Technical University of Denmark



Hydrogen- and helium-implanted silicon: Low-temperature positron-lifetime studies

Mäkinen, S.; Rajainmäki, H.; Linderoth, Søren

Published in: Physical Review B Condensed Matter

Link to article, DOI: 10.1103/PhysRevB.44.5510

Publication date: 1991

Document Version Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Citation (APA): Mäkinen, S., Rajainmäki, H., & Linderoth, S. (1991). Hydrogen- and helium-implanted silicon: Low-temperature positron-lifetime studies. Physical Review B Condensed Matter, 44(11), 5510-5517. DOI: 10.1103/PhysRevB.44.5510

DTU Library Technical Information Center of Denmark

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.

- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Hydrogen- and helium-implanted silicon: Low-temperature positron-lifetime studies

S. Mäkinen and H. Rajainmäki*

Department of Physics, University of Jyväskylä, SF-40100 Jyväskylä, Finland

S. Linderoth

Laboratory of Applied Physics, Technical University of Denmark, DK-2800 Lyngby, Denmark (Received 30 August 1990; revised manuscript received 13 November 1990)

High-purity single-crystal samples of float-zoned Si have been implanted with 6.95-MeV protons and with 25-MeV ${}^{3}\text{He}^{2}$ ions at 15 K, and the positron-lifetime technique has been used to identify the defects created in the samples, and to study the effects of H and He on the annealing of point defects in Si. The results have been compared with those of proton-irradiated Si. A 100-300-K annealing stage was clearly observed in hydrogen (H⁺) -implanted Si, and this stage was almost identical to that in the *p*irradiated Si. The final annealing state of the H⁺-implanted Si started at about 400 K, and it is connected to annealing out of negatively charged divacancy-oxygen pairs. This stage was clearly longer than that for the *p*-irradiated Si, probably due to the breakup of Si—H bonds at about 550 K. The 100-K annealing stage was not seen with the He-implanted samples. This has been explained by assuming that almost all vacancies contained He after the irradiation with ³He. Helium is suggested to be released from vacancies at about 600 K, and small He bubbles seem to have grown at temperatures above 800 K. The specific positron-trapping rate for negatively charged monovacancy-type defects in H⁺-implanted Si has been found to have a $T^{-0.5}$ dependence, whereas for neutral divacancies and monovacancies in Heimplanted Si no dependence on temperature has been observed.

I. INTRODUCTION

Both atomic hydrogen and helium in semiconductors are of great technological and scientific interest.¹ In crystalline silicon, hydrogen is known to have a role of saturating broken chemical bonds.²⁻⁵ For many years this was believed to be the only (and quite harmless) effect that H has on the physical properties of Si. In recent years, much interest has been taken in the role of H in Si since the discovery of its ability to passivate shallow-level and deep-level defects.^{3,4,6} In *p*-type Si, H is found to passivate shallow acceptor impurities causing a dramatic increase in the resistivity of the samples.^{7,8} Also in *n*-type Si, passivation of shallow donor impurities has been seen in experiments.^{9,10} It has also been found that in addition to passivating the existing defects, H can induce microdefects and electronic deep levels in Si.¹¹

Noble-gas impurities in Si are of special interest because they are used for sputtering, ion etching, and gettering. During these processes, a number of gas atoms are retained in the crystal and may therefore affect the annealing of point defects. Also, the effective use of the thermal-helium-desorption spectroscopy $(THDS)^{12,13}$ requires good knowledge about the effects of He on defects in Si. The positron-lifetime technique^{14,15} has proved to be very suitable for studies of He in metals. ^{16–20} However, such studies on He-implanted Si have not yet been reported.

In this paper, we present low-temperature positronlifetime measurements of hydrogen (H^+) -implanted and helium-implanted Si. In a previous work by Mäkinen, Rajainmäki, and Linderoth²¹ we reported on positronlifetime studies of Si irradiated with protons at 15 K. The samples used in these two studies were cut from the same float-zoned (FZ) single-crystal rod, and the results are therefore highly comparable. In the first paper (henceforth referred to as paper I) we suggested that the main positron traps in the proton-irradiated samples were V^- and V_2O^- , and that the specific positron trapping rate μ_+ to these defects varies as $T^{-0.5}$. In the present work, the same temperature dependence was found in the H⁺-implanted samples after annealing at 310 K, but in the He-implanted Si μ_+ was constant with temperature. The main positron traps in the H⁺-implanted samples are suggested to be V^- , V_2^- , and V_2O^- . Hydrogen has been assumed to saturate dangling bonds in the monovacancies, and the dissociation of the Si—H bonds is suggested to happen at about 550 K. In the He-implanted Si, positrons were mainly trapped by V_2^0 and V^0 .

