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Positron annihilation and the charge states of the phosphorus–vacancy pair in silicon

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Abstract. After electron irradiation two positron lifetimes, 250 ± 1 and 268 ± 3 ps, are observed in phosphorus-doped Si ([P] = 3×10^{16} cm^{-3}) depending on the temperature and the electron fluence. The lifetimes are assigned to the negative and neutral charge states of the phosphorus–vacancy pair (P–V). The longer lifetime at the neutral charge state indicates a larger open volume of the vacancy, and implies an outward relaxation of the phosphorus–vacancy pair in the charge-state transition $(P–V)^- \rightarrow (P–V)^0$. A comparison with the theoretical lifetimes yields a breathing-mode relaxation of the nearest-neighbour atoms $\Delta r/r_0 \sim 5.1\%$ (r_0 is the Si–Si bond length), or $\Delta r \sim 0.12$ Å. The positron trapping coefficients 2×10^{16} s^{-1} at 20 K and 2×10^{15} s^{-1} at room temperature at the negatively charged state $(P–V)^-$ are estimated. A weakly bound Rydberg-like precursor state is invoked to explain the temperature dependence of positron trapping at the negatively charged centres $(P–V)^-$ and V^- in Si. The binding energy at the precursor state is 15–30 meV.

1. Introduction

The prevailing observable defect induced by room-temperature electron irradiation of P-doped floating-zone-refined Si is the phosphorus–vacancy pair, or E centre. This defect consists of an Si vacancy trapped next to a substitutional phosphorus atom. The atomic configuration of the phosphorus–vacancy pair closely resembles the isolated Si vacancy. The E centre is known to have two charge states, $(P–V)^0$ and $(P–V)^-$, and there is evidence of a breathing-mode relaxation brought about by electron emission or capture [1, 2]. This defect provides a test case to investigate the effect of lattice relaxation on the positron lifetime as well as the positron trapping at a negatively charged centre.

The change of the open volume associated with the breathing-mode relaxation of the neighbouring atoms around the vacancy should change the positron lifetime. Such relaxations are brought about by electron emission or capture at the deep electronic levels at defects. As an example, in as-grown n-type GaAs the positron lifetimes 258 and 295 ps are seen experimentally. These lifetimes are ascribed to two different charge states of the As vacancy [3, 4], which would indicate a large outward relaxation of the near-neighbour atoms around the neutral As vacancy as compared to its negatively charged state. Evaluation of this phenomenon is of importance in establishing the positron lifetime technique in semiconductors. On the other hand,

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experimental results on the breathing-mode (or symmetry-conserving) relaxations in general are very few even in silicon.

The different charge states have a profound effect on the positron trapping process [5] and therefore the trapping rates. This is of significance in positron lifetime spectroscopy as the trapping coefficient is needed to estimate the defect concentration from the experimental positron lifetime results. The trapping rate can also give information on the positron trap, in particular its charge state. Positive centres repel positrons, and trapping at a positively charged vacancy has not been observed. Negatively charged defects are strongly attractive because of the long-range Coulomb potential.

Previously we have investigated positron annihilation in electron-irradiated pure Si [6]. There, a strong temperature dependence of positron trapping at the negative Si vacancy V^- was observed. Also, the trapping cross section is very large, $\sigma \geqslant 10^{-12}$ cm^2. The cross section is comparable to the capture of free carriers at charged centres in Si and Ge. Positron trapping was ascribed to the weakly bound Rydberg states due to the attractive Coulomb potential acting as precursor states in positron trapping.

In phosphorus-doped Si investigated in this work the positron lifetimes 250 ± 1 and 268 ± 3 ps are observed after room-temperature electron irradiation depending on the electron fluence and the measuring temperature. These lifetimes are typical of positron annihilation at a monovacancy in Si. Positron trapping occurs in the sample Si ($[P] = 3 \times 10^{16}$ cm^{-3}), but not if the phosphorus concentration is $[P] = 4 \times 10^{14}$ cm^{-3}, and the lifetimes induced by electron irradiation can be ascribed to positron trapping at the neutral and negatively charged phosphorus–vacancy pairs. The longer lifetime in the neutral charge state indicates an outward relaxation in the charge-state transition $(P\text{–}V)^- \rightarrow (P\text{–}V)^0$. A comparison with the theoretical lifetimes implies a breathing-mode lattice relaxation $\Delta r/r_0 \sim 5.1\%$, or $\Delta r \sim 0.12$ Å (r_0 is the Si–Si bond length).

The positron trapping coefficients at the negative charge state are equal to or higher than $\mu = 2 \times 10^{16}$ s^{-1} at 20 K and 2×10^{15} s^{-1} at room temperature. The temperature dependence of positron trapping at the negatively charged centre $(P\text{–}V)^-$ is very similar to what was found for the isolated Si vacancy V^- [6]. This can be explained by thermal detrapping from a weakly bound Rydberg-like precursor state.

2. Experimental details

The samples in the experiments were n-type, phosphorus-doped floating-zone-refined (FZ) Si. The resistivities were 10–20 and 0.19–0.31 Ω cm, which correspond to the phosphorus concentrations $[P] = 4 \times 10^{14}$ and 3×10^{16} cm^{-3}, respectively. The orientations of the wafers from which the samples were cut were (1 0 0) in case of $[P] = 4 \times 10^{14}$ cm^{-3} and (1 1 1) for $[P] = 3 \times 10^{16}$ cm^{-3}.

The electron irradiations were carried out in the Van de Graaf accelerator in Laboratoire des Solides Irradies in Ecole Polytechnique in Paris. All the irradiations were done at room temperature. The incident electron energy was 2.0 MeV, and the total fluence ϕ varied from 1×10^{16} to $7 \times 10^{17} e^-$ cm^{-2}. The current of the electron beam was from 2 to 4 μA cm^{-2}.

For the positron lifetime measurements, from 8 to 12 μCi positron source was placed between two identical 5×5 mm^2 pieces of Si. The source was carrier-free $^{22}NaCl$ solution-deposited on a 0.89 mg cm^{-2} Ni foil. The positron lifetimes

were measured using a fast–fast lifetime spectrometer. The time resolution was 232 ps (FWHM, full width at half maximum). Some measurements were done using a different experimental set-up with a time resolution 240 ps. The coincidence count rate when the sample was mounted in a cryostat was typically 80 s^{-1}, corresponding approximately to 10 s^{-1} μCi^{-1}. The number of events collected to each lifetime spectrum varied from (1.5 to 3.5)$\times 10^6$.

The annihilations in the Ni foil and in the source give rise to the lifetime components 150 ps (intensity 3.3%) and 450 ps (2.3%), respectively. The intensity of the source lifetime 450 ps was determined from the measurement of the lifetime in a 10^4 Ω cm FZ Si sample as well as in unirradiated P-doped samples, and it was found to be independent of temperature from 20 to 300 K. The thickness of the [P] $= 3 \times 10^{16}$ cm^{-3} Si wafer was 280 μm. It was sufficiently thin for some positrons emitted from the ^{22}Na source to penetrate through the sample. Their fraction was too small ($< 5\%$) to bear any influence on the lifetime spectrum unless they annihilate with a very long lifetime (typically 1–2 ns) intermixing with the background. To prevent any such annihilation events, pieces of 10^4 Ω cm Si were placed at the back of the samples whereupon the long-lifetime component disappeared. After subtracting the source components the spectra were analysed with either one or two exponential decay components.

The positron lifetimes were measured as a function of temperature from 17 to 300 K using a closed-loop He cryocooler, and in some measurements also a liquid-nitrogen cryostat ($T \geqslant 80$ K).

3. Results

3.1. Analysis of the lifetime spectra

Positron lifetime spectra and their interpretation are described in detail in a number of references [7, 8]. To make the discussion of the experimental results easier, the analysis of the lifetime spectra is very briefly presented below.

