-dependent measurements were carried out at high photon flux; thus equation (6) can be used in estimating the hole recombination cross section of the vacancy clusters. The values of recombination cross sections are shown in the lower panel of figure 4(c).

The decay rate of photoexcitation $g_s$ shows a step-like behaviour at temperatures in the range 100–150 K: the recombination rate is slightly higher at low temperature. The absolute value of the recombination cross-section is very small, in the range of $(2–8) \times 10^{-24} \text{cm}^2$ at 45–300 K. Such small recombination cross-sections have been observed in semiconductor materials containing disordered regions where a physical barrier of some sort is hindering recombination. Examples include grain boundaries in GaN [29] and CVD diamond [30]. It is possible that the large vacancy clusters present in brown diamond could trap charge carriers in a similar manner. However, in the case of trapping into grain boundaries, the recombination is usually thermally activated $\sigma_p = \sigma_o \exp \left( \frac{-\Delta E}{kT} \right)$, where $\Delta E$ is the thermal activation energy. Such a thermally activated recombination process is not observed here. The temperature dependence
of the recombination cross section follows roughly the relation $\sigma_p \propto T^{-1}$. Phonon-assisted capture mechanisms, such as cascade capture \cite{31}, follow such a temperature dependence. However, cascade capture should show a much higher recombination capture cross section.

4. Positron lifetime as a function of temperature and under photoexcitation

Positron lifetime has been measured as a function of temperature with several illumination wavelengths and fluxes. Average positron lifetimes as a function of temperature are shown in figure 5(a) for 3.1 eV illumination with different photon fluxes. The excitation wavelength or the flux does not affect the shape of the average lifetime curve; decreasing the flux only causes a shift in the absolute value. Based on the temperature-dependent transient measurements, the value of $g$ varies from 0.03 to 0.06 s$^{-1}$ in the temperature range 50–300 K. The fraction of negative clusters given by equation (2) is close to saturation in the whole temperature range. With the highest attainable flux of $2 \times 10^{16}$ cm$^{-2}$ s$^{-1}$, the negative fraction is $[V^-]/[V_0^{\text{dark}}] = 0.98$ at 45 K and 0.99 at 300 K. Thus the effect seen with the average lifetime as a function of temperature is not due to the variation of $g$, as a function of temperature, but solely due to the decrease of the trapping coefficient with increasing temperatures. To study the effect, the fitted lifetime components and the intensity of the second component are plotted in figure 5(c). It is clearly seen that the effect in the average lifetime is caused by the decrease of the intensity of the 400 ps lifetime component, and the absolute values of the lifetime components are roughly constant within the measured temperature range. The shorter lifetime component is a superposition of positrons annihilating in the defect-free state with lifetime $\tau_B = 100$ ps and at some defects with open volume roughly corresponding to monovacancy, with lifetimes in the range $\tau_D = 130–145$ ps. The component $\tau_1$ slightly decreases with increasing temperature,
suggesting that at least part of the defects contributing to the lifetime $\tau_1$ have a decreasing trapping coefficient as the temperature increases. It is obvious that the positron lifetime is in saturation at low temperatures with illumination flux $2 \times 10^{16}$ cm$^{-2}$ s$^{-1}$, as the component increases to 140 ps. This is due to the fact that (nearly) all positrons annihilate as trapped at vacancies, i.e. the trapping is in saturation. With the smaller photon flux of $8 \times 10^{15}$ cm$^{-2}$ s$^{-1}$ the attractiveness of the vacancy clusters is not high enough to cause saturation trapping; thus the lifetime is a superposition of $\tau_b$ and $\tau_D$. When the temperature is increased, $\tau_1$ decreases below the value in the dark due to the fact that the effective lifetime seen by positrons in the free state is reduced due to increased trapping at defects. This is due to the fact that the effective bulk lifetime can be written as $\tau_{b \text{, eff}} = (\lambda_b + \kappa_{\text{tot}})^{-1}$, where $\kappa_{\text{tot}}$ is the total trapping rate to defects.