II. EXPERIMENTAL

The single-crystal Si samples were cut from a floatzoned rod grown at Topsil Semiconductor Materials a/s, Denmark. The impurity concentrations were very low: 5.8×10^{-5} ppm P, 2.0×10^{-5} ppm B, < 0.2 ppm O, and < 0.3 ppm C. The material was slightly *n*-type and its resistivity was 2200 Ω cm. The samples were mechanically polished and etched, and samples with thicknesses of $393\pm 3 \mu m$ and $387\pm 1 \mu m$ were prepared. The sandwich geometry was used for the sample packages, i.e., the ²²Na positron source in a thin (1.7 mg/cm²) Havar foil envelope was covered by two identical pieces of Si. For more details of the experimental setup, see paper I.

The positron-lifetime spectra contained about 1.1 mil-

44 5510

lion events, and the data were analyzed by using the Fortran programs Resolution and Positronfit.²² In the analyses of the positron-lifetime spectra, a long-lifetime component of about 1.5 ns with an intensity of about 0.1% was detected. We therefore fixed τ_3 to 1.5 ns and I_3 to 0.1% in the analyses. The variances of the fits were about 1.0–1.2. The time-resolution function was a one component Gaussian function with a full width at half maximum of 217 ps. 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 positron-lifetime spectra were measured at about 15 K. The stepwise annealings were made with an annealing rate of 25 K/h.

The H⁺ implantations were performed with 6.95-MeV protons from the backsides of the $387-\mu m$ Si samples in the sandwich geometry. The sample thickness was sufficient to stop more than 98% of the positrons within the samples.²³ The mean penetration depth and the longitudinal straggling of the 6.95-MeV protons are 370 and 6 μ m, respectively.²⁴ The proton energy was chosen so that the particles could penetrate to a very close distance from the positron source in order to maximize the overlap of the positrons and the electrons in the implanted region. On the other hand, the proton energy was so low that they could not reach the positron source. The proton beam current was about 100 nA/cm^2 . Even though this is much more than the current used in the pirradiations²¹ (12 nA/cm²) it still corresponds to the maximum heating power of only 0.2 W. This is not enough to heat the samples significantly when the sample package is connected to the cryocooler with indium.

The width of the implanted region was widened by using 10- μ m Al foils as degraders between the MC-20 cyclotron and the sample package. The longitudinal straggling of the 6.95-MeV protons (6 μ m) suffices to give a quite homogeneous H profile to the implanted region. We used 0-5 foils, and the final width of the H⁺-implanted region was, hence, about 65 μ m. The samples were irradiated to a H concentration of about 28 ppm.

Two 396- μ m Si samples were He implanted with 25-MeV ${}^{3}\text{He}^{2+}$ ions to a He concentration of about 55 ppm by using the similar irradiation procedure as in the former case. In this case the width of the implanted region was extended to about 70 μ m (by using more Al foils), and the beam current was about 200 nA/cm².

III. RESULTS

A. Hydrogen-implanted Si

After the H⁺ implantation at 15 K, two positronlifetime components were detected in the samples (Si-H), in addition to the fixed long lifetime τ_3 (Fig. 1). The longer component τ_2 was 290±5 ps. This is clearly longer than that in the heavily *p*-irradiated Si-II in paper I, where the value of τ_2 (275±5 ps) was connected to positrons that annihilated in monovacancies. The experimentally suggested monovacancy lifetime in Si is 270–275 ps,^{25–27} and values of about 320 ps are reported for divancancies in Si.^{27–29} Schaefer *et al.*³⁰ have suggested that the 320-ps lifetime is not due to divacancies only, but

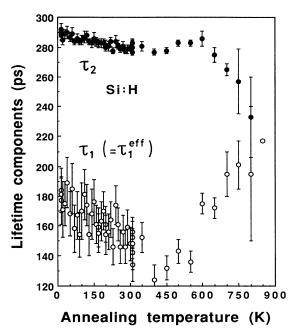


FIG. 1. The positron-lifetime components for the H⁺implanted Si (Si:H) as a function of annealing temperature. The concentration of hydrogen in the 65- μ m-wide implanted region was about 28 ppm after the implantation. The irradiations were carried out at 15 K, and the positron-lifetime spectra were measured at 15 K. See Eq. (4) for the determination of τ_1^{eff} .

also the contribution of larger vacancy agglomerates is important. According to them the positron lifetime in V_2 might thus be slightly shorter than 320 ps. However, this lifetime is theoretically reproduced by including a reasonable lattice relaxation of 2.8% outwards around the V_2 .³¹ Our conclusion is that the implantation produced not only monovacancies in the samples but also a large number of divacancies because τ_2 was clearly longer than the monovacancy lifetime of 270–275 ps.

When termalized near a vacancy, protons are suggested to be situated in the high electron density region around the vacancy, not in the center of the vacancy.^{3,32,33} We therefore assume that the implanted protons do not, significantly, affect the electronic structure and the positron lifetime in a vacancy. However, protons may have strong effects on the mobility and annealing of vacancies or vacancy-impurity pairs when associated with these defects.

