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Defects in electron-irradiated Si studied by positron-lifetime spectroscopy

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Differently doped and undoped silicon was irradiated with electrons to study the formation of nonequilibrium defects and their annealing behavior. The annealing curves, measured by positron lifetime and also partly by the shape parameters of the Doppler-broadened annihilation line, depend strongly on the doping concentration and the oxygen content. In addition, temperature-dependent positron-lifetime measurements starting at 15 K were performed after low-temperature and room-temperature irradiation with different doses and in different annealing states. Shallow positron traps were detected for all conductivity types of irradiated Si. However, the concentration of shallow traps depends on the crystal-growth procedure. Electron-irradiated Czochralski-grown samples contain a higher number of shallow traps than electron-irradiated floating-zone-grown material. Due to the different concentrations of oxygen in these differently grown Si, we conclude that the oxygen atoms are a part of these traps. A possible candidate is the irradiation-induced *A* center. Correlated infrared-absorption investigations were carried out to support this interpretation. [S0163-1829(98)11239-0]

I. INTRODUCTION

The primary process at the irradiation with high energetic particles is the formation of a Frenkel pair, i.e., a vacancy and an interstitial. Vacancies in silicon become mobile above about 70–170 K, depending on their charge state, and then they anneal out or react with each other to divacancies or with impurities or dopants to *A* (*V*O) or *E* ($V+$dopant) centers.[1] These complexes start to anneal at temperatures above 200 K. The vacancies remaining from the complexes by dissociation can cluster during the annealing. These electron-irradiation-induced defects in silicon, and its subsequent annealings, have been the subject of extended investigations by standard methods such as EPR (electron paramagnetic resonance), deep-level transient spectroscopy, and infrared absorption.[2,3] However, the concentration and the behavior of defects formed by irradiation and during the annealing process are partly still under discussion.

The positron annihilation technique is a powerful tool to detect vacancylike defects and, therefore, this method is often used to study irradiation-induced defects. In addition, negative ions and dislocations can be detected by positrons under certain circumstances. The annealing behavior of vacancies and complexes containing vacancies, and also the temperature dependence of the positron trapping in defects for electron-irradiated silicon, were already investigated for individual examples.[4–9] The aim of this work is a systematic study of the formation of vacancy defects and their annealing behavior in electron-irradiated silicon depending on doping and impurity concentration. In addition, temperature-dependent measurements were carried out in different annealing states to investigate shallow positron traps in silicon.

The paper is organized as follows. The material and the experimental details are given in Sec. II. The results obtained and their discussion are presented in Sec. III. Section IV summarizes the paper.

II. MATERIAL AND EXPERIMENTAL PROCEDURES

Samples of different types of Si were investigated by positron-lifetime spectroscopy after irradiation with 2-MeV electrons and fluences between 10^{16} and 10^{19} cm^{-2}. The electron irradiations were performed at 4 K or at room temperature with the Van de Graaff accelerator in the Forschungszentrum Jülich. The characteristics of the samples and the irradiation conditions are listed in Table I. The location of the Fermi level in the band gap was determined by Hall-effect measurements at room temperature after irradiation.

The low-temperature-irradiated samples were mounted in liquid nitrogen in a cryoheater system to prevent warming up. Then, isochronal annealings (15 min) were performed in the range from the temperature of sample installation in the cryoheater system (90 K) to the temperature of complete annealing of vacancy-type positron traps. The positron lifetime was always measured at 90 K with the exception of some marked room-temperature measurements. Temperature-dependent measurements after different annealing steps were carried out starting at 15 K.

The positron-lifetime spectra were obtained using a fast-fast coincidence system having a time resolution FWHM (full width at half maximum) of 260 ps. The samples were sandwiched with the positron source consisting of radioactive ^{22}Na (0.5 MBq) covered with two thin (1 mg/cm^{-2}) Al foils. The lifetime spectra, containing at least 3×10^{6} counts per spectrum, were analyzed after source and background correction[10,11] in terms of the trapping model.[12,13] At low temperatures, the decomposition of the spectra is specially difficult due to the intensified trapping in negative vacancies and in shallow positron traps. Therefore, the spectra were typically decomposed into two components. The accuracy of the average positron lifetime amounts to about 1 ps, and that of the components is shown in the figures or is mentioned in the text.

