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Low-temperature positron-lifetime studies of proton-irradiated silicon

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The positron-lifetime technique has been used to identify defects created in high-purity single-crystal silicon by irradiation with 12-MeV protons at 15 K, and the evolution of the defects has been studied by subsequent annealings between 20 and 650 K. Two clear annealing steps were seen in the samples, the first starting at 100 K and the other at 400 K. The first is suggested to be a result of the migration of free, negatively charged monovacancies, and the second is connected to the annealing of some vacancy-impurity complexes, probably negatively charged vacancy-oxygen pairs. The specific trapping rate of positrons to both of these negatively charged monovacancy-type defects has been found to have a clear $T^{-0.5}$ dependence. The positron lifetime in perfect Si is measured to be 217 ± 1 ps, and the monovacancy lifetime is found to be 275 ± 5 ps. Also the negatively charged vacancy-oxygen complexes were found, both experimentally and theoretically, to give rise to a positron lifetime of about 275 ps.

I. INTRODUCTION

Silicon is technologically the most important semiconductor so far. It is employed in almost all modern high-technology products such as chips, solar cells, and transistors. At the moment the industry can produce quite high-quality Si-based components thanks to the development of the crystal growth and thin-film techniques. However, present techniques cannot prevent the existence of different atomic-size defects[1] in silicon. In many cases, such as the space technology, also particle radiation induces point defects in the Si-based components. These point defects can often have drastic effects on the electrical and optical properties of Si.[2,3] It is thus important to achieve knowledge about the properties of the defects, as well as the changes they cause to the electronic structure and the carrier densities in the host matrix. In addition to its technological importance, the study of point defects in Si also gives fundamental knowledge about the properties of atomic-size defects in semiconductors in general, and can aid the investigations of, e.g., the more complex GaAs.

Various experimental techniques have been developed for studies of point defects in solids since the early 1950's. For semiconductors the methods most often used are the electron paramagnetic resonance (EPR),[4] infrared spectroscopy (IR),[5] transient capacitance spectroscopy (TCS),[6] deep-level transient spectroscopy (DLTS),[7] high-voltage electron microscopy,[8] and positron-annihilation spectroscopies (PAS).[9–11] Due to the positive charge of positrons the positron-lifetime technique is selectively sensitive to negatively charged and neutral vacancy-type defects. The electron density in a vacancy is lower than that in the interstitial regions of the perfect lattice. Therefore, the lifetime of positrons trapped at a monovacancy in Si is about 25% longer than the lifetime of those positrons that annihilate in the perfect crystal.[12] The sensitivity of the positron-lifetime technique to open-volume defects is excellent: in semiconductors, defect concentrations of the order of 0.1 ppm or less can be detected by this method.[13]

The density of states in semiconductors is characterized by the band gap, and in totally pure intrinsic conditions the Fermi level is (at zero temperature) in the middle of the gap. However, semiconductors always contain at least a small amount of point defects which can create electron energy levels in the gap. According to the occupation of these levels the Fermi level can vary from the top of the valence band to the bottom of the conduction band. The value of the Fermi energy determines the charge state of the vacancy, which in the case of Si is $-2e$, $-e$, 0, or $2e$ (V^+ is found to be unstable[14–16]). The vacancy charge state makes the trapping of positrons very complex. In spite of intensive studies all the effects are not yet fully understood.

We have employed the positron-lifetime technique to study the annealing of vacancies in Si. High-purity single-crystal samples have been irradiated at 15 K with 12 MeV protons and the samples have, thereafter, been isochronally annealed up to 650 K. The positron-lifetime spectra were measured at 15 K. Two annealing steps were clearly seen. The first started at about 100 K where free, negatively charged monovacancies are believed to become mobile.[17] The other annealing step started at about 400 K, and the samples were totally annealed at 600 K. We have also studied the dependence of the relative vacancy concentration on the dose. With a dose of 2.3×10^{14} protons/cm^2 the defect concentration, as observed by the positron-lifetime technique, was about eight times larger than the concentration produced by a

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3.0×10^{13} p/cm^2 irradiation. We have studied the temperature dependence of the positron trapping rate in proton-irradiated Si and found good agreement with a theory recently proposed by Puska *et al.*[18]

II. EXPERIMENT

The Si samples were cut from a high-purity floating-zone (FZ)-grown single crystal rod made at Topsil Semiconductors a/s, Denmark. The resistivity of the material was 2200 Ω cm and the material was slightly *n*-type. The concentrations of phosphorus and boron were 5.8×10^{-5} ppm P and 2.0×10^{-5} ppm B. The carbon and oxygen contents were <0.3 ppm C and <0.2 ppm O. The samples were mechanically polished with 50 mol % Al_2O_3, 30 mol % SiO_2 powder to a thickness of 467 μm. After polishing, the Si samples were washed in deionized water and acetone before etching in 95 vol % HNO_3 and 5 vol % HF for $1-1\frac{1}{2}$ hours. Samples with thicknesses of 396 ± 3 μm and 387 ± 1 μm were prepared. Finally, the samples were rinsed in deionized water and acetone again.