After subtracting the source components, either one or two exponential decay components were used in the positron lifetime spectra $n(t)$ to analyse the experimental data

$$n(t) = n_0 \left(I_1 e^{-\lambda_1 t} + I_2 e^{-\lambda_2 t}\right). \tag{1}$$

The annihilation rate λ_i ($i = 1,2$) is the inverse of the positron lifetime, $\lambda_i = \tau_i^{-1}$, I_1 and I_2 denote the relative intensities of the two lifetime components, and n_0 is the total number of counts. The decomposition is conceivable if the lifetime ratio τ_2/τ_1 is larger than ~ 1.3. If there is more than one type of positron trap, it is usually not possible to decompose the lifetime spectrum into more than two decay components. In the present case the shortest lifetime is clearly separated in the two-component analysis.

In terms of the lifetimes τ_i and their intensities I_i the average positron lifetime reads

$$\tau = I_1\tau_1 + I_2\tau_2. \tag{2}$$

The average lifetime coincides with the centre of mass of the spectrum, typically within 2 ps, and it can be accurately determined even if it is not possible to make a reliable decomposition.

3.2. Positron lifetime results

The positron lifetime was measured in unirradiated Si samples Si ([P] = 3×10^{16} cm^{-3}) from 20 to 300 K. In the whole temperature range there is only one decay component in the lifetime spectra. At 20 K the lifetime is 216.7 ± 0.3 ps and at 300 K it is 217.9 ± 0.3 ps. The lifetime exhibits a weak linear temperature dependence $\tau = \tau_0 + \alpha T$, and the temperature coefficient is $\alpha = (0.34 \pm 0.10) \times 10^{-2}$ ps K^{-1}. This lifetime is typical of positron annihilation in Si if there is no positron trapping [9]. The temperature dependence of the positron lifetime is in accordance with the thermal expansion of the lattice.

Figure 1 shows the average lifetime and the decomposition of the lifetime spectra as a function of the measuring temperature from 17 to 300 K after 2.0 MeV electron irradiation $\phi = 2 \times 10^{16} e^-$ cm^{-2} at room temperature. The lifetime spectra were analysed with two decay components. At 300 K the lifetime is $\tau = 223$ ps, indicating a 5 ps increase of the average lifetime compared to the unirradiated sample. From 300 to 17 K the average lifetime increases continuously to 239 ps at 17 K. The most interesting discovery in this sample is the temperature dependence of the lifetime τ_2. From 17 to 90 K, the lifetime $\tau_2 = 251 \pm 1$ ps is independent of temperature. Above 175 K the lifetime is 268 ± 3 ps, which is 17 ± 3 ps longer than the lifetime below 100 K. Hence a transition between two well defined lifetimes 250 ± 1 ps and 268 ± 3 ps takes place between 100 and 150 K. Associated with the lifetime transition the increase of the intensity I_2 becomes steeper below 150 K, and at 20 K $I_2 = (91 \pm 1)\%$. Also, the average lifetime increases from 233 to 239 ps between 100 and 17 K although the lifetime τ_2 is constant. The increase of the average lifetime thus has contributions from the change of the positron lifetime τ_2 and the temperature dependence of the trapping rate as indicated by the increase of the intensity I_2 below 100 K.

Figure 2 shows the average positron lifetime and the decomposition of the lifetime spectra as a function of the measuring temperature from 30 to 300 K after 2.0 MeV electron irradiation $\phi = 3 \times 10^{17} e^-$ cm^{-2}. The lifetime spectra can be decomposed into two components. The average lifetime increases continuously from 225 ps at 300 K to 241 ps at 30 K. Compared with the electron irradiation $2 \times 10^{16} e^-$ cm^{-2} the average lifetime is from 2 to 4 ps larger between 30 and 300 K. The lifetime $\tau_2 = 267 \pm 3$ ps is independent of temperature between 100 and 300 K. Below 100 K, it decreases continuously to the lowest measuring temperature, and at 30 K $\tau_2 = 256 \pm 1$ ps. The intensity $I_2 = 60 \pm 5\%$ is constant above 175 K, and from 175 to 30 K it increases to (88 ± 1)%.

Two more electron irradiations of the [P] = 3×10^{16} cm^{-3} Si samples were made. In the first, the irradiated sample was a 10×12 mm^2 piece from which the lifetime samples were cut after irradiation. The fluence was not measured but it was of the order of $10^{16} e^-$ cm^{-2}. The average positron lifetime at 25 K is 232 ps as compared to 239 ps in figure 1 after the fluence $\phi = 1 \times 10^{16} e^-$ cm^{-2}. The lifetimes $\tau_2 = 250 \pm 1$ ps are the same, and the shorter average lifetime is due to the smaller intensity I_2, which is now (85 ± 1)% at 25 K (in figure 1, $I_2 = (91 \pm 1)\%$). This indicates that the concentration of positron traps is smaller. Assuming the rate of defect production is approximately constant for $\phi \leqslant 2 \times 10^{16} e^-$ cm^{-2}, the positron trapping rates (section 4) imply that the irradiation fluence is $1 \times 10^{16} e^-$ cm^{-2}. The irradiation fluences are not needed in the estimation of the trapping coefficients, and below this sample is referred to as $\phi = 1 \times 10^{16} e^-$ cm^{-2}. In this sample the average

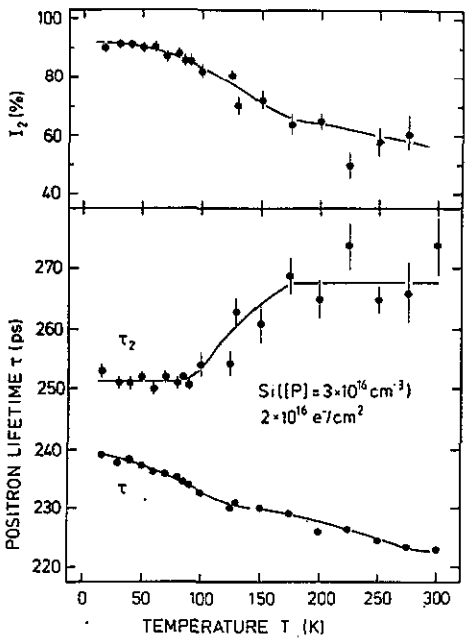

Figure 1. The average positron lifetime and decomposition of the lifetime spectra as a function of temperature in phosphorus-doped Si ([P] = 3×10^{16} cm^{-3}) after 2.0 MeV electron irradiation at 300 K. The irradiation fluence is $2 \times 10^{16} e^-$ cm^{-2}.

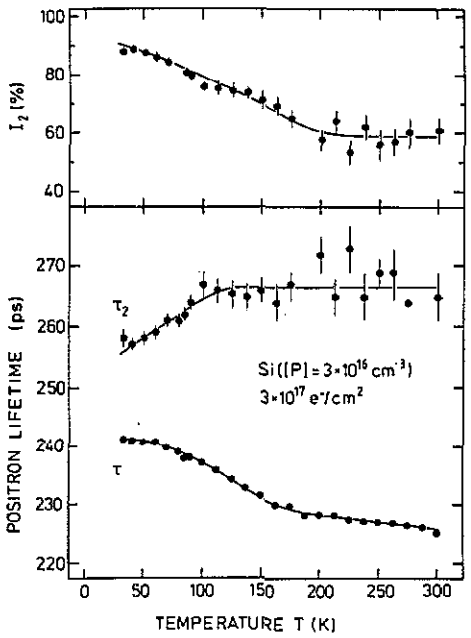

Figure 2. The average positron lifetime and decomposition of the lifetime spectra as a function of temperature in phosphorus-doped Si ([P] = 3×10^{16} cm^{-3}) after 2.0 MeV electron irradiation at 300 K. The irradiation fluence is $3 \times 10^{17} e^-$ cm^{-2}.

lifetime increases from 220 ps at 300 K to 232 ps at 25 K. The average lifetime 221 ps at 260 K is rather close to the bulk lifetime, but it was still possible to decompose the lifetime spectrum. This is due to the fact that the intensity $I_2 > 50\%$ because of the small value of the lifetime τ_2 ($\tau_2/\tau_1 = 1.35$ at 260 K). Also, to improve the decomposition the number of events in a lifetime spectrum was increased to 3.5×10^6. The lifetime τ_2 is 250 ± 3 ps from 20 K to room temperature. The intensity I_2 is (55 ± 5)% at room temperature and (85 ± 1)% at 25 K, and the variation of the average lifetime is due to the increase of I_2.