The details of the positron trapping in defects and of the positron trapping model were the same as earlier.[14,15] Fits according to this trapping model were applied to temperature-dependent positron lifetime measurements (see Sec. III). Positron trapping in and detrapping from Rydberg states of shallow traps and of negatively charged vacancy

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TABLE I. Characteristics of the investigated Si samples. The specified Fermi levels were determined at a sample temperature of 300 K after 4-K electron irradiation.

Sample no.	Doping characteristics	Oxygen conc. $[O_i]$ (10^{17} cm^{-3})	irrad. dose Φ (cm^{-2})	irrad. temperature T_{irr} (K)	Fermi level E_f-E_v (eV)
1	undoped, $\rho=200\ \Omega$ cm	6.0 (Cz)	$10^{16},\ldots,10^{19}$	4, 300	0.55
2	P doped, $\rho=5000\ \Omega$ cm	0.2 (FZ)	10^{18}	4, 300	0.56
3	P doped, $\rho=0.001\ \Omega$ cm	5.0 (Cz)	10^{18}	4	within conduction band
4	P doped, $\rho=0.6\ \Omega$ cm	7.6 (Cz)	10^{18}	4	0.56
5	B doped, $\rho=0.0025\ \Omega$ cm	7.0 (Cz)	10^{18}	4	within valence band
6	B doped, $\rho=1.3\ \Omega$ cm	0.1 (Fz)	10^{18}	4	0.26
7	B doped, $\rho=5.7\ \Omega$ cm	8.4 (Cz)	10^{18}	4	0.63
8	B doped, $\rho=0.015\ \Omega$ cm	7.0 (Cz)	10^{18}	4	-
9	B doped, $\rho=2.65\ \Omega$ cm	7.0 (Cz)	10^{18}	4	-
10	As doped, $\rho=1.2\ \Omega$ cm	5.0 (Cz)	10^{18}	4	0.78
11	As doped, $\rho=0.0016\ \Omega$ cm	7.0 (Cz)	10^{18}	4	within conduction band
12	Sb doped, $\rho=0.04\ \Omega$ cm	6.0 (Cz)	10^{18}	4	within conduction band
13	Sb doped, $\rho=0.009\ \Omega$ cm	7.0 (Cz)	10^{18}	4	within conduction band

defects and also direct trapping by a vacancy without Rydberg states were taken into account in the trapping model.

Some annealing experiments were performed by the variable-energy positron annihilation spectroscopy (slow-positron beam technique).[16] The Doppler broadening of the emitted γ radiation is mainly caused by the momentum of the annihilating electrons. Thus the shape of the 511-keV annihilation line is sensitive to the electron momentum distribution in the solid. This distribution differs in open-volume defects compared to the defect-free bulk. The line-shape parameter S is the measurement quantity in the conventional Doppler spectroscopy. This annihilation parameter changes when positrons are trapped in defects. The S parameter is defined as the ratio between the number of counts in the center (511 ± 0.8 keV) to the total peak area of the annihilation line in our experimental setup. The γ annihilation spectrum was recorded with a high-purity Ge detector having an energy resolution of 1.5-keV FHWM at 514 keV.

The infrared-absorption measurements were carried out at a Fourier-transform spectrometer (Bruker IFS66). A halogen lamp was used as source in the near-IR range. The beam splitter of the Michelson interferometer was made of CaF_2. An InSb detector acted as signal indicator. The range of sensitivity was 15 000–2000 cm^{-1}. A globar produced the radiation in the middle IR range, and the beam cutter consisted of KBr. The detector was sensitive in the range between 5000 and 400 cm^{-1}. The measurements were performed at a resolution of 1 cm^{-1} at a sample temperature of 20 K. This temperature was ensured by a cryostat construction which sample chamber was equipped with KBr windows.

III. RESULTS AND DISCUSSION

Undoped, *p*-type (B doped), and *n*-type (P, As, and Sb doped) silicon samples were investigated after low-temperature (4 K) electron irradiation in the annealing range above 90 K. The temperature dependence of the positron lifetime was also studied after different annealing steps. Additional dose and irradiation-temperature-dependent studies were correlated with IR-absorption measurements to identify the kind of shallow traps.