The samples were packed in the standard sandwich geometry[19] to let the positron source be covered by two identical pieces of Si. The ^{22}NaCl positron source was deposited onto thin Havar foil (1.7 mg/cm^2) and then developed. The proton irradiations were carried out by the JYFL low-temperature irradiation facility[20] where the temperature of the specimens can be kept continuously at 15 K during and after irradiation, and annealings could thus be started from 15 K. The lifetime spectrometer consists of a plastic scintillator for the start gamma (1.275 MeV) and of a BaF_2 scintillator for the stop gamma (511 keV). Each positron-lifetime spectrum contained about 1.1 million events. The annealing rate was 25 K/h, and the isochronal annealings were carried out either in vacuum ($T_{ann}\leq320$ K) or in flowing argon ($T_{ann}>320$ K).

The time resolution of the lifetime spectrometer was determined by measuring perfect Mo and Si samples and analyzing the lifetime spectra with the FORTRAN program RESOLUTION.[21] The resolution function was found to be a one-component Gaussian function with a full width at half maximum (FWHM) of 217 ps. Also the contributions of the Havar foil and of the ^{22}NaCl salt were obtained by the program. The total intensity of the source components was found to be 16% with lifetimes of 170 ps (13.5%) and 450 ps (2.5%). The lifetime data were analyzed with the FORTRAN program POSITRONFIT[21] by using this resolution function and these source components.

The 12-MeV proton irradiations were performed from both sides of the sample set to obtain a homogeneous defect distribution. The penetration depth and the longitudinal straggling of 12-MeV protons in Si are 950 and 15 μm, respectively,[22] hence all protons penetrated the total sample set. The samples were packed with indium to maximize the heat transfer from the samples to the cold head. The current of the proton beam was kept low (~6 nA) in order to keep the sample temperature below 20 K. In the first irradiation (Si-I) the samples were irradiated at 15 K to a dose of 2.4×10^{13} protons/cm^2. These samples were then annealed isochronally up to 150 K in 10-K steps, after which the temperature dependence of the specific trapping rate of positrons was studied by measuring the positron-lifetime spectra at temperatures between 15 and 140 K. Then the sample set was further irradiated at 15 K to a total dose of 2.3×10^{14} p/cm^2 (Si-II). A third proton irradiation (Si-III) to a total dose of 3.0×10^{13} p/cm^2 was performed on another sample set.

In the analysis of the positron-lifetime spectra a lifetime component of about 1.5 ns was found. The intensity of this lifetime component was about 0.05% in the less-irradiated samples and about 0.1% in the heavily irradiated Si. We therefore fixed τ_3 to 1.5 ns and I_3 either to 0.05% (Si-I and Si-III) or to 0.1% (Si-II). This component is probably due to orthopositronium that annihilated in the bulk or on the surfaces of the Si samples. The variances of the fits were between 1.0 and 1.2 for most spectra.

III. RESULTS AND DISCUSSIONS

A. As irradiated

The positron lifetime in the perfect Si crystal was measured prior to the irradiations, and a lifetime of 217 ± 1 ps was found at 15 K. This is in excellent agreement with the earlier reported value of 218 ps.[23–25] The calculated positron lifetime of Puska *et al.* is 219 ps.[26]

The Si samples were irradiated at 15 K with 12-MeV protons to a dose of 2.4×10^{13} p/cm^2 (Si-I). The samples were then annealed in 10-K steps with an annealing rate of 25 K/h. All positron-lifetime spectra were measured at 15 K. After the irradiation two lifetime components could clearly be detected. The longer lifetime was 273 ± 6 ps which is in good agreement with the experimentally suggested monovacancy lifetimes of 270–275 ps in Si.[27–29] Also the calculated positron lifetime of 270 ps (Ref. 12) in a neutral Si monovacancy with a realistic breathing-mode relaxation (4.2% outwards) is close to our experimental result. The intensity of 50 ± 7 % of the defect-related component is high when compared to the irradiation dose. This indicates that positrons trap very effectively to the defects produced in the samples. The specific positron-trapping rate to negatively charged vacancies in Si has recently been estimated to be as high as $10^{17}-10^{18}$ s^{-1} at low temperatures,[27] whereas for neutral vacancies this value has been estimated to be only of the order of 10^{15} s^{-1}.[18] Thus, we conclude that the samples contained negatively charged monovacancies.

The Si-I samples were annealed up to 150 K, after which the temperature dependence of the positron-lifetime parameters was studied by measuring positron-lifetime spectra at temperatures from 15 to 140 K. These results will be discussed in Sec. III C.