The other pair of samples was irradiated to the total fluence $\phi = 7 \times 10^{17} e^-$ cm^{-2}. The average positron lifetime and the decomposition of the lifetime spectra are very similar to those after the electron irradiation $\phi = 3 \times 10^{17} e^-$ cm^{-2}. The increase of the average lifetime compared to the smaller electron fluence is 1 ps or smaller, independent of temperature between 20 and 300 K. The intensity I_2 is also the same within the experimental errors indicated in figure 2. The only difference is a small increase of the lifetime τ_2. After this highest electron irradiation τ_2 is constant above 150 K, but its value 272 ± 2 ps is a few picoseconds longer than after the electron irradiations $\phi = 2 \times 10^{16}$ and $3 \times 10^{17} e^-$ cm^{-2}. Below 100 K, the continous decrease of τ_2 is the same as observed for $\phi = 3 \times 10^{17} e^-$ cm^{-2} in figure 2, and at 30 K $\tau_2 = 257 \pm 1$ ps. The positron lifetimes τ_2 after electron irradiations $\phi = 1 \times 10^{16}$ and $7 \times 10^{17} e^-$ cm^{-2} are shown in figure 3.

The Si samples Si ([P] = 4×10^{14} cm^{-3}) were irradiated to $\phi = 2 \times 10^{16}$ and $7 \times 10^{17} e^-$ cm^{-2}. The average lifetimes at 300 K are 218 and 219 ps, respectively.

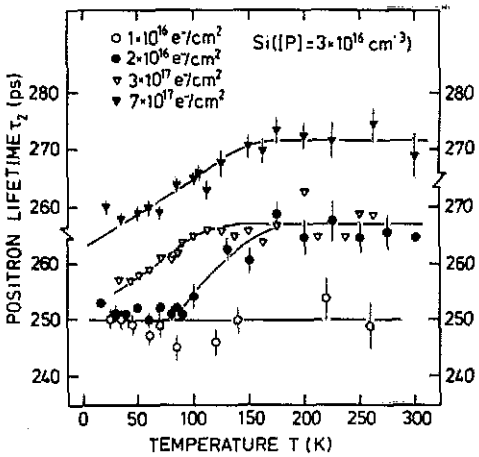

Figure 3. Temperature dependence of the positron lifetime τ_2 in phosphorus-doped Si ([P] = 3×10^{16} cm^{-3}) after 2.0 MeV electron irradiation at 300 K. The irradiation fluences are 1×10^{16}, 2×10^{16}, 3×10^{17} and $7 \times 10^{17} e^-$ cm^{-2}.

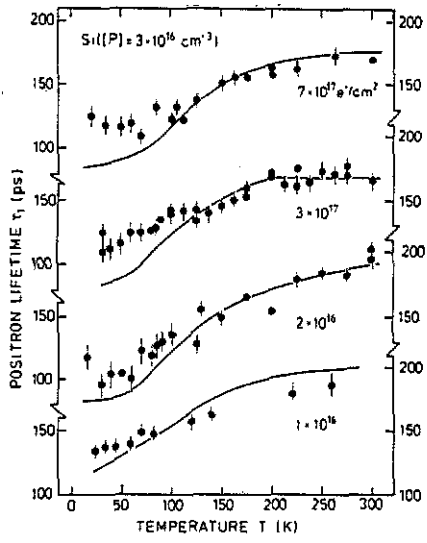

Figure 4. Temperature dependence of the positron lifetime τ_1 in phosphorus-doped Si ([P] = 3×10^{16} cm^{-3}) after 2.0 MeV electron irradiation at 300 K. The irradiation fluences are the same as in figure 3. The full curves indicate the lifetime $\tau_{1,calc}$ calculated from the two-state trapping model (equation (7)).

The average lifetime at 85 K is 220 ps if the electron fluence is $2 \times 10^{16} e^-$ cm^{-2}, corresponding to a 2 ps increase from room temperature and a 3 ps increase compared with the positron lifetime measured in the unirradiated sample at 85 K. After the higher electron fluence the average lifetime at 150 K and above is smaller than 220 ps. Below 85 K the average lifetime is 227 ± 1 ps, and the lifetime τ_2 is between 260 and 270 ps.

Table 1. Experimental positron lifetimes τ_2 in electron-irradiated Si in the temperature range indicated. The phosphorus-doped samples Si ([P] = 3×10^{16} cm^{-3}) were irradiated at 300 K. The lifetimes measured in electron-irradiated samples Si ([P] = 1×10^{20} cm^{-3}) are from [6].

Sample	E_{irr} (MeV)	Fluence (e^- cm^{-2})	τ_2 (ps)	Temperature (K)
[P] = 3×10^{16} cm^{-3}	2.0	1×10^{16}	250±3	25–300
		2×10^{16}	251±1	17–90
			268±3	150–300
		3×10^{17}	267±3	100–300
		7×10^{17}	272±3	100–300
[P] = 10^{20} cm^{-3}	1.5	3×10^{17}	250±2	4–300
		3×10^{18}	250±2	4–300

To make a summary of the results of the positron lifetime experiments, the lifetimes τ_2 measured in the samples [P] = 3×10^{16} cm^{-3} are represented in figure 3

as a function of temperature, and the different values are collected in table 1. Two values of the lifetime τ_2 were observed depending on the measuring temperature and the electron irradiation, $\tau_2 = 250 \pm 1$ and 268 ± 3 ps. When $\phi = 1 \times 10^{16} e^- cm^{-2}$, the lifetime τ_2 is 250 ● 3 ps from 20 K to room temperature. When $\phi = 2 \times 10^{16} e^- cm^{-2}$, there is a transition between these two lifetimes. The lifetime 250 ps is observed below 90 K, and the longer lifetime 268 ± 3 ps is observed above 150 K. The lifetime 268–272 ps is found above 100 K when the electron fluence is equal to or higher than $3 \times 10^{17} e^- cm^{-2}$. Table 1 also includes the lifetimes τ_2 measured in electron-irradiated Si ($[P] = 10^{20} cm^{-3}$) [6]. Irradiation with 1.5 MeV electrons was carried out at 20 K, and the fluences were 3×10^{17} and $3 \times 10^{18} e^- cm^{-2}$. The higher fluence gives rise to saturation of positron trapping. The lifetime τ_2 in those samples is 248–252 ps from 4 to 300 K. Unlike in Si ($[P] = 3 \times 10^{16} cm^{-3}$), the samples with the phosphorous concentration $[P] = 4 \times 10^{14} cm^{-3}$ showed practically no positron trapping after electron irradiation.

4. Positron traps

The positron lifetime in unirradiated Si samples increases from 216.7 ps at 20 K to 217.9 ps at 300 K. This lifetime is the bulk lifetime in Si [9]. There is also a good agreement with the theoretical lifetime of 219–221 ps in Si [10]. The increase of the average lifetime after electron irradiation indicates positron trapping at vacancy defects. In the following the experimental results presented in section 3 are examined to identify the positron traps induced by room-temperature electron irradiation.