A. Undoped silicon

Silicon materials grown by the Czochralski (Cz) and by the floating-zone (FZ) method were available for the annealing studies. The dose-dependent investigations and the irradiations at different temperatures were performed for Cz-Si.

1. Annealing experiments

The undoped Cz-Si sample was n type ($n\approx2\times10^{13}$ cm^{-3}) prior to irradiation, and the Fermi level E_f was located at $E_v+0.76$ eV. The Fermi level was shifted in a midgap position at $E_v+0.55$ eV by the electron irradiation (2 MeV, 4 K, 10^{18} cm^{-2}). The monovacancy and the divacancy should be negatively charged in this sample state. All statements to the charge states of the monovacancy and divacancy in this paper are based on our Hall-effect measurements and the ionization level schema according to Corbett.[17]

Figure 1 shows the average positron lifetime $\overline{\tau}$, the defect-related positron lifetime τ_2, and the corresponding intensity I_2 in dependence on the annealing temperature for irradiated undoped Cz-Si. The lines in the figures are guide for the eye in general. If they represent fits according to the trapping model, it is mentioned in the text and in the respective figure caption.

$\overline{\tau}$ increases from the bulk value of 218 ± 2 ps, measured before irradiation treatment, to 260 ps by the electron irradiation. Two annealing stages at 170 and 270 K were observed. Then, the average positron lifetime weakly increases above 350 K and it subsequently reaches the bulk value in a

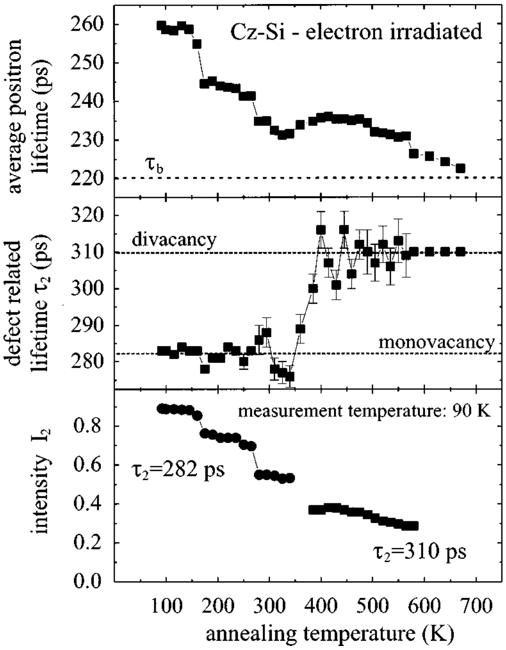

FIG. 1. The average positron lifetime, the defect-related positron lifetime, and the corresponding intensity as functions of annealing temperature for electron-irradiated (2 MeV, 4 K, 10^{18} cm^{-2}) undoped Cz-Si. The positron measurements were performed at 90 K. τ_b is the bulk lifetime. The different symbols for the intensity indicate the different defect types (monovacancy and divacancy).

wide stage between 500 and 670 K. The defect-related lifetime is constant $\tau_2=282$ ps up to room temperature. τ_2 increases in the further course of the annealing and comes up to the value of 310 ps at 400 K. The intensity I_2 of the defect component also reflects the annealing stages.

The first annealing stage can be attributed to the annealing of monovacancies. The defect-related positron lifetime ($\tau_2=282$ ps) is in a good agreement with the theoretically and experimentally determined values for V_{Si}.[18,7,4] The annealing temperature of 170 K is equal to that accepted and obtained by deep-level transient spectroscopy measurements.[19] The monovacancy becomes mobile and interacts with other vacancies or with impurities in this temperature range.[2]

The second annealing stage at 270 K must be caused by the annealing of a defect, having an open volume similar to that of a monovacancy and being connected with oxygen. These properties must be derived from the defect-related positron lifetime, $\tau_2=282\pm3$ ps, and from the absence of this annealing stage in FZ silicon with a low content of oxygen (see Fig. 2).