According to Fig. 2, where the mean positron lifetime $\overline{\tau}$ is shown as a function of annealing temperature, the samples annealed strongly at temperatures between 100 and 300 K. The total irradiation dose used in the H⁺ implantation was about 70 times larger than in the Si-II experiment in paper I. Therefore, the intensity of the defect-related lifetime component, I_2 , after the implantation was about 10% higher than in the former case (see Fig. 3). This intensity is almost constant at the annealing temperatures below 400 K, which could indicate that positron trapping was saturated, at 15 K, through the annealing temperature range of 15–400 K.

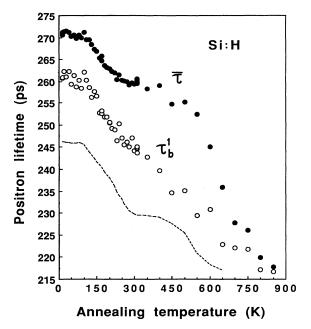


FIG. 2. The mean positron lifetime $\overline{\tau}$ (solid circles) and the bulk lifetime calculated by the one-trap model τ_b^1 (open circles) as a function of annealing temperature for the H⁺-implanted Si. The dotted line is the average lifetime vs annealing temperature for the *p*-irradiated Si-II samples (paper I).

In Fig. 2, two clear annealing stages are seen in the mean lifetime: the first at 100 to 300 K and the other beginning at about 400 K and lasting up to 850 K. When compared to the proton-irradiated Si (Si-II in paper I) the 100-300-K annealing stage seems to be much weaker in the Si-H samples than in the Si-II samples (Fig. 2). How-

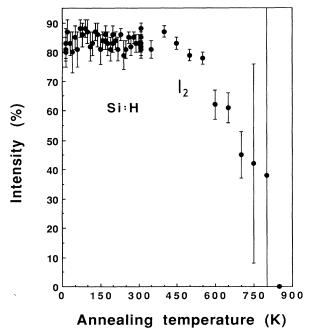


FIG. 3. The intensity of the long-lifetime component τ_2 vs annealing temperature for the H⁺-implanted Si samples.

ever, due to the much larger vacancy concentration in the Si-H samples and due to the sigmoidal dependence of $\overline{\tau}$ on the vacancy concentration, ³⁴ the weaker decrease in $\overline{\tau}$ does not necessarily mean that the change in the vacancy concentration was any smaller. In paper I, we suggested that the annealing stage at 100–300 K is due to migration of free, singly negatively charged monovacancies. We adopt this suggestion and propose that this first annealing stage was due to the migration of V^- .

In the Si-H samples the first annealing stage continues up to 850 K, about 250 K higher than in the Si-II samples. The reason for the delayed annealing is presumably the dissociation of Si-H bonds at hydrogen-containing monovacancies. Protons would thus stabilize free monovacancies and hinder them from annealing out at temperatures between 100 and 300 K.²¹ In deuteriumimplanted Si, the annealing out of deuterium-containing monovacancies has been suggested to take place at about 500 K.³² In amorphous Si, the Si—H bonds have been suggested to break up at about 600 K, and this process is seen to continue up to about 800 K.³⁵ The strong annealing at 550-700 K, seen in Fig. 2, could thus be due to dissociation of Si-H bonds in the hydrogenmonovacancy complexes. The possibility of the annealing out of divacancy-hydrogen complexes cannot be excluded.

Another possibility for the long 400-K annealing stage could be the annealing out of singly negatively charged divacancies which is reported to take place at about 550 K.^{36,37} However, it is hard to believe that the annealing of divacancies could last from 550 to 850 K. The length of this stage could also result from the presence of dislocation lines or loops in the samples. The possibility of creating dislocations is now greater than in the case of the proton irradiations because protons are known to produce large cascades of atomic displacements near the region where they stop in a crystal.³⁸ The slow annealing at 700–850 K (Fig. 2) is most probably due to annealing out of vacancies trapped at dislocation lines or loops.

The temperature dependence of the positron-trapping rate κ was studied after annealing the H⁺-implanted Si samples at 310 K. The behavior was qualitatively the same as for the *p*-irradiated Si samples,²¹ i.e., κ was proportional to $T^{-0.5}$. This behavior is expected for negatively charged defects^{21,39} and, thus, indicates that in this case the main positron traps were negatively charged even after annealing at 310 K. This supports the negative charge state of the divacancies, which presumably started to anneal out above 550 K. After the annealings above 310 K, the value of τ_2 was significantly lower than the suggested positron lifetime in V_2^- (320 ps). Therefore, also monovacancy-type defects should have been present in addition to the divacancies. Our conclusion is that, as in the case of the *p*-irradiated Si,²¹ these traps were nega-tively charged divacancy-oxygen pairs, V_2O^- . In paper I the annealing out of these pairs was suggested to start at about 400 K, which is consistent with our present results (Fig. 2).