4.1. The trapping model

In the perfect lattice, positrons annihilate with a single lifetime τ_b. In the presence of vacancy defects, positrons get trapped. When trapped at a vacancy, the electron density around the positron is lower, and it annihilates with a different lifetime $\tau_d > \tau_b$. In the simple two-state trapping model [7, 8] only one type of positron trap is assumed. The experimental lifetimes τ_i and the intensities I_i ($i = 1, 2$) are related to the characteristic lifetimes τ_b and τ_d by

$$\tau_1^{-1} = \tau_b^{-1} + \kappa \tag{3}$$

$$\tau_2 = \tau_d \tag{4}$$

$$I_2 = 1 - I_1 = \kappa/(\kappa + \lambda_b - \lambda_d). \tag{5}$$

Here κ is the trapping rate, which is proportional to the concentration c_d of positron traps, $\kappa = \mu c_d$. The trapping coefficient μ is related to the trapping cross section as $\mu = \sigma \nu_{th}$, where ν_{th} is the thermal positron velocity. In semiconductors, temperature can strongly affect the cross section σ, and thus the positron trapping rate at vacancies.

The lifetime $\tau_2 = \tau_d$ is characteristic of the defect trapping a positron. The trapping rate in the two-state trapping model is calculated from the average lifetime using equations (2) and (3)–(5) as

$$\kappa = [(\tau - \tau_b)/(\tau_d - \tau)]\lambda_b. \tag{6}$$

The comparison of the lifetime

$$\tau_{1,calc} = (\lambda_b + \kappa)^{-1} = \tau_b(\tau_2 - \tau)/(\tau_2 - \tau_b) \tag{7}$$

calculated from the two-state trapping model with the experimental lifetime τ_1 is used to test whether the two-state trapping model is valid. This comparison is done in figure 4, which shows the lifetime τ_1 from the decompositions of the lifetime spectra. The full curves correspond to the lifetime calculated from equation (7). Above 125 K the two-state trapping model is in accordance with the experimental results to a good approximation. Below 100 K the experimental lifetime τ_1 is somewhat larger than expected from equation (7). The difference $\tau_1 - \tau_{1,\mathrm{calc}}$ is from 10 to 30 ps at 20 K. Partly this is due to the very small value of the lifetime τ_1, which is close to the limit of experimental resolution. The small discrepancy appears at low temperatures when the second lifetime is 250 ps or a superposition of the two experimental lifetimes 250 and 268 ps. The small deviation may be due to a small amount of residual acceptors acting as shallow traps for positrons. However, the overall agreement with the two-state trapping model is acceptable.

4.2. Phosphorus–vacancy pair in Si

The phosphorus–vacancy pair (E centre) is the predominant defect produced by room-temperature electron irradiation of P-doped floating-zone-refined Si. This defect consists of an Si vacancy trapped next to a substitutional phosphorus atom. The migration energy of the phosphorus–vacancy pair is 0.95–1.25 eV depending on its charge state, and it is stable up to 450 K [11]. The P and Si atoms are of nearly the same size, and the introduction of a phosphorus atom at a subsitutional site does not cause any significant lattice distortion. Therefore the E centre forms an open volume trap to a positron that is similar to the Si vacancy. We argue below that the two experimental lifetimes τ_2 can both be ascribed to positron trapping at the phosphorus–vacancy pair.

The positron lifetimes $\tau_2 = 250 \pm 1$ and 268 ± 3 ps observed after electron irradiation are independent of the electron fluence. When either of these lifetimes is observed, the two-state trapping model is valid to a good approximation. This suggests that both lifetimes are due to annihilation from a well defined state. The values between 250 and 268 ps observed from 100 to 150 K when $\phi = 2 \times 10^{16} \mathrm{e}^-$ cm^{-2} or below 100 K when $\phi \geqslant 3 \times 10^{17} \mathrm{e}^-$ cm^{-2} then arise from the superposition of the lifetimes 250 and 268 ps in a two-component analysis.

The 2.0 MeV electron energy is sufficient to produce both vacancies and divacancies in the Si lattice. The isolated monovacancy can be ruled out as it migrates below 200 K in any of its charge states [12], well below the irradiation temperature (300 K). The vacancies remain in the lattice only if they are bound to impurities such as phosphorus or oxygen, forming vacancy–impurity complexes. Below we consider positron trapping at such complexes and at divacancies.

Previously we have found the lifetime 273 ± 3 ps for the negatively charged vacancy V^- in electron-irradiated $10^4 \Omega$ cm Si [6]. The positron lifetime calculated from the self-consistent electron structure of an ideal unrelaxed Si vacancy is 250–260 ps [10]. The experimental lifetimes for the Si divacancy fall typically in the range 300–330 ps. Fush *et al* [13] have attributed the lifetime 318 ps to divacancies in Si after 1 MeV electron irradiation at $7 \times 10^{18} \mathrm{e}^-$ cm^{-2} and annealing above 150 K. The lifetimes 310–330 ps have also been reported after 2 MeV electron irradiations at 300 K if the electron fluence is $\phi \geqslant 1 \times 10^{18} \mathrm{e}^-$ cm^{-2} [14, 15]. The theoretical lifetime predicted for the Si divacancy is 306–309 ps [16, 17]. Comparison of the lifetimes indicates that the positron lifetimes $\tau_2 \leqslant 270$ ps are far too short to be associated with the divacancy and suggests that the lifetimes 250 and 268 ps are due

to positron annihilation at monovacancy defects. This is further supported by the lifetime ratio τ_d/τ_b, which is 1.15 and 1.23 for $\tau_d = 250$ and 268 ps, respectively. These values are close to or smaller than the ratios for the lifetimes reported in GaAs or electron-irradiated Ge and interpreted as positron annihilation at monovacancies [3, 18].

Phosphorus atoms have a strong effect on the production of vacancy defects in electron irradiation. When $\phi = 7 \times 10^{17} e^- \text{ cm}^{-2}$, the positron trapping rate is approximately an order of magnitude higher at the phosphorus concentration [P] $= 3 \times 10^{16} \text{ cm}^{-3}$ than at [P] $= 4 \times 10^{14} \text{ cm}^{-3}$. For smaller electron fluences, the difference is even larger. The defect production thus increases with the number of phosphorus atoms in Si. Further, the concentration of vacancies saturates in the [P] $= 3 \times 10^{16} \text{ cm}^{-3}$ samples. The saturation of vacancy concentration can be seen from the positron lifetime results, which do not change when the fluence is raised from 3×10^{17} to $7 \times 10^{17} e^- \text{ cm}^{-2}$. This can be understood so that after the electron irradiation $3 \times 10^{17} e^- \text{ cm}^{-2}$ practically all the phosphorus atoms are transformed to phosphorus–vacancy pairs.

The absolute lifetimes directly point to the conclusion that the positron lifetimes $\tau_2 = 250$ and 268 ps in the electron-irradiated Si ([P] $= 3 \times 10^{16} \text{ cm}^{-3}$) samples are both associated with monovacancies. These vacancy defects appear only if the concentration of phosphorus atoms is sufficiently high. The defect produced by room-temperature electron irradiation and observed by the positron lifetime measurement can therefore be identified as the phosphorus–vacancy pair. The maximum concentration of (P–V) pairs is the concentration $3 \times 10^{16} \text{ cm}^{-3}$ of P atoms.