The average positron lifetime increases in the temperature range above 350 K due to the increase in the defect-related positron lifetime to 310 ps, which is typical of a divacancy. The calculated positron lifetime of the divacancy is 306 ps,[18] and the experimentally determined values are in the range from 318 to 327 ps.[20–22] The annealing range of the investigated sample (see Fig. 1) agrees with the annealing range of the divacancy between 450 and 623 K which was found by EPR measurements.[23] Therefore, we conclude in agreement to earlier results that the divacancy is formed above 350 K, and anneals between 500 and 650 K.

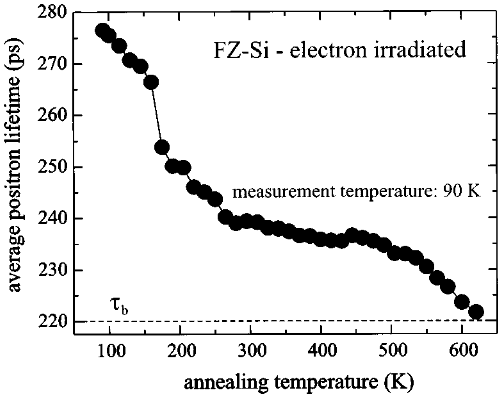

FIG. 2. Change of the average positron lifetime with the annealing temperature in electron-irradiated (2 MeV, 4 K, 10^{18} cm^{-2}) undoped FZ-Si. The measurement temperature was 90 K. The dashed line indicates the bulk lifetime τ_b.

Figure 2 shows the annealing behavior of electron-irradiated (2 MeV, 4 K, 10^{18} cm^{-2}) FZ-Si. The sample is nominally phosphorus doped, but the specific resistivity is 5000 Ω cm and, thus, the phosphorus concentration is lower than 10^{12} cm^{-3}. Therefore, the influence of the dopant on the positron lifetime can be neglected, and the sample can be considered as undoped. The position of the Fermi level was measured to be $E_v+0.56$ eV after irradiation and annealing up to 300 K analogous to Cz-Si. Then the monovacancy and the divacancy are negatively charged.

The average positron lifetime of 277 ps after electron irradiation and annealing at 90 K is distinctly higher compared to the value measured for Cz silicon. This is because of the higher concentration of shallow positron traps in Cz-Si (see discussion in Sec. III A 2). These shallow traps decrease the average positron lifetime at low temperatures. Assuming that the negatively charged monovacancy with the defect-related positron lifetime of $\tau_V=\tau_2=282$ ps is the dominant positron trap in FZ silicon at 90 K, the positron trapping rate of $\kappa_V=5\times10^{10}$ s^{-1} can be calculated. Then, by means of

$$C_V=\frac{\kappa_V}{\mu}=\frac{1}{\mu\tau_b}\,\frac{\bar{\tau}-\tau_b}{\tau_V-\bar{\tau}}, \tag{1}$$

the vacancy concentration of $C_V=1.5\times10^{17}$ cm^{-3} can be estimated with the trapping coefficient of $\mu=1.8\times10^{16}$ s^{-1} for negatively charged VP centers.[24] This value was used because no experimentally determined trapping coefficient of the monovacancy in silicon is known. It follows that the introduction rate of monovacancies is 0.15 cm^{-1}. This value is high compared with values of 0.03 cm^{-1} for p-Si and 0.003 cm^{-1} for n-Si determined by EPR measurements.[2] The defect introduction rates in Si were recently discussed in the literature. A Huang diffuse scattering study resulted in a total introduction rate of 1 cm^{-1}.[25]

Two distinct annealing stages at 170 and 450 K were observed for FZ-Si. These stages can be attributed to the annealing of monovacancies and divacancies. The stage at 270 K, which was observed for Cz-Si, was very weakly detected. The main difference between FZ- and Cz–Si is the oxygen content, and, therefore, we conclude that this annealing effect at 270 K is due to oxygen. The defect-related