One cannot be sure about the presence of the V_2O^- defects in the samples, and one should actually bear in mind the possibility of vacancy-carbon complexes also. How-

ever, the role of carbon on the defect recovery is not known. The V-P pairs are excluded because the concentration of P is only 5.8×10^{-5} ppm.

Our studies about the temperature dependence of the positron-trapping rate clearly indicate negatively charged defects, but Lee and Corbett⁴⁰ have only found neutral V_2O defects in Si with their EPR studies. Additionally, they only found V_2O defects in Czhoralski-grown (CZ) Si, not in FZ material. This was probably due to the larger concentration of oxygen in the CZ grown Si than in the FZ material.

The bulk lifetime calculated by the one-trap model⁴¹, τ_b^1 , is also shown in Fig. 2. The model fails drastically in reproducing the experimental bulk lifetime of 217 ps, and we can conclude that the Si-H samples consisted of at least two kinds of positron traps, almost until the end of the annealing process. This supports the existence of dislocations, because they usually anneal out at higher temperatures.

The behavior of the lifetime components as a function of annealing temperature (Fig. 1) is unusual and needs some discussion. Three different kinds of regions can be distinguished. The first starting from 15 K and lasting up to 100 K is quite stable (see also Figs. 2 and 3), informing that no annealing takes place in the samples. From 100 to about 400 K both lifetimes decrease; especially τ_1 that decreases by about 45 ps. τ_1 should increase towards the bulk lifetime as the samples anneal, if the simple one-trap model⁴¹ holds. An explanation for the observed behavior can be conducted from the fact that after the implantation the samples consisted of two different kinds of regions from the positron point of view. The first, about a $10-\mu$ m-wide region consisted of perfect Si crystal where positrons could only annihilate from the delocalized bulk state, resulting in the positron lifetime of 217 ps. Outside this region positrons were able either to annihilate in the bulk or to get trapped by point defects. This gives rise to the modified bulk lifetime τ_1 and to the long defectrelated lifetime τ_2 . The number of positrons at time t can thus be written as

$$N_{+}(t) = I_{0}e^{-\lambda_{b}t} + I_{1}e^{-\lambda_{1}t} + I_{2}e^{-\lambda_{2}t}, \qquad (1)$$

where I_0 , I_1 , and I_2 are the intensities of the bulk lifetime $(\tau_b = 1/\lambda_b)$, the modified bulk lifetime $(\tau_1 = 1/\lambda_1)$, and the defect-related lifetime $(\tau_2 = 1/\lambda_2)$, respectively.

To find out if these two regions can be thought to be separated from the positron point of view, one must think of the diffusion length of positrons at these temperatures. The diffusion length L_+ can be written as⁴²

$$L_{+} = \left[\frac{D_{+}}{\lambda_{b} + \kappa}\right]^{1/2}, \qquad (2)$$

where D_+ is the diffusion constant, λ_b is the bulk annihilation rate, and κ is the trapping rate of positrons. If we use the one-trap model⁴¹ to roughly estimate the value of κ ,

$$\kappa = \frac{\overline{\tau} - \tau_b}{\tau_2 - \overline{\tau}} \lambda_b \quad , \tag{3}$$

and a value of 3.0 cm²/s for D_+ at 300 K,⁴³ we get that $L_+ \sim 0.1 \,\mu\text{m}$. If we further take into account that $D_+ \propto T^{-0.5}$ (Ref. 42), we find that $L_+ \sim 0.3 \,\mu\text{m}$ at 15 K. This value is small when compared to the width of the perfect crystal region, and we can conclude that a significant number of positrons only experience perfect crystal before the annihilation.

The intensities of the modified bulk lifetime τ_1 and of the defect-related lifetime τ_2 can be estimated by calculating the fraction of positrons that were stopped in the 10- μ m-wide region of the perfect Si crystal. This can be done by using the exponential law for the absorption and by using the formula of Linderoth *et al.*²³ for the mass absorption coefficient. This gives that after the implantation 10% of the positrons emitted by the ²²Na source stopped in the defect-free region, i.e., I_0 is 0.10 in Eq. (1). Thus, I_1 is 6%, because the value of I_2 was about 84% at 15 K (Fig. 3).

The effective bulk lifetime seen in the measurements τ_1^{eff} can be determined as

$$\tau_1^{\text{eff}} = \frac{I_0 \tau_b + I_1 \tau_1}{I_0 + I_1} , \qquad (4)$$

where τ_b is the bulk lifetime, τ_1 is the modified bulk lifetime, and I_0 and I_1 are the corresponding intensities, respectively. The value of the modified bulk lifetime at 15 K can roughly be estimated by using the one-trap model

$$\frac{1}{\tau_1} = \frac{1}{\tau_b} + \frac{I_2}{I_1} \left| \frac{1}{\tau_b} - \frac{1}{\tau_2} \right| , \qquad (5)$$

which gives that $\tau_1 \approx 50$ ps. If this value is used for τ_1 in Eq. (4), and if I_0 and I_1 are assumed to be 0.10 and 0.06, respectively, one gets that τ_1^{eff} is about 155 ps. As can be seen in Fig. 1, this is close to the value of the short life-time component seen in our measurements.