The sample set was further irradiated at 15 K with 12-MeV protons to a total dose of 2.3×10^{14} p/cm^2 (Si-II). Isochronal annealings were carried out from 15 to 320 K in 10-K steps and above 320 K in 20- or 50-K steps. After the irradiation two lifetimes, in addition to the fixed long lifetime τ_3, were detected: $\tau_2=277\pm4$ ps, cor-

responding to positrons that annihilated in monovacancies, and $\tau_1 = 131 \pm 9$ ps, which is the modified bulk lifetime (Fig. 1). The intensity of the τ_2 component, I_2, was higher than 75% after the irradiation (see Fig. 2). This intensity stays constant up to annealing temperatures of about 150 K, after which it decreases almost linearly, within statistics, to become zero at 600 K. The corresponding positron lifetime remains at about 275 ps in the whole annealing temperature range, which means that (i) either the defects remain the same but decrease in number above 150 K, or that (ii) new defects, created when the primary defects migrate above 150 K and get trapped by impurities, give rise to similar positron lifetimes as the primary defects. We shall later in this chapter argue that the secondary defects are negatively charged complexes of a Si monovacancy and a nearest-neighbor substitutional oxygen atom, V_2O^-, and our calculations indeed yield that the positron lifetime is almost identical in pure monovacancies and in these V_2O^- pairs.

When high-energy protons are used in irradiations, the possibility of creating divacancies in addition to monovacancies must be considered. This is due to the large displacement cascades created by the protons. The experimental positron-lifetime value for divacancies in Si is about 320 ps.[23,28,30] We tried to analyze our positron-lifetime spectra by fixing τ_2 to 270 ps and τ_3 to 320 ps and by searching for the modified bulk lifetime τ_1 and for the intensities I_1, I_2, and I_3 in order to see if divacancies, besides monovacancies, were present in the samples. No systematic behavior could be seen in the intensities of τ_2 and τ_3: I_2 had values from 46% to 110% with no decreasing trend, and I_3 fluctuated randomly between -19% and 11%. We therefore believe that the number of divacancies was negligible in the samples, and that the results can be understood by assuming only a single-trap state. The validity of this assumption was investigated by using the one-trap model.[31] In this model the bulk lifetime is calculated as

$$\tau_b = \left[\sum_{i=1}^{2} \frac{I_i}{\tau_i} \right]^{-1} \tag{1}$$

As can be seen from Fig. 3, the model gives reasonable results for τ_b (the measured bulk lifetime is 217 ps). This supports the idea that the Si-II samples consisted only of monovacancy-type defects. The situation is not totally clear if the charge state of monovacancies was negative and that of divacancies was neutral. In this case positrons would have gotten trapped much more effectively by monovacancies than by divacancies, and the intensity of the 320-ps-lifetime component would therefore have been extremely low.

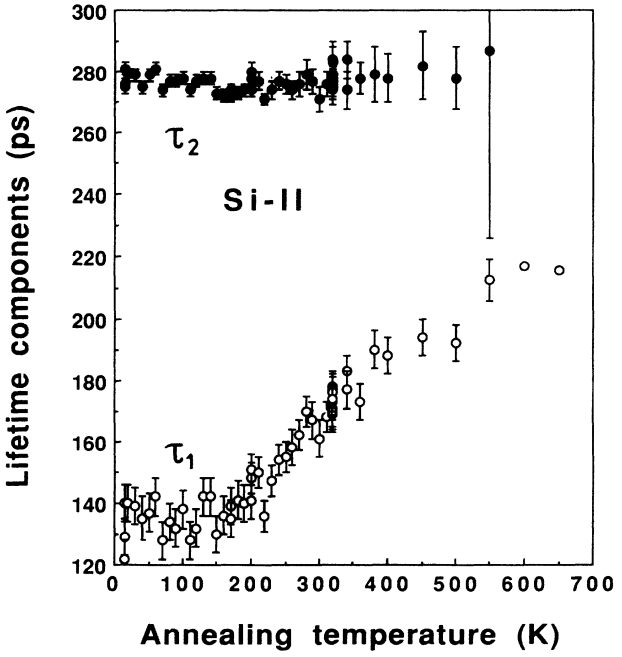

FIG. 1. The positron-lifetime components for the proton-irradiated Si. The irradiation dose was 2.3×10^{14} protons/cm^2 (Si-II) and the lifetime spectra were measured at 15 K. The irradiations were also carried out at 15 K.

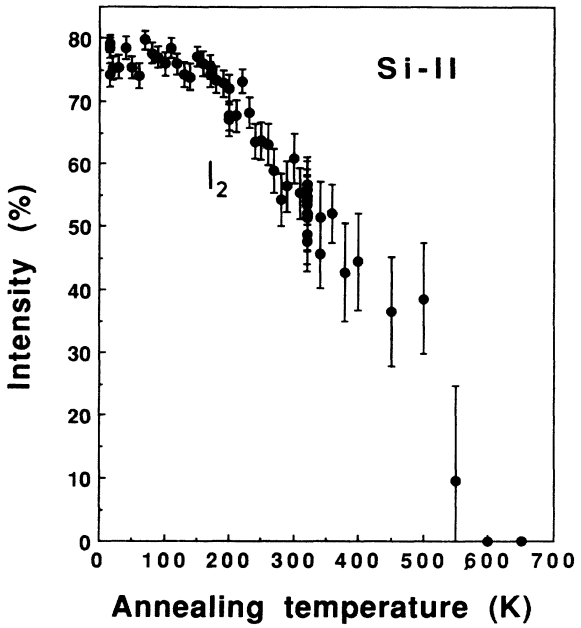

FIG. 2. The intensity of the defect-related lifetime (τ_2) in proton-irradiated Si-II.