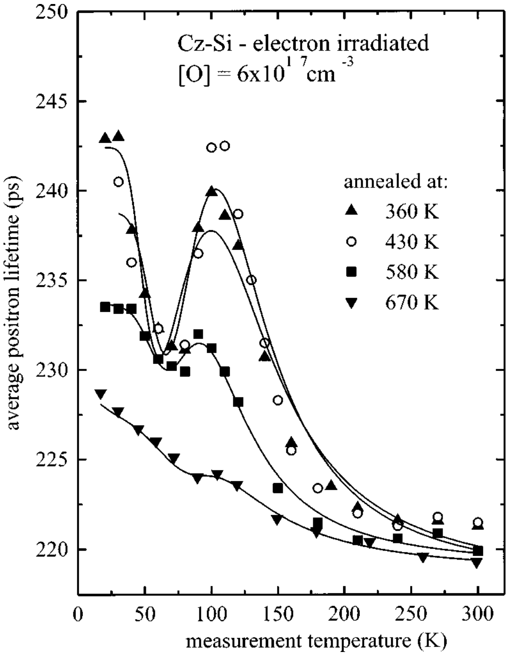

FIG. 3. Average positron lifetime as a function of the sample temperature in electron-irradiated ($E=2$ MeV, $T_{\rm irr}=4$ K, $\Phi=10^{18}$ cm^{-2}) Czochralski-grown Si after different annealing steps. The lines correspond to fits according to the trapping model.

positron lifetime for electron-irradiated FZ-Si cannot be separated up to 200 K due to the nearly complete positron trapping in vacancies. Above an annealing temperature of about 200 K, $\tau_2=300$ ps. This value can be considered as an average of the defect-related lifetimes of divacancies and monovacancylike defects. Monovacancies agglomerate or interact with oxygen if they become mobile. The divacancy is the dominant defect in FZ silicon after annealing at about 200 K due to the low oxygen concentration.

2. Temperature-dependent investigations

Temperature-dependent positron-lifetime measurements were performed after different annealing treatments in undoped Cz- and FZ-Si after electron irradiation ($E=2$ MeV, $T_{\rm irr}=4$ K, $\Phi=10^{18}$ cm^{-2}). The positron lifetime depends distinctly on temperature. However, the observed temperature dependence of average positron lifetime is different from the one expected for negatively charged open-volume defects, such as irradiation-induced vacancies and divacancies. It is rather typical for the competitive trapping in vacancies and in shallow traps.

Figure 3 shows temperature-dependent measurements after different annealing steps for electron-irradiated Cz-Si. The positron lifetime increases up to 100 K with decreasing temperature. This behavior can be attributed to negatively charged vacancy defects. After annealing at 360 K, the monovacancies vanished and divacancies were formed. The positron lifetime in the defect was determined to be 310 ±5 ps. This value is in good agreement with calculated, and also earlier measured positron lifetimes in Si divacancies.[26,20] Below a measurement temperature of 100 K, the positron lifetime at first decreases due to the effectiveness of shallow positron traps. After the disappearance of the detrapping from these defects below 60 K (see Fig. 3), the negative divacancies act as dominant trapping centers and the positron lifetime continues to increase.

TABLE II. Annealing temperature T_a and fitted values for concentration of shallow traps $C_{\rm st}$ and vacancy defects C_V in electron-irradiated undoped Cz-Si. The irradiation was performed at 4 K with 2-MeV electrons and a dose of 10^{18} cm^{-2}.

T_a (K)	$C_{\rm st}$ (10^{16} cm^{-3})	C_V (10^{16} cm^{-3})
360	4.95±1.86	21.60±8.52
430	4.88±2.37	21.47±9.22
580	1.82±0.43	4.85±1.15
670	1.03±0.37	1.94±0.65

The temperature-dependent average positron lifetime was fitted to the trapping model.[12,13] Two negatively charged defect types (shallow traps and divacancies) were taken into account. At first, free fits were performed. Then the mean values of positron binding energies of Rydberg states of the shallow traps and of the vacancy defects, and both trapping coefficients were fixed in the following fit procedures. The mean positron binding energy of shallow traps was determined to be $E_{\rm st}=48.6\pm10.0$ meV and of the precursor Rydberg state of vacancy defects $E_R=22.4\pm7.8$ meV. The mean trapping coefficient at 25 K of shallow traps was $\mu_{\rm st0}=(9\pm4)\times10^{17}$ s^{-1} and of the Rydberg states of negative vacancies $\mu_{R0}=(7\pm3)\times10^{16}$ s^{-1}. Table II summarizes the other most important fitting parameters. As mentioned above, one has to assess the uncertainties in the fitting procedure very critical due to the partial correlation of the fitting parameters. Since the fitting results are in rational restrictions, it is possible to draw qualitative conclusions.