Silicon divacancies are produced by 2 MeV electron irradiation. After MeV electron irradiations they have been clearly identified by electron paramagnetic resonance (EPR), electron–nuclear double resonance (ENDOR) and deep-level transient spectroscopy (DLTS) measurements [12, 19, 20]. It is worth while to consider whether the divacancies have any effect on positron trapping or the lifetime τ_2. When [P] $= 4 \times 10^{14} \text{ cm}^{-3}$ and $\phi = 2 \times 10^{16} e^- \text{ cm}^{-2}$, the average positron lifetime at 300 K is the same as in the unirradiated samples, indicating that the defect concentration is too small to be detected. This asserts that the lifetime 268 ± 3 ps observed for [P] $= 3 \times 10^{16} \text{ cm}^{-3}$ after the same electron fluence and also when $\phi = 3 \times 10^{17} e^- \text{ cm}^{-2}$ has no contribution from positron trapping at divacancies. After the electron irradiation $\phi = 7 \times 10^{17} e^- \text{ cm}^{-2}$ of the Si ([P] $= 4 \times 10^{14} \text{ cm}^{-3}$) samples, we observe a very small ($\leqslant 1$ ps) increase of the average positron lifetime at 300 K. The trapping rate $\kappa \sim 10^8 \text{ s}^{-1}$ at neutral divacancies can be estimated from the reported trapping rates after 2 MeV electron irradiations of Si at 300 K [14, 15]. The trapping rate in Si ([P] $= 3 \times 10^{16} \text{ cm}^{-3}$) after electron irradiations $\phi \geqslant 3 \times 10^{17} e^- \text{ cm}^{-2}$ is an order of magnitude higher, $8 \times 10^8 \text{ s}^{-1}$. From these trapping rates one expects a 2–3 ps increase of the lifetime τ_2 after electron irradiation $7 \times 10^{17} e^- \text{ cm}^2$ of the Si ([P] $= 3 \times 10^{16} \text{ cm}^{-3}$) due to divacancies. This could explain the increase of τ_2 from 268 ps to 272 ± 3 ps.

In [6], the lifetime 248–252 ps was observed from 4 to 300 K in electron-irradiated Si in which the P concentration is 10^{20} cm^{-3}. Because of the high phosphorus concentration it was identified as the phosphorus–vacancy pair although the samples were Czochralski-grown Si. In those samples the doping is sufficiently high for the Fermi level to lie in the conduction band after electron irradiation. The position of the Fermi level as compared to the ionization level (−/0) at $E_C - 0.44$ eV [21] (E_C is the bottom of the conduction band) corresponds to the negative charge state of

the phosphorus–vacancy pair. The lifetime 250 ps in the present case can therefore be assigned to the negatively charged $(P–V)^-$ pair. The negative charge state is in accordance with the strong temperature dependence of the positron trapping rate (section 5).

We attribute the lifetime $\tau_2 = 268 \pm 3$ ps, which is typical of a monovacancy and only appears if the phosphorus concentration is $[P] = 3 \times 10^{16}$ cm^{-3}, to the neutral charge state $(P–V)^0$ of the phosphorus–vacancy pair. This is supported by the following observations:

(i) The positron lifetime 250 ps is observed after electron irradiations $\phi \leqslant 2 \times 10^{16}e^-$ cm^{-2}. The phosphorus concentration 3×10^{16} cm^{-3} corresponds to the Fermi level position above the ionization level (–/0). The transition to the lifetime 268 ± 3 ps occurs as a result of increasing the irradiation fluence, which lowers the position of the Fermi level. In EPR measurements the E centre does not appear at the initial stages of electron irradiation but only after the Fermi level has receded close to the acceptor level $E_C - 0.44$ eV and the E centre becomes neutral [22].

(ii) The transition 250→268 ps occurs also if temperature increases and the lifetime is 250 ps at low temperatures ($\phi \geqslant 2 \times 10^{16}e^-$ cm^{-2}). Similarly to the increasing electron fluence, this lowers the position of the Fermi level in the energy gap. Comparing the electron irradiations $\phi = 2 \times 10^{16}$ and 3×10^{17}e$^-$ cm^{-2}, the transition occurs at a lower temperature for the higher fluence.

(iii) As a result of the transition the positron trapping rate decreases. At 100 K the trapping rate after electron irradiation $\phi = 2 \times 10^{16}$e$^-$ cm^{-2} is $\kappa = 4.2 \times 10^9$ s^{-1} ($\tau_2 = 250$ ps), and $\kappa = 3 \times 10^9$ s^{-1} when $\phi = 3 \times 10^{17}$e$^-$ cm^{-2} ($\tau_2 = 268$ ps). An implication of the smaller trapping rate even though ϕ is an order of magnitude higher is that the 250 ps defect disappears. This can follow from the change of the charge state of the E centre.

In summary, there are clear grounds for ascribing the lifetimes induced by electron irradiation to positron trapping at the phosphorus–vacancy pair. Also, the concentration of divacancies is too small to bear any observable influence on positron trapping or the defect lifetime apart from a possible small increase of τ_2 at the highest irradiation fluence. Below we discuss the consequences of this interpretation of the experimental lifetime results. In particular, it implies that the change of the charge state of the phosphorus–vacancy pair in Si causes a change of the positron lifetime.

5. Relaxation of the phosphorus–vacancy pair

Above, the lifetimes 250 ± 1 and 268 ± 3 ps induced by electron irradiation in phosphorus-doped Si were ascribed to the negative and neutral charge states of the phosphorus–vacancy pair. One of the results of the theoretical calculations of positron lifetimes in semiconductors is that the lifetime is nearly independent of the charge state of the vacancy if the atomic configurations are the same at the different charge states [10]. Taking the Si vacancy as an example, the calculated positron lifetime increases from 249 ps for V^0 by only 2 ps to 251 ps if the vacancy becomes negatively charged [23]. Therefore we anticipate that the transition 250→268 ps of the positron lifetime is connected with the volume relaxation of the phosphorus–vacancy pair. The DLTS experiments discussed in more detail below indicate that such breathing-mode relaxation is associated with the emission of an electron in the transition $(P–V)^-$→$(P–V)^0$. In the following the amplitudes of the relaxations are estimated by comparing the

experimental and theoretical positron lifetimes. We consider separately the *difference* in the lifetime τ_2 between the different charge states and the absolute positron lifetimes at each state.

The difference in the positron lifetimes 250 ± 1 and 268 ± 3 ps between the negative and the neutral charged states $(P–V)^-$ and $(P–V)^0$ is 18 ± 3 ps. The longer lifetime in the neutral charge state indicates a larger open volume, and hence an *outward* relaxation in the transition $(P–V)^- \rightarrow (P–V)^0$. The magnitude of the lattice relaxation can be estimated from the calculated positron lifetimes. In [24] the positron lifetime for both the Si vacancy and the phosphorus–vacancy pair were calculated as a function of the bond length around a vacancy assuming a symmetrical breathing-mode relaxation of the nearest-neighbour atoms. The positron lifetime was found to change in proportion to the nearest-neighbour bond length. An 18 ps change of the lifetime at the (P–V) pair corresponds to the amplitude of the lattice distortion $\Delta r/r_0 \sim 5.1\%$, or $\Delta r \sim 0.12$ Å (r_0 is the Si–Si bond length 2.35 Å).

The estimation of the amplitude of the relaxation assumes that the relaxation is taken up by the first-shell atoms only. For the Si vacancy the theoretical results show that the distortion amplitude for the next-nearest Si atoms is approximately half of the nearest-neighbour atoms, and it becomes negligibly small at four bond lengths away from the vacancy [25, 26]. The wavefunction of a positron trapped at the Si vacancy is rather well localized. The fraction of the positron density inside the nearest-neighbour shell of the vacancy is about 70% [10]. The positron lifetime is therefore determined mainly by the relaxation of the nearest-neighbour atoms. Also, the breathing-mode relaxation is not symmetric as there is a superimposed symmetry-breaking Jahn–Teller distortion associated with the formation of the (P–V) centre [22].