B. Annealing behavior

The average positron lifetime, or the statistical mean of the positron-lifetime distribution, is defined as

$$\bar{\tau} = \sum_{i=1}^{N} I_i \tau_i \ , \tag{2}$$

where N is the number of lifetime components, τ_i is a positron-lifetime component, and I_i is the corresponding intensity. The values of $\bar{\tau}$ for the Si-II experiment are shown in Fig. 3 as a function of annealing temperature. Two clear annealing steps can be seen. The first step

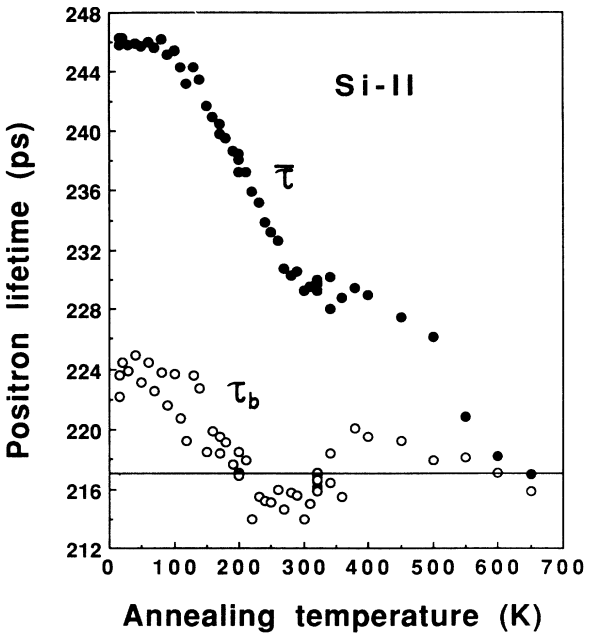

FIG. 3. The mean positron lifetime $\bar{\tau}$ (solid circles) and the bulk lifetime τ_b calculated by the one-trap model (open circles) as a function of annealing temperature. The lifetime spectra were measured at 15 K and the Si samples were irradiated at 15 K with 12-MeV protons to a dose of 2.3×10^{14} protons/cm^2 (Si-II). The line indicates the measured bulk lifetime of 217 ps.

starts at about 100 K and continues until 300 K. This step was also detected in the Si-I experiment, although the annealings were then performed only up to 150 K. Note that the onset of this stage is seen at 150 K in the two-component analysis (see Figs. 1 and 2). This is probably due to the fluctuations in the analysis. The average lifetime is less sensitive to small fluctuations and thus more reliable (but less informative). Kimerling *et al.* have studied the annealing kinetics of Si by the EPR technique and found that in FZ Si, $E2$ centers start to anneal out at 120 K.[17] The $E2$ center is proposed to correspond to the negatively charged monovacancy.[17] According to EPR and DLTS studies of Watkins *et al.* the doubly negative monovacancy in Si starts to anneal out at about 70 K, and the neutral monovacancy at about 210 K.[32] We thus conclude that our samples consisted mainly of singly negative monovacancies which started to anneal out at about 100 K.

This first annealing stage is rather long. It thus seems that free, negatively charged monovacancies annealed out slowly at temperatures between 100 and 300 K. A similar annealing stage has also been observed in electron-irradiated Si by the Doppler-broadening measurements of Fuhs *et al.*[23] This long annealing stage might be due to weak trapping of the migrating monovacancies by some impurity atoms. Another possibility for this long stage might be that the negative vacancies annealed out at the range of 100 to about 200 K, after which the Fermi level decreased below a certain level in the band gap[24] and the vacancies became neutral, continuing to anneal out from 200 K (Ref. 32) to 300 K. Theoretical calculations have shown that if atomic relaxation is omitted, the positron lifetime in V^- is almost the same as that in V^0.[12,33] Also, experimental results indicate no difference in positron lifetimes at V^- and V^0. However, the specific positron-trapping rate to neutral vacancies in Si is believed to be about 100–1000 times smaller than that to negatively charged vacancies.[18,27] If the latter assumption was correct, even though it is hard to find any reason why the Fermi level would have moved to such a low position[24] in the gap, we should therefore have seen a strong decrease in I_2 at the transition region. The values of I_2 did not show this kind of behavior: I_2 decreased smoothly from 75% to zero at temperatures between 150 and 600 K (see Fig. 2).