The behaviour of the positron trapping can be studied by analysing the trapping rates given by equations (14) and (15). The trapping rates $\kappa_1$ and $\kappa_2$ in the dark and with high illumination flux are plotted in figure 5(b). The trapping is not in saturation in the dark even at low temperatures as $\kappa_1 \approx \lambda_B$, $\kappa_1$ shows temperature dependence of $\kappa_1 \propto T^{-0.3}$ whereas the component $\kappa_2$ is rather independent of the measurement temperature. Due to the fact that $\kappa_1$ depends on the temperature less than, e.g., for a negative vacancy, the trapping rate $\kappa_1$ has been modelled using equation (12) with the diffusion-limited part of the trapping following the relation $\kappa_{\text{diff}} = 1.7 \times 10^{10} \text{s}^{-1} (\frac{T}{100 \text{K}})^{-1/2}$ and the transition-limited trapping being temperature independent $\kappa_{\text{trans}} = 3.5 \times 10^{10} \text{s}^{-1}$, with the numerical values of $\kappa_{\text{diff}}$ and $\kappa_{\text{trans}}$ having been obtained from fitting equation (12). The resulting fit is shown in figure 5(b). The fact that $\kappa_1$ is a sum of two components is not surprising, as the smaller lifetime component can be at least partially attributed to dislocations [15] and the trapping to dislocations is very often diffusion limited [21]. When the samples are illuminated with photon flux of $2 \times 10^{16}$ cm$^{-2}$ s$^{-1}$, it is seen that the trapping rate to the small defect $\kappa_1$ increases at low temperatures, but close to room temperature it is similar to the situation without illumination. This suggests that the defects corresponding to $\kappa_1$ do not show optical activity and that $\kappa_1$ estimated using equation (14) increases at low temperatures with high illumination flux of $2 \times 10^{16}$ cm$^{-2}$ s$^{-1}$ only as an artefact of the analysis as the overall trapping at defects is approaching saturation.

Positron trapping to the vacancy clusters in the dark ($\kappa_2$) is temperature independent in the temperature range 50–300 K as can be seen in figure 5(b). The temperature independence is important as it means that the positron trapping to the vacancy clusters is not diffusion limited and that the cluster is in the neutral charge state. The fact that under illumination the positron trapping is approaching saturation below 200 K means that the trapping rate $\kappa_1$ increases artificially and the estimate of $\kappa_2$ results in too high values. In the temperature range 200–300 K the values of $\kappa_1$ are similar irrespective of the illumination flux. Assuming that the ‘real’ $\kappa_1$ under illumination can be assumed to behave in a similar manner as in the dark, the value of the trapping rate to the vacancy cluster $\kappa_2$ can be estimated using equation (15) by using the value $\kappa_1$ from the measurements in the dark in the estimation. Even if this assumption does not hold, it should be noted that $\kappa_2$ increases by a factor of $>10$ at low temperatures, whereas the estimate of $\kappa_1$ for the analysis increases only by a factor of 2. The estimated $\kappa_2$ is plotted in figure 5(b). The illumination results in a massive increase in the trapping rate. The shape of $\kappa_2$ is similar to the average lifetime, showing an interesting downward bend at around 150 and 300 K, suggesting that detrapping of positrons from the shallow Rydberg-like states occurs. For the neutral cluster the trapping rate is constant, $\kappa^0 = 1 \times 10^9$ s$^{-1}$. Under illumination the vacancy cluster is in the negative charge state and the temperature dependence has to be taken into account. In figure 5(b), the trapping rate has been fitted as a sum $\kappa_2 = \kappa_{V, Ry} + \kappa_V$. 

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i.e. trapping to the vacancy can occur either directly ($\kappa_V$) or through Rydberg-like precursor states ($\kappa_{V,Ry}$). $\kappa_V = 1 \times 10^{10}(\frac{T}{100 \text{ K}})^{-1/2}\text{s}^{-1}$ and $\kappa_{V,Ry} = c \mu_R$, where $\mu_R$ is given by equation (13) with the fitted value for binding energy being $E_b = (75 \pm 5)\text{meV}$, the trapping rate to the Rydberg state $\kappa_R = 3.6 \times 10^9(\frac{T}{100 \text{ K}})^{-1/2}\text{s}^{-1}$ and the fitted ratio $\mu_R/\eta_R = 40$ at 100 K. The fit given by equation (13) corresponds to the experimental data very well. Above 300 K the experimental points decrease more rapidly than the fit, suggesting that there is a second detrapping step present. However, this is not fitted due to the lack of experimental points above 300 K. The trapping rate is fitted when the samples are illuminated by a smaller flux of $1 \times 10^{14}\text{cm}^{-2}\text{s}^{-1}$. The $\kappa_{V,Ry}$ and $\kappa_V$ both decrease approximately by a factor of 2, agreeing also with equation (2).