Samara [1, 2] has investigated the breathing-mode relaxations of the phosphorus–vacancy pair in Si. Those experiments were based on DLTS measurements under hydrostatic pressure, and the pressure dependence of the annealing kinetics of the (P–V) pair in its neutral and negative charge states. The results indicate an outward breathing-mode relaxation accompanying electron emission, and the volume change in the charge state transition is 2.5–5 Å^3 per defect. The pressure dependence of annealing kinetics yields the volume changes $\Delta V = 10.0$ and 5.2 Å^3 for $(P–V)^0$ and $(P–V)^-$, respectively. This indicates an outward relaxation in both charge states. The volume changes imply the amplitudes of lattice distortion $\Delta r/r_0$ of 6.1% for $(P–V)^0$ and 3.2% for $(P–V)^-$ assuming a symmetrical relaxation of the nearest-neighbour atoms only [1, 2].

Experimental positron lifetimes indicate the relaxation of a vacancy in the transition $(P–V)^- \rightarrow (P–V)^0$ in the same direction as the DLTS experiments. Also the amplitude of relaxation $\Delta r/r_0 = 5.1\%$ or $\Delta r = 0.12$ Å is in fair agreement with $\Delta r/r_0 = 2.9\%$ or $\Delta r = 0.07$ Å reported by Samara [1].

Comparison with the theoretical positron lifetime at an ideal vacancy gives the direction of the relaxation separately for different charge states. In [10] the calculated lifetimes for an unrelaxed Si vacancy in neutral or negatively charged states are 259–261 ps. The lifetimes were calculated from the self-consistent electron structure using the standard local-density scheme. However, it appears that the calculation of the annihilation rate directly from the total electron density without dividing it into valence and core electron contributions gives a considerably shorter positron lifetime [23]. For the Si vacancy the calculated lifetimes are 249 and 251 ps for the neutral and negatively charged states [23]. The lifetime 250 ps for unrelaxed

vacancy would correspond to a very small breathing-mode lattice distortion for the negatively charged (P–V) centre, and approximately 5% outward relaxation for the neutral state. Here we have used the theoretical lifetime for an isolated Si vacancy as there are no calculations for the (P–V) pair that use the self-consistent electron density. The positron lifetime is not affected by the phosphorus atom [24]. These values are in fair agreement with the DLTS measurements [1, 2] ($\Delta r/r_0 = 3.2$ and 6.1% for $(P–V)^-$ and $(P–V)^0$, respectively). The agreement is in fact even better. The DLTS experiments measure the total volume relaxation ΔV per defect, and therefore overestimate Δr if only the relaxation of the nearest-neighbour atoms is assumed. According to Samara, the true relaxation amplitudes of the nearest-neighbour atoms may be even 30% smaller [1, 2].

The relaxation amplitudes estimated separately for different charge states depend on the accuracy of the theoretical positron lifetimes. However, as a function of the amplitude of the breathing-mode relaxation, the *change* of the positron lifetime is rather independent of the approximations. Different calculations yield the lifetime change 3.3–3.6 ps for the relaxation $\Delta r/r_0 = 0.01$ for the Si vacancy and (P–V) centre in Si and the As vacancy in GaAs [24, 27].

Another complication arises if the localized positron influences the ionic relaxations around the vacancy. In GaAs, the theoretical positron lifetimes at As and Ga vacancies are considerably lower than the experimental ones if one assumes the ionic relaxations of vacancies predicted from recent first-principles molecular-dynamics calculations [27]. This would indicate that positron trapping can cause additional distortion of ions around the vacancy, increasing the positron binding energy and its lifetime. The good agreement with the DLTS experiments suggests that the effect is unimportant in the case of the phosphorus–vacancy pair in Si.

These results can be compared to the positron lifetime experiments in GaAs. There the positron lifetimes $\tau_2 = 257$ and 295 ps at the as-grown vacancies in n-type GaAs are observed [3, 4]. The lifetime transition 257→295 ps is associated with an energy level at $E_C - 30$ meV, and it has been interpreted as the (0/1−) ionization level of the As vacancy [4]. This would indicate an outward relaxation in electron emission $V_{As}^- \rightarrow V_{As}^0$, and the magnitude of the relaxation is almost a factor of 2 larger than in the case of the (P–V) centre in Si.

6. Positron trapping

6.1. Trapping rates

Comparison of the experimental lifetime τ_1 with the trapping model in figure 4 indicated that the two-state trapping model is valid, and the trapping rate κ can be calculated from equation (6). In the following we first estimate the positron trapping coefficients for both charge states of the (P–V) centre, and discuss the trapping mechanisms at negatively charged vacancies.

In the Si ($[P] = 3 \times 10^{16}$ cm^{-3}) samples the positron lifetime τ_2 is 250 ± 1 ps from 25 K to room temperature after the electron irradiation $\phi = 1 \times 10^{16}$e$^-$ cm^{-2}, and from 17 to 100 K when $\phi = 2 \times 10^{16}$e$^-$ cm^{-2}. To calculate the trapping rate the lifetime τ_2 has been fixed at 250 ps in the decomposition in the case of the smaller fluence. Also, the temperature coefficient 0.34×10^{-2} ps K^{-1} of the bulk lifetime τ_b in equation (6) was taken into account. Figure 5 shows the trapping rate κ as

a function of temperature for the $\tau_2 = 250$ ps defect identified as the negatively charged centre $(P\text{–}V)^-$.

The electron irradiation $\phi = 2 \times 10^{16} e^- \text{ cm}^{-2}$ gives rise to the positron trapping rate $9.5 \times 10^9 \text{ s}^{-1}$ at 20 K, and it decreases to $4 \times 10^9 \text{ s}^{-1}$ at 100 K. A similar decrease from $4 \times 10^9 \text{ s}^{-1}$ at 25 K to $1.5 \times 10^9 \text{ s}^{-1}$ at 100 K is seen after the smaller irradiation fluence $1 \times 10^{16} e^- \text{ cm}^{-2}$. In the latter case the calculation of the trapping rate can be extended to 300 K as the lifetime τ_2 indicates that the phosphorus–vacancy pair remains negatively charged. Above 100 K the trapping rate decreases continuously, and at 300 K it is $\kappa = 3 \times 10^8 \text{ s}^{-1}$.

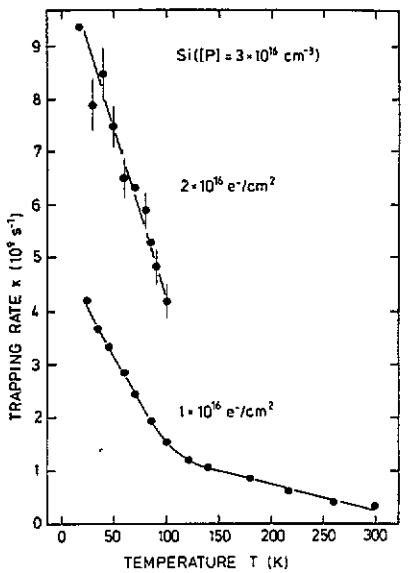

Figure 5. Positron trapping rate κ calculated from equation (7) as a function of temperature in phosphorus-doped Si ($[P] = 3 \times 10^{16} \text{ cm}^{-3}$) after 2.0 MeV electron irradiation at 300 K. The trapping rate is calculated for the positron lifetime 250 ps, which is observed from 17 to 100 K when $\phi = 2 \times 10^{16} e^- \text{ cm}^{-2}$, and from 25 K to room temperature when $\phi = 1 \times 10^{16} e^- \text{ cm}^{-2}$. This defect was identified as the negatively charged $(P\text{–}V)^-$ pair.