It could also be possible that free, negatively charged monovacancies annealed out rather fast above 100 K, after which some vacancy-impurity pairs started to dissociate. The EPR and DLTS studies[32] of Watkins *et al.* show that at the temperature range of 100 to 300 K only monovacancy pairs with boron and germanium could migrate in Si, in addition to free monovacancies. However, the existence of these complexes can most probably be excluded because the samples should not contain Ge and the concentration of B was very low ($\sim2\times10^{-5}$ ppm).

Oxygen and carbon were the most significant impurities in the samples. The presence of complexes of a substitutional oxygen atom and a nearest-neighbor Si monovacancy, V_2O,[34] could therefore be possible. Lee *et al.* have reported that neutral V_2O complexes start to anneal only at about 620 K (Ref. 34), which strongly suggests that even the negatively charged V_2O defects do not anneal at temperatures below 300 K. One cannot rule out the possibility of forming V-C complexes during the vacancy migration but the role of carbon on the defect recovery is not known. Our conclusion is that free, singly negatively charged Si monovacancies annealed out slowly at temperatures between 100 and 300 K.

The second annealing step begins at about 400 K (see Fig. 3). One could suggest that this annealing stage is due to migration of divacancies which might have grown by agglomeration of migrating monovacancies above 100 K. However, divacancies in Si are known to become mobile only at about 550 K (Refs. 32 and 35) and, as discussed earlier in this chapter, we do not believe that the samples did contain a detectable amount of divacancies. Another possibility for explaining this step could be the annealing of V·P pairs[12,36] as they have been observed to anneal out at about 400 K.[32,37] However, the concentration of phosphorus was so small in the samples that V·P complexes were most probably out of our detection limit. Also the experimentally observed positron lifetime in the V·P defect is against the existence of these pairs: the measured values are in the range of 248–255 ps (Refs. 27 and 29), clearly shorter than τ_2 in our experiments. It therefore seems that the annealing step above 400 K shall be explained by annealing out of V_2O complexes that were created during the first annealing stage between 100 and 300 K, when migrating monovacancies were trapped by "substitutional" oxygen atoms (A centers).[4]

The annealing of neutral V_2O complexes have been

suggested to start at about 620 K.[34] On the other hand, our studies on the temperature dependence of the specific trapping rate of positrons (see Sec. III C) indicate that the charge state of the main positron traps was negative even after annealing at 300 K. If the samples did contain V_2O defects at 400 K, their charge state would therefore have been negative. We calculated the positron wave function and annihilation characteristics for the case where one of the nonrelaxed nearest-neighbor Si atoms around a vacancy was replaced by an oxygen atom (the V_2O complex) by using the method of Puska and Nieminen.[38,39] The wave function was strongly localized at the vacancy, and the positron lifetime was only 2 ps shorter than that for a free monovacancy. The lifetime components corresponding to these two defects are thus not distinguishable in experiments. Since the value of τ_2 did not change significantly from the monovacancy lifetime after the first annealing step (see Fig. 1), it is possible that V_2O^- complexes were created in this step, and that these defects are then those that annealed out above 400 K.

The third proton irradiation (Si-III) was also performed with 12-MeV protons, but this time the dose was only about 3.0×10^{13} p/cm^2, i.e., a factor of 10 smaller than that for Si-II. Now the main interest was to compare the annealing behavior in these two experiments. The 100–300-K annealing step was clearly detected also in the Si-III samples: the mean lifetime decreased linearly from 224 to 218 ps, i.e., the bulk positron lifetime was reached after annealing at 300 K and therefore no further annealing stage could be seen. The vacancy concentration was probably too low to produce a detectable amount of monovacancy-oxygen pairs in the samples. The value of the long-lifetime component was, within uncertainties, the same (271±11 ps) as that in the Si-I and in the Si-II samples.

C. Trapping of positrons

The trapping rate of positrons to a lattice defect, κ, is written as

$$\kappa=\mu_+ c_v \ , \tag{3}$$

where μ_+ is the specific trapping rate of positrons to the defect in question, and c_v is the defect concentration. In the one-trap model[31] κ is given as

$$\kappa=\frac{\bar{\tau}-\tau_b}{\tau_d-\bar{\tau}}\lambda_b \ , \tag{4}$$

where τ_d is the defect-related lifetime (τ_2), τ_b is the bulk lifetime, and λ_b is the positron-annihilation rate in the perfect crystal ($=\tau_b^{-1}$). The temperature dependence of κ was studied by measuring positron-lifetime spectra at different temperatures after the samples were annealed at a certain higher temperature and by using the one-trap model [Eq. (4)]. In this way every lifetime spectrum corresponded to the same concentration of vacancies, i.e., c_v was constant in Eq. (3). Thus, the temperature dependence of κ gave the temperature dependence of the specific positron-trapping rate for the defect.