It is obvious from the fitting results that the concentrations of divacancies and also of shallow traps decrease during annealing. This annealing behavior is also visible in Fig. 3. The average positron lifetime decreases with increasing annealing temperature in the whole temperature range, and the minimum between 40 and 100 K is not as pronounced as before. After annealing at 670 K, only a weak shoulder is detectable in this temperature range.

Figure 4 shows results of analogous temperature-dependent measurements on FZ-Si. The average positron lifetime increases with decreasing temperature, and at about 75 K a small plateau was observed. This weak indication of a curve minimum is a hint to a lower concentration of shallow traps than found in Cz-Si. The fits to the positron lifetime according to the trapping model (shallow positron traps and negative divacancies) are drawn in Fig. 4 as solid lines. The average binding energies are $E_{\rm st}=48\pm10$ meV and $E_R=25\pm8$ meV. These values are in good agreement with the ones of Cz-Si. The other important results are summarized in Table III.

Here the concentration of both defect types also decreases with increasing annealing temperature, which is also detected by average positron lifetime (see Fig. 4). The difference between Cz and FZ materials is the concentration of shallow traps. FZ-Si contains only about the fourth part of this defect type. This dependence was also found in doped material. The only difference between these Si materials is the concentration of oxygen and, therefore, we conclude that shallow traps are directly connected with oxygen. Consider-

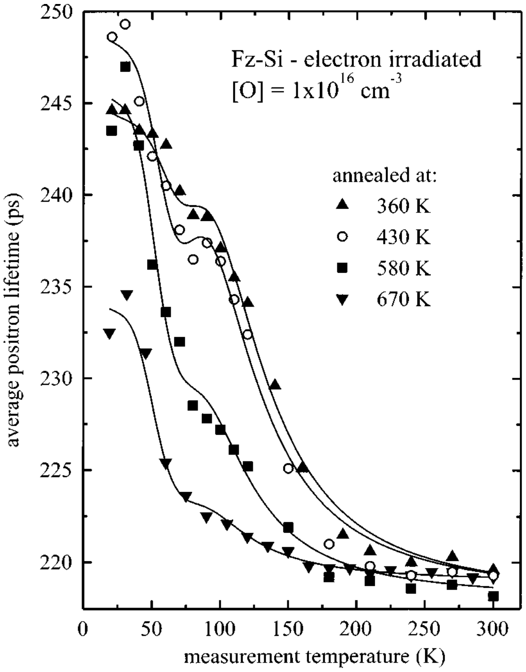

FIG. 4. The temperature-dependent average positron lifetime in floating-zone-grown Si after low-temperature irradiation with 2-MeV electrons (10^{18} cm^{-2}) at different annealing states. The lines are trapping-model fits (see text).

ing that oxygen in its usual interstitial configuration in Si is electrically inactive, we can consequently conclude that oxygen is only a constituent of these shallow traps. Shallow traps should also be irradiation induced, since a negatively charged defect with such a high concentration is unknown for as-grown material. A further possible explanation could be that a neutral defect with small open volume forms a shallow potential from which positrons can escape at high temperatures after its trapping. The *A* center is a candidate for this trap in weakly *n*-conductive, semi-insulating, and *p*-type silicon.

The existence of shallow positron traps in *n*-type Cz silicon after room-temperature irradiation was earlier detected by temperature-dependent measurements.[5] These defects were attributed to the negatively charged *A* center with a lifetime close to the bulk value, 225 ps. In slightly *n*- and *p*-type materials and also in FZ-Si, no shallow positron traps were observed up till now. The *A* center has an ionization level 0/− at 170 meV below the conduction band edge.[27] This means that the *A* center is neutral in our undoped and *p*-type samples which were compensated after irradiation or remained of *p* type, respectively (see Table I).

TABLE III. Annealing temperature T_a and fitted values for concentration of shallow traps C_{st} and vacancy defects C_V in FZ-Si after 2-MeV electron irradiation at 4 K to a dose of 10^{18} cm^{-2}.