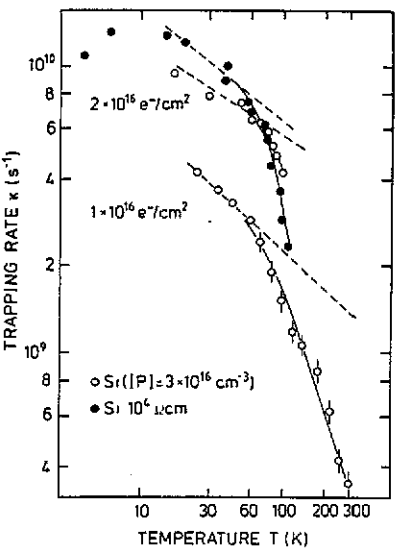

Figure 6. Temperature dependence of the positron trapping rate κ at $(P\text{–}V)^-$ in electron-irradiated phosphorus-doped Si ($[P] = 3 \times 10^{16} \text{ cm}^{-3}$) also shown in figure 5 but plotted as $\ln \kappa$ versus $\ln T$. The trapping rate at a negative Si vacancy V^- is from [6]. The full curves are fits to the two-stage trapping model given in equations (8) and (9), and also depicted in figure 7.

The temperature dependence in figure 5 is very similar to that found for positron trapping at the negatively charged vacancy V^- in electron-irradiated $10^4 \Omega$ cm Si from 4 to 120 K [6]. For the isolated vacancy the measuring temperature was limited by vacancy migration at 150 K. The same kind of temperature dependence has been reported by Mascher *et al* [15] for negatively charged divacancies in electron-irradiated Si.

We have estimated the trapping coefficient μ at the neutral and negatively charged states from the saturation of the concentration of phosphorus–vacancy pairs in the Si ($[P] = 3 \times 10^{16} \text{ cm}^{-3}$) samples. Comparing the electron irradiations $\phi = 3 \times 10^{17}$ and $7 \times 10^{17} e^- \text{ cm}^{-2}$, the positron lifetime measurements indicate that the

concentration of the traps does not increase. It implies that the fluence $3 \times 10^{17} e^- cm^{-2}$ is sufficiently high for the electron irradiation to produce a concentration of phosphorus–vacancy pairs that is close to the original concentration of phosphorus atoms. Assuming the concentration 3×10^{16} cm^{-3} of the phosphorus–vacancy pairs, the trapping rate 0.8×10^9 s^{-1} yields the trapping coefficient $\mu^0(300\ K) = 1.3 \times 10^{15}$ s^{-1} for the neutral charge state $(P\text{–}V)^0$ at 300 K. For the electron irradiation $2 \times 10^{16} e^-$ cm^{-2} the trapping rate at 300 K is 0.5×10^9 s^{-1}. Because of the same positron lifetime $\tau_2 = 268 \pm 3$ ps, the ratio of the trapping rates due to the electron irradiations 2×10^{16} and $3 \times 10^{17} e^-$ cm^{-2} directly yields the estimate 1.9×10^{16} cm^{-3} for the defect concentration. The trapping rate 9.3×10^9 s^{-1} then gives the trapping coefficient $\mu^-(20\ K) = 2.4 \times 10^{16}$ s^{-1} at the negatively charged $(P\text{–}V)^-$ pair ($\tau_2 = 251 \pm 1$ ps) at 20 K. Further, estimating the concentration of (P–V) pairs due to the $1 \times 10^{16} e^-$ cm^{-2} electron irradiation from the ratio of the trapping rates at 20 K yields 1×10^{16} cm^{-3}. This corresponds to the trapping coefficient $\mu^-(300\ K) = 2.0 \times 10^{15}$ s^{-1} at the negatively charged $(P\text{–}V)^-$ centre at room temperature.

The values given above are lower limits for the trapping coefficient as the concentration of the (P–V) centres is equal to or smaller than the concentration 3×10^{16} cm^{-3} of P atoms. The trapping coefficients estimated here are in good agreement with the values 1×10^{15} and 3.5×10^{15} s^{-1} reported for the neutral and negatively charged divacancies in electron-irradiated Si at 300 K [15].

6.2. *Trapping mechanisms*

Non-radiative mechanisms of free-carrier capture at defects include the phonon-assisted processes and the various Auger processes, which involve excitations of electrons. Similar mechanisms are expected for the trapping of positrons at vacancy defects. Below we discuss the trapping mechanisms for V^- and $(P\text{–}V)^-$ in the light of the experimental temperature dependence of the positron trapping rate.

The trapping rate κ as a function of temperature is represented in figure 6 as an $\ln \kappa$ versus $\ln T$ plot. Positron trapping at the phosphorus–vacancy pair $(P\text{–}V)^-$ is characterized by (i) a strong temperature dependence of the trapping rate κ and (ii) a large trapping coefficient 2.4×10^{16} s^{-1} at low temperatures (20 K). This corresponds to the trapping cross section 2×10^{-13} cm^2. In analogy with electron or hole capture, these characteristics are typical of trapping at an attractive Coulomb centre. This also supports the assignment of the lifetime 250 ps to the negatively charged state. For comparison the trapping rate at the negative Si vacancy V^- is reproduced from [6]. If the trapping rate is described by $\kappa \sim T^{-n}$, the temperature dependence between 15 and 60 K is approximately given by $n = 0.5$ in both cases. Above 70 K the temperature dependence corresponds approximately to $n = 1.5$ in P-doped Si, and 2.5 in $10^4 \Omega$ cm Si.

The large cross sections and the strong temperature dependence of positron trapping at V^- or $(P\text{–}V)^-$ cannot be explained in terms of multiphonon emission or Auger processes. The capture cross section for multiphonon emission varies over many orders of magnitude but is not expected to exceed 10^{-14} cm^2 [28]. Also the temperature variation in figure 6 is different from that expected if the energy dissipation occurs by multiphonon emission. Jaros [29] has proposed that many of the capture cross sections for free carriers as high as 10^{-13} cm^2 can be explained by Auger processes. Also, Puska *et al* [5] have calculated trapping coefficients of the order of 10^{16} s^{-1} for positron trapping at negative vacancies for interband electron–hole excitation and electron excitation from localized levels at the vacancy. Auger

processes, however, typically exhibit a much weaker temperature dependence than that in figure 6.

In an attempt to explain the strong temperature dependence and the large cross section of positron trapping at the negatively charged Si vacancy, the phonon cascade model was proposed in [6, 30]. Within the semiclassical approach, the cross section of the cascade capture varies with temperature as T^{-3} [31]. In that model a positron is initially captured by a cascade process where the Coulomb field supports the necessary distribution of excited states. Trapping of a positron is detected as a change of its lifetime only if it gets to the ground state at the vacancy. The phonon cascade process cannot describe the transition into the deep ground state at the vacancy as the transition rate between the Rydberg states is $< 10^7 s^{-1}$ [5], which is much smaller than the positron annihilation rate $1/\tau_b = 4.6 \times 10^9\ s^{-1}$ in Si.

In consequence, if the excited Rydberg states act as an intermediate precursor state for positron trapping, only one state can be involved. For the charge carriers, the model due to Gibb *et al* [32] treats two-step capture with thermal re-emission from a single excited state. If the re-emission dominates the capture cross section, it leads to a temperature dependence similar to that in figure 6.

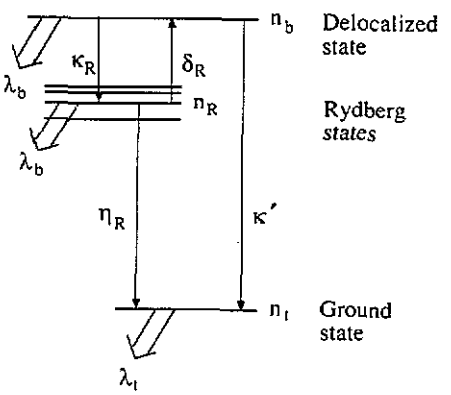

Figure 7. A schematic picture of positron trapping at a negative vacancy in Si (from [5]).