The vacancy cluster concentration has been estimated by combining optical absorption and positron measurements as $4 \times 10^{15}\text{cm}^{-3}$. The trapping coefficient to the vacancy clusters can be estimated using the equation $\mu_D = \kappa_D \frac{N_0}{\tau_D}$. For the neutral vacancy cluster, the trapping coefficient in the dark is temperature independent $\mu_{Cl}^0 = 4 \times 10^{16}\text{s}^{-1}$. This is interesting, as the relation between the vacancy size and the trapping coefficient has been theoretically estimated to follow a linear relation $\mu_{Cl} = i \mu_V$, where $\mu_{Cl}$ is the trapping coefficient of a vacancy cluster, $i$ is the number of missing atoms ($i \leq 5$) and $\mu_V$ is the trapping coefficient for a monovacancy [32]. The limitation for $i$ stems from the requirement that the trapping is transition limited as it seems to be in our case, even though the vacancy clusters are larger than the limit. In our case, we get $\mu_{Cl}^0/\mu_V = 40$, where $\mu_V = 1 \times 10^{15}\text{s}^{-1}$ is the typical value of the trapping coefficient of a neutral monovacancy [1]. This is in surprisingly good agreement with the vacancy cluster size (40–60 missing atoms) estimated from the value of the lifetime component [15], even with this large a size of the cluster.

Under photoexcitation at 50 K the trapping coefficient for the negative vacancy cluster is $\mu_{Cl}^-(50 \text{ K}) = 5 \times 10^{17}\text{s}^{-1}$ and at 300 K $\mu^-(300 \text{ K}) = 1 \times 10^{17}\text{s}^{-1}$. The ratios of trapping coefficients at different temperatures and charge states are thus $\mu_{Cl}^-/(50 \text{ K})/\mu_{Cl}^-(300 \text{ K}) = 4.0$ and $\mu_{Cl}^-(300 \text{ K})/\mu_{Cl}^0(300 \text{ K}) = 2.7$. The stronger than $T^{-1/2}$ temperature dependence for negative clusters is due to the detrapping from the Rydberg states, similar to what has been reported for Ga vacancies in GaAs under photoexcitation [24]. The ratio $\mu^-(300 \text{ K})/\mu^0(300 \text{ K})$ is similar to what is typical of monovacancies [1, 2]. Generally, it seems that the positron trapping at the vacancy clusters producing the 400 ps lifetime component in natural diamond behaves very similarly to positron trapping at monovacancy defects. Hence, all evidence suggests that, in natural diamond, trapping is transition limited also for large vacancy clusters. It seems that the vacancy size does not dictate the dominant trapping mechanism (diffusion or transition limited).

As the last step in analysing the temperature-dependent behaviour of the positron trapping under illumination, the average lifetime has been modelled based on the trapping rate $\kappa_2$ given by the detrapping model (13) and the trapping rate $\kappa_1$ given by equation (12). The average lifetime has been calculated using equation (17) with the values $\tau_R = 100\text{ps}$, $\tau_1 = 145\text{ps}$ and $\tau_2 = 420\text{ps}$. The results are shown in figure 5(a). The match between the experimental points and the estimate is very good, providing evidence that the discussed model is justified. It should be noted that the modelling procedure is independent of $\tau_{\text{ave}}$. Another point worth noting is that the binding energy $E_b$ does not depend on the illumination flux, suggesting that the charge state of the vacancy cluster seen by positrons does not vary as a function of photon flux; only the fraction in the negative charge state varies.
5. Summary

In summary, we have presented a positron lifetime method that can be used to study the time-dependent charge transfer processes of vacancies in semiconductors. The method has been applied to high-purity type IIa diamond, which shows a large increase of positron lifetime under photoexcitation. A simple two-stage model has been used to analyse the experimental results. Alternative models are also discussed. Positron lifetime has been measured during and after a light pulse, showing that the decay of the photoexcitation effect is independent of the presence of illumination photons. The effect of varying the intensity of the illumination has been studied, showing that the decay rate is independent of the illumination flux. Finally, the temperature dependences of transient and steady-state illumination were presented. It was found that the positron trapping at vacancy clusters in diamond behaves very similarly to trapping at monovacancies, suggesting that size is not the dominant factor determining the trapping mechanism at vacancies and vacancy clusters.

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