T_a (K)	C_{st} (10^{16} cm^{-3})	C_V (10^{16} cm^{-3})
360	1.52 ± 0.25	11.26 ± 1.83
430	0.97 ± 0.25	6.47 ± 1.56
580	1.21 ± 0.35	7.68 ± 2.07
670	0.94 ± 0.31	3.03 ± 0.90

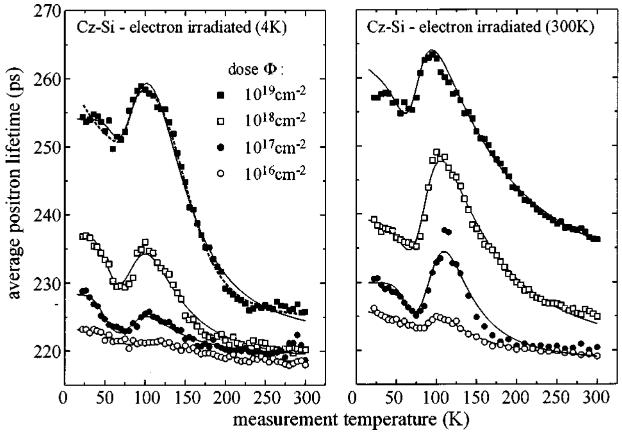

FIG. 5. A comparison between the positron trapping behavior in undoped Cz-Si after irradiation at room temperature and at 4 K (subsequent annealing at 300 K) with different doses ($\Phi = 10^{16},\ldots,10^{19}$ cm^{-2}, $E = 2$ MeV). The solid lines correspond to the trapping model taking into account a negatively charged vacancy defect and a negative ion as shallow positron trap. The dashed line shows the fit which considers a negatively charged vacancy and a neutral defect with a small open volume acting as a shallow trap.

In order to act as a shallow positron trap, it is usually assumed that a non-open-volume defect must carry a negative charge. The positron is then captured by a shallow Coulomb potential at low temperatures. The *A* center does not form such a potential in its neutral charge state. Nevertheless it may be an effective shallow trap. The attraction between the positron and the *A* center is only based on the open volume which, however, is rather small for this particular defect.[27] Thus, the positron binding energy must be small and the defect-related lifetime is very close to the bulk lifetime of a defect-free sample. A similar case was predicted for the positron trapping in an undisturbed dislocation line.[28]

3. Dose and irradiation-temperature dependence of positron trapping behavior in Si

Dose-dependent positron-lifetime measurements after irradiation at different temperatures (4 and 300 K) correlated with infrared-absorption studies were performed to identify the shallow positron traps. Figure 5 shows the temperature-dependent positron lifetime in Cz-Si after 2-MeV electron irradiation at 4 K, subsequently annealed at 300 K, and after irradiation at 300 K with different doses ($10^{16},\ldots,10^{19}$ cm^{-2}).

The fundamental course of the temperature dependence of $\bar{\tau}$ is independent of the irradiation temperature, and typical of the simultaneous positron trapping in deep and shallow traps (see the discussion in Sec. III A 2). The average positron lifetime increases when lowering the sample temperature in the range from 300 to 100 K due to negatively charged vacancy defects. Then $\bar{\tau}$ decreases in the range down to about 60 K due to the shallow traps, and it increases again to 20 K.

The average positron lifetime increases when raising the dose in the whole measurement range for both irradiation temperatures. This means that the concentration of vacancy defects increases. We can also conclude that the concentration of shallow positron traps increases by irradiation because the competitive trapping in shallow traps was detected for all doses. A difference caused by the irradiation temperature is the higher positron lifetime after room-temperature irradiation in the whole temperature range and for all doses. It is possible that the ratio of the concentrations of the irradiation-induced neutral and negatively charged divacancies and shallow traps causes this behavior.