As the annealing temperature exceeds 100 K the free, singly negatively charged monovacancies become mobile and some of them begin to penetrate through the region of the perfect crystal, in order to get to the surface of the sample. The migrating monovacancies can then be trapped by some impurity atoms, forming vacancyimpurity pairs; also in the 10-µm-wide region of perfect Si. In this region, the density of positrons is very high due to the exponential absorption. The relative number of positrons that annihilate at the bulk state thus decreases strongly, giving rise to the decrease of the short-lifetime component τ_1^{eff} seen in Fig. 1. As in the Si-II experiment in paper I, these vacancy-impurity complexes are suggested to be singly negatively charged divacancyoxygen pairs, V_2O^- , because the final annealing step started at the same temperature of 400 K in these two experiments. We conclude that the decrease seen in the short-lifetime component at temperatures between 100 and 400 K is due to the decrease in the number of positrons that annihilate in the perfect crystal closest to the positron source.

Another explanation for the unusual behavior of τ_1 would be the trapping of positrons by, e.g., interstitial clusters. One can assume that at these defects the positron lifetime is close to the bulk lifetime, and that the

modified bulk lifetime would then easily be mixed to this lifetime component in the analysis, resulting in the τ_1 component of Fig. 1. If the number of these defects decreased as the annealing temperatures increased from 15 to 400 K, the values of τ_1 would behave as seen in our analysis (Fig. 1). This explanation assumes that the interstitial clusters trap positrons at the measuring temperature of 15 K. The existence of two different kinds of traps would also lead to the observed low values of I_2 in the saturated state.

Also the long-lifetime component τ_2 decreased as the annealing temperature went from 100 to 400 K (Fig. 1). This might be due to a different kind of atomic relaxation around a pure monovacancy and around a V_2O^- pair. If the positron lifetime at a pure monovacancy was a few picoseconds longer than at a V_2O^- pair, the decrease in τ_2 would just be a consequence of the decrease in the relative number of positrons annihilating at pure monovacancies as the free monovacancies migrate and trap at monovacancy-oxygen pairs, V(O).

At 400 K, the migration of monovacancies is finished and τ_1 begins to grow (Fig. 1). Also τ_2 rises by about 10 ps as the annealing temperature goes from 400 to 600 K. This could indicate that divacancies were formed when the V_2O^- pairs broke up. Above 600 K τ_2 starts to decrease, while the increase in τ_1 proceeds, which indicates that τ_1 and τ_2 were connected to each other in the analysis of the positron-lifetime spectra, as also follows from the trapping model.⁴¹

B. He-implanted Si

Two identical 396- μ m-thick Si samples were implanted by 25-MeV ³He²⁺ ions at 15 K to a He concentration of about 55 ppm. The reason for using ³He instead of ⁴He was a solely technical one; the maximum kinetic energy that can be achieved for ⁴He by the MC-20 cyclotron is 20 MeV which was insufficient for our experiment. Furthermore, ³He ions are more penetrating than ⁴He ions.

In Fig. 4, the mean positron lifetime is plotted against annealing temperature. After the 320-K annealing the samples were accidentally annealed at 320 °C (593 K), which is seen in the figure as a lack of data point between 320 and 593 K. Fortunately, no drastic changes in the positron-lifetime parameters seem to have happened in this temperature range—although the 400-K annealing step, seen in the Si-II and Si-H experiments, could thereby not be studied in this case.

No annealing can be distinguished at temperatures between 100 and 300 K, in contrast to the p-irradiated and H⁺-implanted Si. Another interesting phenomenon is that τ_1 was very high after the implantation, about 220 ps (Fig. 5). This is close to the positron lifetime in the perfect lattice (217 ps), although defect trapping should lead to a τ_1 considerably lower than the bulk lifetime. An explanation for this could be the existence of irradiationinduced monovacancy-He complexes, giving rise to a positron lifetime close to the bulk lifetime. If this lifetime was mixed to the modified bulk lifetime in the analysis of the positron-lifetime spectra, and if the number of these complexes was high enough, the experimentally seen short-lifetime component could be close to the perfect lattice lifetime. Also the relatively low I_2 values (Fig. 6) after the irradiation suggest this assumption.