The assumption that the samples consisted only of one type of defect was most reasonable for the Si-I and Si-III samples where the irradiation doses were low. After the Si-I samples were annealed at 150 K, the positron-lifetime spectra were measured at the temperature range of 15 to 140 K. The mean lifetime $\bar{\tau}$ calculated by Eq. (2) is plotted in Fig. 4 as a function of measuring temperature. As can be seen, $\bar{\tau}$ decreases very strongly as the temperature rises. The trapping rate values were calculated for these results by fixing τ_2 to its average value in the spectra in question, and by using Eq. (4). In the calculations 217 ps was used for the bulk lifetime. Naturally, also the temperature dependence of κ (see Fig. 5) is qualitatively the same as that for $\bar{\tau}$.

The trapping of positrons to a negatively charged vacancy is believed to go either through direct electron-hole excitations or through Rydberg states at the Coulomb tail of the vacancy,[18,27] leading to huge positron-trapping probabilities. These Rydberg states are assumed to be shallow traps for positrons, and the detrapping of positrons from these states should therefore be possible at high temperatures. From this, and by using the two-stage capture model of Gibb *et al.*,[40] the experimentally observed temperature dependence of the specific positron trapping rate to V^- in Si has recently been suggested to follow an $e^{E/kT}$ law above 60 K.[27] Here E is the binding energy of a positron to this shallow Rydberg-state trap, and a value of 20±2 meV has been proposed for V^-.[27] We have plotted the logarithm of κ as a function of $1/T$ for the points in Fig. 5 (see Fig. 6) in order to check the $e^{E/kT}$ dependence. Although a line could somehow be drawn through the points corresponding to temperatures above ~60 K, no strong evidence about this kind of temperature dependence can be seen.

The temperature dependence of μ_+ to negatively charged vacancies in Si has often been studied by using Lax's calculations[41] about the trapping of electrons and

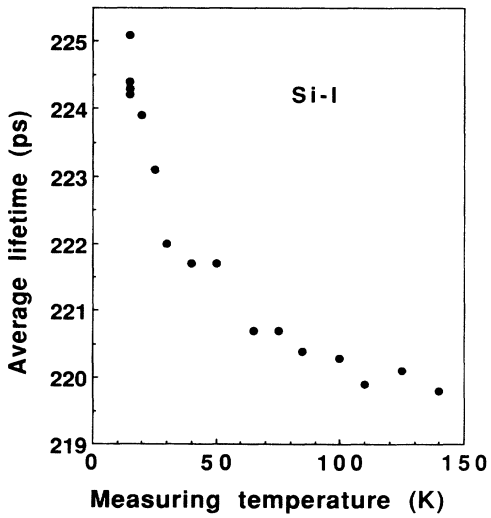

FIG. 4. The mean positron lifetime as a function of measuring temperature. The samples were irradiated with 12-MeV protons to a dose of 2.4×10^{13} protons/cm^2 (Si-I) and the samples were annealed at 150 K before the measurements.

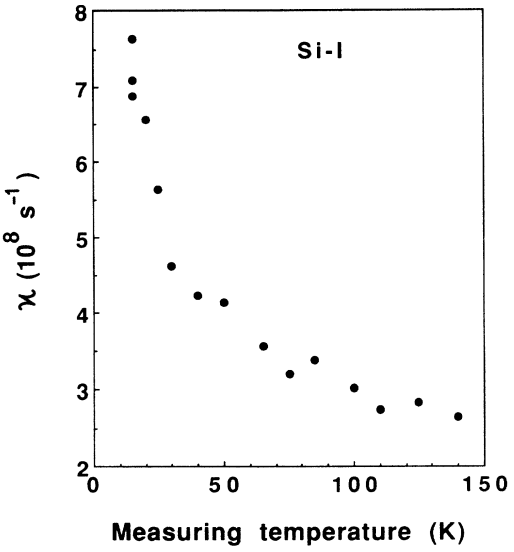

FIG. 5. The trapping rate of positrons vs temperature. κ is calculated by using the one-trap model and the data in Fig. 4.

holes by charged defects. Positrons are first thought to be captured in a highly excited state, a shallow positron trap with the binding energy of about kT. Thereafter, positrons are thought to lose their energy by phonon emission until they reach the ground state. If positrons get trapped at negatively charged vacancies by emission of optical phonons, μ_+ should be proportional to $T^{0.5-n}$, where n is 1 at low temperatures and 4 at high temperatures. On the other hand, if the trapping goes through acoustic phonons, μ_+ should vary as T^{-1}. According to Lax, the acoustic-phonon contribution predominate at low temperatures and optical phonons are important only at room temperature.[41] Dannefaer *et al.* have found that for negatively charged divacancies, V_2^-, in p-type single crystal Si, μ_+ is proportional to $T^{-0.5}$ at temperatures below 40 K (Ref. 42) and that at temperatures above 40 K, μ_+ varies as $T^{-3.5}$ (Ref. 42) or as $T^{-2.28}$. Mascher *et al.* have recently reported that for V_2^- in slightly n-type Czochralski-grown Si, μ_+ has a T^{-2}-dependence.[43] Moreover, Brandt *et al.*[44] and Fuhs *et al.*[45] have reported that μ_+ varies as $T^{-1.5}$ for these defects. The positron-lifetime results of Mäkinen *et al.*[27] for V^- in n-type FZ Si can also be explained by assuming a $T^{-2.6}$ dependence in μ_+ at temperatures between 60 and 120 K.