In the following we examine the two-stage trapping model including a single precursor state. This model was presented by Puska *et al* [5], and it is schematically shown in figure 7. In the model the transition from the delocalized state to a precursor state occurs with the rate κ_R, from the precursor state to the ground state at the rate η_R, and from the delocalized state directly to the ground state at the rate κ'. An annihilation rate at the precursor state equal to the bulk annihilation rate λ_b is assumed. The relationship between this two-stage capture mechanism and the two-state trapping model used in the analysis of the experimental lifetime spectra is (see [5])

$$\kappa = \eta_R \kappa_R / (\eta_R + \delta_R). \tag{8}$$

In equation (8) the annihilation in the precursor state is neglected ($\eta_R \gg \lambda_b$), and the direct transition rate is assumed to be small ($\kappa' \ll \lambda_b$). When the delocalized and localized states are in thermal equilibrium, the detrapping rate δ_R is given by [33]

$$\delta_R / \kappa_R = (1/c_v)\,(m_+ k_B T / 2\pi\hbar^2)^{3/2} \exp(-E_b / k_B T) \tag{9}$$

where m_+ is the effective positron mass, and E_b is the binding energy of the precursor state.

The full curves in figure 6 are fits of the two-stage trapping model to the experimental trapping rate. Thermal re-emission from the weakly bound precursor state leads to a rapid decrease of κ observed experimentally. The fitted parameters are the binding energy E_b and the factor $\eta_R c_v$. In the case of the negative phosphorus–vacancy pair, the binding energy is $E_b \sim 15$ meV, and $\eta_R c_v$ is $3 \times 10^{27} s^{-1}$ cm^{-3} for $\phi = 1 \times 10^{16} e^-$ cm^2 and 8×10^{27} s^{-1} cm^{-3} for $\phi = 2 \times 10^{16} e^-$ cm^2. A similar analysis of the trapping rate at the negative Si vacancy V^- yields the binding energy $E_b \sim 27$ meV, and the factor $\eta_R c_v$ is 0.6×10^{27} s^{-1} cm^{-3}. Some implications of the two-stage trapping model are considered below:

(i) In view of this model the trapping rate κ is equal to κ_R below 60 K ($\delta_R = 0$, no detrapping). If the trapping rate to the ground state is very fast ($\eta_R \gg \lambda_b$) the initial trapping event limits the overall trapping rate. The model thus imposes the trapping coefficient 2×10^{16} s^{-1} at 20 K from the delocalized state to the precursor state in the case of $(P–V)^-$ and approximately an order of magnitude higher for V^-. The trapping coefficient for the isolated vacancy V^- is based on the reported vacancy production rates 0.01–0.001 cm^{-1} in n-type Si for MeV electron irradiation [34]. The trapping rate increases roughly as $T^{-0.5}$ below 60 K. This temperature dependence of the trapping rate κ_R was extrapolated to higher temperatures (broken lines in the figure).

(ii) The binding energy of the precursor state is between 15 and 30 meV. The binding energies are sensitive to the actual potential of the deep trap but 15–30 meV would correspond to a rather small quantum number n of the excited Rydberg state, typically from $n = 2$ to $n = 4$.

(iii) The factor $\eta_R c_v$ extracted from the two-stage trapping model yields an estimate for the transition rate η_R if the defect concentrations estimated in the preceding section are used. For the phosphorus–vacancy pair $(P–V)^-$, the transition rate is approximately 3×10^{11} s^{-1}. This value is large compared to the annihilation rate λ_b at the precursor state, as assumed in equation (8). It means that a positron makes a transition to the ground state once it has been trapped at the Rydberg state. For the negatively charged Si vacancy V^- the factor $\eta_R c_v$ is clearly smaller. The transition rate from the Rydberg state to the ground state at the vacancy very much depends on the quantum numbers of the state [5], but the lifetime results do not show annihilation from the precursor state indicating that the transition rate is $\eta_R \gg \lambda_b$. If one assumes the same transition rate as in the $(P–V)^-$ pair, the vacancy concentration is $c_v = 1 \times 10^{15}$ cm^{-3}. This is in relatively good agreement with the reported vacancy production rates 0.001–0.01 for 1.5 MeV electron irradiation [34]. It would also imply a very large trapping coefficient $\mu \geqslant 10^{17}$ s^{-1} for positron trapping at V^- at low temperatures [6].

The actual trapping process is more complicated as the different Rydberg states act in parallel. The weakly bound state in the two-stage trapping model describes the Rydberg states in the sense of some average. The model calculation shows, however, that the capture rates from a delocalized state to a Rydberg state and from a Rydberg state to the ground state vary by orders of magnitude depending on the quantum numbers of the states [5]. This makes the contribution of the various excited states to the positron trapping process very different.

Positron trapping in electron-irradiated Si in the case of very high phosphorus

doping [P] = 10^{20} cm^{-3} gives evidence of the important role of the Rydberg-like precursor state in positron capture. Positrons are trapped at the negatively charged phosphorus–vacancy pair, but the trapping rate is independent of temperature from 4 to 300 K [6]. This can be attributed to the efficient screening of the Coulomb potential. The phosphorus concentration is higher than the critical concentration 3.75×10^{18} cm^{-3} of the metal–insulator transition in P-doped Si [35]. The Thomas–Fermi screening length is only ~ 4 Å, and a positron can no longer be bound at a Rydberg-like state. Trapping occurs via a direct transition to the ground state and the trapping rate is independent of temperature as the negative charge of the vacancy is screened.

In GaAs, positron trapping and thermal detrapping at negatively charged ion-type centres has been ascribed to the Rydberg states [36, 37]. The positron binding energy is typically 40 meV corresponding to the Rydberg state $n \simeq 3$ [37].

7. Conclusions

In this work we have investigated positron annihilation in electron-irradiated phosphorus-doped FZ Si. Electron irradiation induces the positron lifetimes τ_2 = 250 ± 1 and 268±3 ps. There is a transition 250→268 ps that takes place with increasing electron fluence and increasing measuring temperature. These lifetimes are both ascribed to positron trapping at the phosphorus–vacancy pair, which is the dominant defect in electron-irradiated P-doped Si. It has the charge states $(P–V)^0$ and $(P–V)^-$. The change of the positron lifetime indicates that the open volume of the vacancy increases in the transition $(P–V)^- \rightarrow (P–V)^0$, which means that there is an outward lattice relaxation associated with electron emission. The difference in the lifetime corresponds to 5% relaxation of the nearest-neighbour atoms around the vacancy. Comparing with the most recent theoretical lifetimes, the breathing-mode relaxation of the negatively charged state is approximately 5% whereas the neutral state is almost unrelaxed. These observations are in accordance with the previous DLTS measurements due to Samara [1, 2].

The results demonstrate the effect of lattice relaxation around the vacancy on positron lifetime. The positron lifetime technique combined with theoretical calculations could be used to measure the symmetry-conserving relaxations of vacancy defects, which are not very well known even in Si. There is considerable uncertainty on the direction of the relaxation as well as its magnitude, both in experiments and in theory.

Positron trapping at the negatively charged phosphorus–vacancy pair is characterized by a strong temperature dependence and a relatively large trapping coefficient 2×10^{16} s^{-1} at 20 K. The temperature dependence is quite similar to what was previously observed for the negatively charged Si vacancy V^-. This temperature dependence was ascribed to the attractive Coulomb potential between a positron and a negatively charged centre, which gives rise to a series of Rydberg states acting as a precursor state in the positron capture. In such a two-stage trapping model, thermal detrapping from a weakly bound precursor state can explain the strong temperature dependence observed experimentally. The binding energy E_b ~15–30 meV at the precursor state was estimated.

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