We estimated the positron lifetime at a monovacancy-

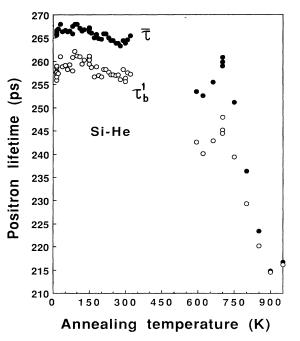


FIG. 4. The mean positron lifetime $\overline{\tau}$ (solid circles) and the bulk lifetime calculated by the one-trap model τ_b^1 (open circles) as a function of annealing temperature for the He-implanted Si.

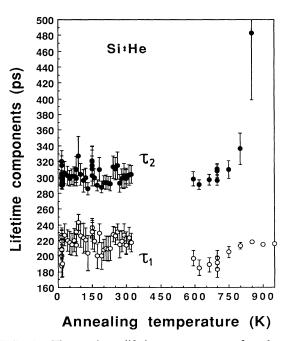


FIG. 5. The positron-lifetime components for the Heimplanted Si (Si:He) as a function of annealing temperature. The concentration of He was about 55 ppm in the implanted region of 70 μ m. The irradiations were performed with ³He²⁺ ions at 15 K.

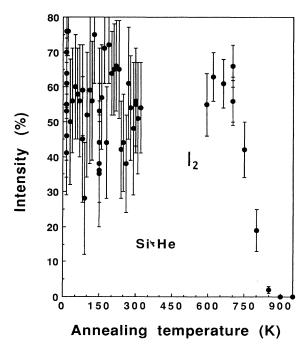


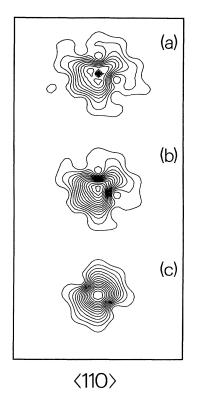
FIG. 6. The intensity of the defect-related lifetime component τ_2 vs annealing temperature for the He-implanted Si.

He pair by calculating the positron-annihilation characteristics at a Si monovacancy containing a He-atom in the middle of the vacancy. The calculations were performed by using the model of Puska and Nieminen⁴⁴ with no atomic relaxation around the vacancy. According to these calculations, the positron is trapped at this defect with a binding energy of about 0.14 eV, and it results in a positron lifetime of about 227 ps. This explains the long τ_1 values seen in the Si-He samples (Fig. 5), which in all probability are mixtures of the modified bulk lifetime, due to positrons that were trapped at monovacancies in the He-free region, and of the lifetime of positrons annihilating in He-containing monovacancies. The contour plots of the positron wave function localized at a monovacancy, a divacancy, and a monovacancy containing a He-atom are shown in Fig. 7.

After the He-implantation, the value of the defectrelated lifetime component τ_2 was about 300 ps, significantly longer than in the proton-irradiated and H⁺-implanted samples. This lifetime is suggested to be due to positrons trapped at divacancies. The experimentally suggested divacancy lifetime in Si is about 320 ps.²⁷⁻²⁹

The temperature dependence of the positron-trapping rate was studied after annealing the Si-He samples at 80 and at 300 K. No changes were observed in κ as a function of the measuring temperature. This indicates that in this case the charge state of the main positron traps was neutral, in contrast to the *p*-irradiated and H⁺-implanted samples, where the $T^{-0.5}$ dependence of κ suggests for negatively charged defects.

At temperatures between 600 and 700 K, $\bar{\tau}$ increases by about 7 ps (Fig. 4). We suggest that heliummonovacancy pairs were dissociated at these tempera-



Ê

FIG. 7. Contour plots of the positron wave function localized at (a) a Si monovacancy including a He atom, (b) at a monovacancy, and (c) at a divacancy. Atomic relaxation around the vacancy was not included in the calculations, and the vacancy charge state was neutral.

tures, leaving the vacancies free to migrate, to be lost at sinks or to agglomerate. At 700 K, $\bar{\tau}$ and I_2 start to decrease strongly as the final annealing begins. At the same time as I_2 goes down, τ_2 starts to increase, reaching a value of about 480 ps at 850 K. This could mean that He bubbles were created in the samples. However, the value of I_2 is only about 2% for the 480-ps lifetime. The value of τ_2 is already high at 800 K, about 335 ps, with a remarkable intensity of 19±6%. We thus assume that cavities, probably small He bubbles, were grown in the samples at temperatures above 800 K.

Gorelkinskii, Nevinny, and Ajazbaev⁴⁵ have studied ³He-implanted Si by using the EPR technique, and found two EPR active centers that anneal out at about 450 K. They tentatively suggested that these centers are due to neutral vacancy-He complexes. Unfortunately, we cannot draw any clear conclusions about this temperature region because of the accidental annealing at 593 K after 320 K. Also THDS and transmission electron microscopy have been used to study He-implanted Si.^{46,47} However, these studies have dealt with large cavities and blistering effects, and the annealing out of monovacancies or divacancies have not been studied.