In the light of the results discussed above, we assume that μ_+ is proportional to T^{-n} for the negative vacancy-type defects V^- and V_2O^- in our Si samples. If the vacancy concentration is assumed to be constant after the 150-K annealing, the temperature dependence of κ directly gives the temperature dependence of μ_+. We plotted $\ln\kappa$ as a function of $\ln T$ for the points in Fig. 5 and made a least-squares fit to the data in order to find the value of the exponent from the slope of the line. A value of about -0.5 was found. Also, in other measurements for the temperature dependence of μ_+ (Si-I, $T_{ann}=150$ K; Si-II, $T_{ann}=150$ and 300 K; Si-III, $T_{ann}=90$ and 200 K), which will be discussed later in this chapter, the same value was obtained. This means that the specific trapping rate of positrons to V^- and to V_2O^- is proportional to $T^{-0.5}$. This can clearly be seen in Fig. 7, where the measured κ is plotted as a function of $T^{-0.5}$ for the points corresponding to the Si-I samples after annealing at 150 K.

Also, Puska *et al.* have recently derived theoretically that in the case of negatively charged vacancies in Si μ_+ is proportional to $T^{-0.5}$.[18] This decreasing trend is a result of the Coulomb-wave behavior of the initial positron wave function: the amplitude of the wave function increases strongly at the vacancy when its energy eigenvalue decreases. Our results agree very well with this model.

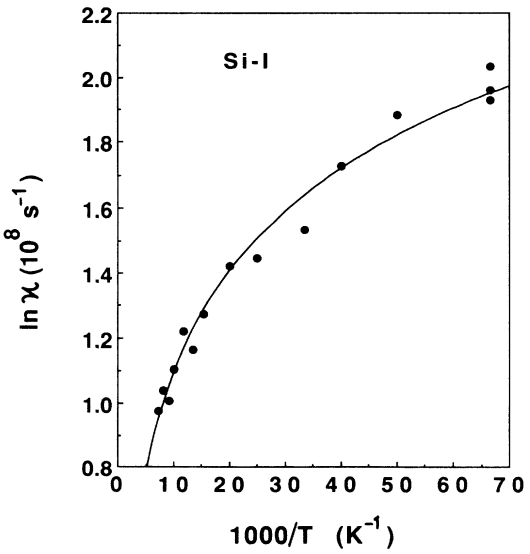

FIG. 6. Natural logarithm of κ as a function of $1/T$ for the data in Fig. 5. The line shows the behavior corresponding to the $T^{-0.5}$ dependence.

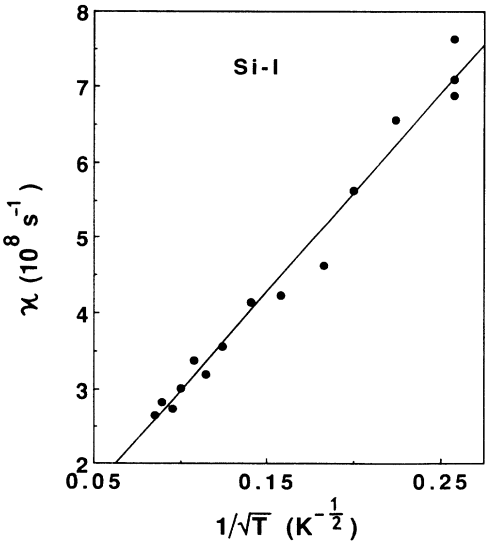

FIG. 7. The trapping rate of positrons as a function of $1/\sqrt{T}$ for the points in Fig. 5. The line corresponds to a least-squares fit to the data.

This confirms our suggestion that the monovacancies in our samples were negatively charged, and that no detrapping took place as the temperature dependence can be understood by assuming only trapping.

We also calculated how $\ln\kappa$ should behave as a function of $1/T$ if the $T^{-0.5}$ dependence was correct. If the trapping rate is written as

$$\kappa=\kappa_0+A\frac{1}{\sqrt{T}}\ , \tag{5}$$

we get that

$$\ln\kappa=\ln\left[\frac{A+\kappa_0\sqrt{T}}{\sqrt{1000}}\right]+\tfrac{1}{2}\ln\left[\frac{1000}{T}\right]\ . \tag{6}$$

The resulting curve is drawn in Fig. 6, and it fits very well in the data points. Here κ_0 is the high-temperature limit of the positron trapping rate, and it should therefore be zero. A is related to the number of defects giving the $T^{-0.5}$ dependence in κ, i.e., A is proportional to the concentration of V^- and V_2O^-. For the Si-II samples the value of A decreased from about 122 to 40 (in units of 10^8 $K^{1/2}/s$) as the annealing temperature went from 150 to 300 K, and for the Si-III samples A was about 31 after annealing at 90 K, decreasing to a value of about 12 (in the same units) after annealing at 200 K.