IV. CONCLUSIONS

Single-crystal Si samples were implanted with 6.95-MeV protons and with 25-MeV ${}^{3}\text{He}^{2+}$ ions, and the in-

teractions of H and He with the irradiation-induced defects were studied by using the positron-lifetime technique. Nothing was found to happen at temperatures between 15 and 100 K. In the H⁺-implanted samples a strong annealing step was seen at 100 to 300 K. This stage is connected to the annealing out of free, singly negatively charged monovacancies. At 300-400 K the vacancy concentrations were more or less unchanged, and the final annealing step started at about 400 K. At temperatures above 400 K, divacancy-oxygen pairs are suggested to anneal out. The Si-H bonds in hydrogencontaining monovacancies are suggested to break up above 550 K. Also singly negatively charged divacancies are believed to anneal out above 550 K. The last annealing at 700-850 K is most probably due to the escape of vacancies from dislocation lines or loops created in the samples during the implantation.

- *Present address: Outokumpu Poricopper Oy, P. O. Box 60, SF-28101 Pori, Finland.
- ¹Proceedings of the Fifteenth International Conference on Defects in Semiconductors, Hungary, 1988, Materials Science Forum, Vols. 38-41, edited by G. Ferenczi (Trans Tech, Ltd, Aedermannsdorf, Hungary, 1989).
- ²G. G. DeLeo, W. B. Fowler, and G. D. Watkins, Phys. Rev. B **29**, 1819 (1984).
- ³S. J. Pearton, M. Stavola, and J. W. Corbett, in the Proceedings of the Fifteenth International Conference on Defects in Semconductors, 1988, Ref. 1, p. 25.
- ⁴S. K. Estreicher, L. Throckmorton, and D. S. Marynick, Phys. Rev. B 39, 13 241 (1989).
- ⁵G. Müller, Appl. Phys. A **45**, 41 (1988); Phys. Rev. B **39**, 13 241 (1989).
- ⁶S. J. Pearton, J. W. Corbett, and T. S. Shi, Appl. Phys. A 43, 153 (1987).
- ⁷J. I. Pankove, D. E. Carlson, J. E. Berkeyheiser, and R. O. Wance, Phys. Rev. Lett. **51**, 2224 (1983).
- ⁸C. T. Sah, J. Y.-C. Sun, and J. J.-T. Tzou, Appl. Phys. Lett. **43**, 204 (1983).
- ⁹N. M. Johnson, C. Herring, and D. J. Chadi, Phys. Rev. Lett. 56, 769 (1986).
- ¹⁰K. Bergman, M. Stavola, S. J. Pearton, and J. Lopata, Phys. Rev. B **37**, 2770 (1988).
- ¹¹N. M. Johnson, F. A. Ponce, R. A. Street, and R. J. Nemanich, Phys. Rev. B 35, 4166 (1987).
- ¹²A. A. van Gorkum and E. V. Kornelsen, Vacuum **31**, 89 (1981).
- ¹³E. V. Kornelsen and A. A. van Gorkum, Vacuum **31**, 99 (1981).
- ¹⁴Positrons in Solids, edited by P. Hautojärvi, Topics in Current Physics, Vol. 12 (Springer, Heidelberg, 1979).
- ¹⁵Positron Solid State Physics, Proceedings of the Enrico Fermi International School of Physics, "Enrico Fermi," Course LXXXIII, Varenna, 1981, edited by W. Brandt and A. Dupasquier (North-Holland, Amsterdam, 1983).
- ¹⁶C. L. Snead, A. N. Goland, and F. W. Wiffen, J. Nucl. Mater. 64, 195 (1977).
- ¹⁷H. Rajainmäki, S. Linderoth, H. E. Hansen, R. M. Nieminen, and M. D. Bentzon, Phys. Rev. B 38, 1087 (1988).
- ¹⁸H. E. Hansen, H. Rajainmäki, R. Talja, M. D. Bentzon, R. M. Nieminen, and K. Petersen, J. Phys. F 15, 1 (1985).

In the He-implanted Si no annealing was seen at temperatures between 100 and 300 K, indicating that nearly all monovacancies contained He and that the concentration of free monovacancies was therefore very small. Helium is suggested to be released from vacancies at about 600 K. Small He bubbles may have grown at temperatures above 800 K.

ACKNOWLEDGMENTS

The authors want to thank M. Manninen, M. J. Puska, and P. Hautojärvi for many helpful discussions. We are also grateful to T. Visler at Topsil Semiconductor Materials a/s for the Si samples and for the impurity analysis. One of us (S.M.) wants to thank the Emil Aaltonen foundation for financial support.

- ¹⁹K. O. Jensen and R. M. Nieminen, Phys. Rev. B 36, 8219 (1987).
- ²⁰K. O. Jensen, M. Eldrup, B. N. Singh, and M. Victoria, J. Phys. F 18, 1069 (1988).
- ²¹S. Mäkinen, H. Rajainmäki, and S. Linderoth, Phys. Rev. B 42, 11 166 (1990) (paper I).
- ²²P. Kirkegaard, M. Eldrup, O. E. Mogensen, and N. J. Pedersen, Comput. Phys. Commun. 23, 307 (1981).
- ²³S. Linderoth, H. E. Hansen, B. Nielsen, and K. Petersen, Appl. Phys. A 33, 25 (1984).
- ²⁴U. Littmark and J. F. Ziegler, Handbook of Range Distributions for Energetic Ions in All Elements (Pergamon, New York, 1980).
- ²⁵J. Mäkinen, C. Corbel, P. Hautojärvi, P. Moser, and F. Pierre, Phys. Rev. B **39**, 10162 (1989).
- ²⁶R. Würschum, W. Bauer, K. Maier, A. Seeger, and H.-E. Schaefer, J. Phys. Condens. Matter 1, SA33 (1989).
- ²⁷S. Dannefaer, G. W. Dean, D. P. Kerr, and B. G. Hogg, Phys. Rev. B 14, 2709 (1976).
- ²⁸W. Fuhs, U. Holzhauser, S. Mantl, F. W. Richter, and R. Sturm, Phys. Status Solidi. B 89, 69 (1978).
- ²⁹S. Dannefaer, in Proceedings of the Eighth International Conference on Positron Annihilation, Gent, Belgium, 1988, edited by L. Dorikens-Vanpraet, M. Dorikens, and D. Segers (World Scientific, Singapore, 1989), p. 86.
- ³⁰H.-E. Schaefer, R. Würschum, R. Schwarz, D. Slobodin, and S. Wagner, Appl. Phys. A 40, 145 (1986).
- ³¹S. Mäkinen and M. J. Puska, Phys. Rev. B 40, 12 523 (1989).
- ³²B. Bech Nielsen, Ph.D. thesis, University of Aarhus (1987); see also B. Bech Nielsen, Phys. Rev. B 37, 6353 (1988).
- ³³V. A. Singh, C. Weigel, J. W. Corbett, and L. M. Roth, Phys. Status. Solidi. **81**, 637 (1977); see also S. T. Picraux and F. L. Vook, Phys. Rev. B **18**, 2066 (1978).
- ³⁴G. Dlubek, O. Brümmer, F. Plazaola, and P. Hautojärvi, Phys. C 19, 331 (1986).
- ³⁵H. J. Stein and P. S. Peercy, Phys. Rev. B 22, 6233 (1980).
- ³⁶G. D. Watkins, in *Deep Centers in Semiconductors, A State-of-the-Art Approach*, edited by S. T. Pantelides (Gordon and Breach, New York, 1986), p.147.
- ³⁷J. W. Corbett, J. K. Karins, and T. Y. Tan, Nucl. Instrum. Methods **182&183**, 457 (1981).
- ³⁸J. Keinonen, M. Hautala, E. Rauhala, M. Erola, J. Lahtinen, H. Huomo, A. Vehanen, and P. Hautojärvi, Phys. Rev. B 36,

1344 (1987); J. Keinonen, M. Hautala, E. Rauhala, V. Karttunen, A. Kuronen, J. Räisänen, J. Lahtinen, A. Vehanen, E. Punkka, and P. Hautojärvi, *ibid.* **37**, 8269 (1988).

- ³⁹M. J. Puska, C. Corbel, and R. M. Nieminen, Phys. Rev. B **41**, 9980 (1990).
- ⁴⁰Y.-H. Lee and J. W. Corbett, Phys. Rev. B 13, 2653 (1976).
- ⁴¹See, e.g., R. N. West, in *Positrons in Solids*, edited by P. Hautojärvi, Topics in Current Physics, Vol. 12, (Springer, Heidelberg, 1979), p. 89.
- ⁴²K. G. Lynn, in *Positron Solid State Physics*, Proceedings of the Enrico Fermi International School of Physics, "Enrico Fermi", Course LXXXIII, Varenna, 1981, edited by W. Brandt

and A. Dupasquier (North-Holland, Amsterdam, 1983), p. 609.

- ⁴³J. Mäkinen, C. Corbel, P. Hautojärvi, A. Vehanen, and D. Mathoit, Phys. Rev. B 43, 12 114 (1991).
- ⁴⁴M. J. Puska and R. M. Nieminen, J. Phys. F 13, 333 (1983),
 M. J. Puska, Phys. Status. Solidi. A 102, 11 (1987).
- ⁴⁵Yu. V. Gorelkinskii, N. N. Nevinnyi, and S. S. Ajazbaev, Phys. Lett. 110A, 157 (1985).
- ⁴⁶C. C. Griffioen, J. H. Evans, P. C. DeJong, and A. van Veen, Nucl. Instrum. Methods B 27, 417 (1987).
- ⁴⁷J. H. Evans, A. van Veen, and C. C. Griffioen, Nucl. Instrum. Methods B 28, 360 (1987).