We measured the temperature dependence of κ also for the Si-III samples after annealing at 90 and 200 K. These results also clearly agree with the $T^{-0.5}$ dependence for κ (and μ_+). We did the same for the Si-II samples after annealing at 150 and 300 K and, again, the results strongly support the $T^{-0.5}$ dependence. These results are shown in Fig. 8 together with the results for the Si-I experiment.

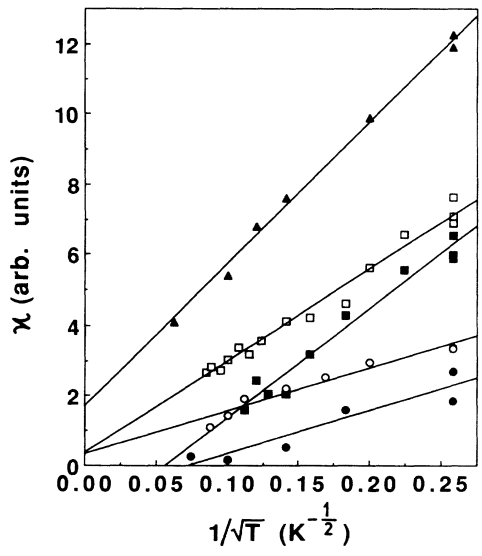

FIG. 8. Same as Fig. 7 but for the proton-irradiated samples annealed at 90 K (Si-III, solid squares), 150 K (Si-I, open squares; Si-II, open circles), 200 K (Si-III, solid circles), and 300 K (Si-II, solid triangles).

All data points are nicely described by straight lines. The values of κ are not fully comparable in Fig. 8, and they should only be taken as a proof of the $T^{-0.5}$ law. It should be noted that the same temperature dependence is seen also after annealing at 300 K, where the V^- defects had already disappeared. This means that the temperature dependence of μ_+ for V_2O^- complexes is the same as that for V^-.

If the trapping of positrons was assumed to be diffusion limited, μ_+ would vary as $D_+(T)T^{-1}$, where D_+ is the diffusion constant.[46] As D_+ is proportional to $T^{-0.5}$ (Ref. 46), the specific positron-trapping rate would be proportional to $T^{-1.5}$. This was not observed, and we conclude that the positron trapping was only transition limited. Also, the measuring temperatures were so low that the presence of phonons limiting the diffusion of positrons was not probable.

It is interesting to note that κ_0 is not equal to zero for the cases in Fig. 8, i.e., the trapping rate does not go to zero at the high-temperature limit. This could indicate that our samples included also neutral vacancy-type traps in addition to the negatively charged monovacancy-type traps V^- and V_2O^-. Other possibilities are that the $T^{-0.5}$ behavior is not exactly valid for the defects in question or that the values of κ are somewhat inaccurate. The last assumption is reasonable, because κ_0 could be made to be zero by changing the value of τ_b by only 1–3 ps in Eq. (4). These small changes had almost no effect on the values of A in Eq. (5) and on the variances of the linear fits to the data points, which again supports the $T^{-0.5}$ dependence of μ_+.

In principle, the monovacancy concentration can be estimated by using Eq. (3) and the one-trap model for κ [Eq. (4)]. The problem is that the value of the specific trapping rate μ_+ is not known. In the model calculations of Puska *et al.*[18] the value of μ_+ is estimated to be of the order of 10^{16} s^{-1} for positrons that trap to a negatively charged vacancy through direct electron-hole excitations at about 10–20 K. If the trapping goes through Rydberg states this value can be much higher. If μ_+ is roughly estimated to be 10^{16} s^{-1} at 15 K, the upper limit of the monovacancy concentration is 0.05 ppm for the Si-III samples after the irradiation. The relatively high irradiation dose used in the Si-II experiment results in a maximum vacancy concentration of about 0.4 ppm. These results correspond to a maximum effective vacancy production rate of about four vacancies per proton during its path through the specimens. The number of atomic displacements ought to be considerably higher. The reason for the low vacancy production is the high mobility of the interstitial Si atoms at the irradiation temperature of 15 K (even at 1.5 K),[47] so that the irradiation-induced Frenkel pairs annihilated very effectively.

IV. CONCLUSIONS

High-purity single-crystal Si samples were irradiated at 15 K with 12-MeV protons, and the annealing of the created vacancies was studied by the positron-lifetime

method. A strong annealing stage was seen between 100 and 300 K. It is connected to the migration of free, singly negatively charged monovacancies. From 300 to 400 K the vacancy concentration was almost unchanged. The second annealing stage between 400 and 600 K is, tentatively, suggested to be due to annealing out of negatively charged complexes of a Si monovacancy and a nearest-neighbor substitutional oxygen atom (V_2O^-).

The temperature dependence of the specific positron trapping rate μ_+ to V^- and to V_2O^- was studied in the range of 15 to 280 K, and at these temperatures a $T^{-0.5}$ dependence was clearly observed.

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