Fits according to the trapping model taking into account negatively charged divacancies ($\tau_d = 305$ ps) and negatively charged shallow positron traps in principle describe the temperature-dependent courses of $\overline{\tau}$ (see Fig. 5). The resulting positron binding energies to shallow traps, $E_{\mathrm{st}} = 55.3 \pm 10.3$ meV for low-temperature irradiation and $E_{\mathrm{st}} = 66.8 \pm 9.8$ meV for the 300-K irradiation, and that of the Rydberg states of the negative vacancy defects, $E_R = 24.8 \pm 9.0$ meV for the 4-K irradiation and $E_R = 20.4 \pm 8.3$ meV for the room-temperature irradiation, are in a good agreement. It seems that the same defect types give rise to the positron trapping.

The quantitative fit results of defect concentrations are statistically unsafe. Nevertheless, as general statements, it can be concluded that the vacancy and the shallow trap concentrations increase with increasing dose, and that the positron trapping rate of shallow traps is about one order of magnitude higher than that of negative vacancy defects at low temperatures. In addition, the fits result in an increase in C_V and C_{st} by one order of magnitude in the dose range from 10^{16} to 10^{18} cm^{-2} after low-temperature irradiation. Then the defect concentrations again increase tenfold at a dose of 10^{19} cm^{-2}. After room-temperature irradiation, the defect concentrations evenly increase.

Considering that the neutral *A* center can act as a shallow trap due to the small open volume, we modified the trapping model and also took into account a negative vacancy and a neutral trap from which positrons are strongly detrapped with increasing temperature. The fits yield curves which are similar to that of the other model. An example is shown in Fig. 5 for the dose of 10^{19} cm^{-2} after 4-K irradiation. The dashed line corresponds to the trapping model considering a negative vacancy and a neutral shallow trap. The positron binding energies both of the shallow trap and of the Rydberg state of the vacancy are likewise shifted to higher values after low- and room-temperature irradiation. The increase of the defect concentration with increasing dose and the decrease with progressive annealing is also an analogous result of the fits. Thus, one cannot distinguish between neutral and negative shallow traps by the temperature-dependent positron lifetime measurements and by fits according to the trapping model.

In summary of positron results, it may be said that after electron irradiation divacancy defects and shallow positron traps connected with oxygen can be observed independent of irradiation temperature. The concentration of both defect types increases with the dose.

4. Dose and irradiation-temperature dependence of IR absorption in Si

IR-absorption measurements in the wave number range from 400 to 5000 cm^{-1} (resolution: 1 cm^{-1}) were performed for all eight samples (two different irradiation temperatures and four different doses) at 20 K. Figure 6 shows the dose dependence of the intensity of the local vibrational mode at 835 cm^{-1} being typical of the neutral *A* center,[29] and with its concentration in arbitrary units for both irradiation temperatures in electron-irradiated silicon. Other complexes as VO_2, VO_3, V_2O, and so on, usually appearing after annealing at higher temperatures, are not detectable in our electron-irradiated silicon.

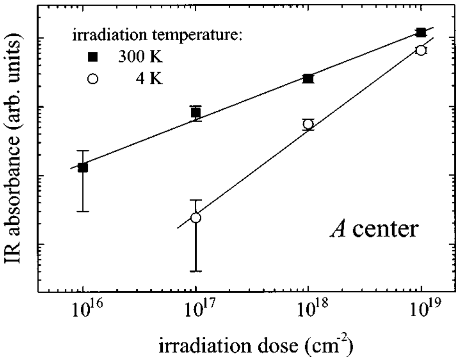

FIG. 6. Dose dependence of the intensity of the local vibrational mode of the neutral *A* center (835 cm^{-1}) for different irradiation temperatures in Cz-Si.

The neutral *A* center is detectable after room-temperature irradiation in all Cz silicon samples, and its concentration increases with the electron dose. C_A is proportional to $\Phi^{0.6}$. The introduction rate of the neutral *A* center is lower at low-temperature irradiation. This defect was not observed after 4-K irradiation with a dose of $\Phi = 10^{16}$ cm^{-2} by IR-absorption measurements. The concentration linearly increases in the dose range between 10^{17} and 10^{19} cm^{-2}. Therefore, the concentration difference for the two irradiation temperatures decreases from more than two orders of magnitude to a factor 2 in the investigated dose range.

A possible explanation of the different dose dependences of the *A* center concentration would be that two different defect formation processes happen. First, the *A* center is directly formed by the irradiation proportional to the dose, and this process is the dominating one at low-temperature irradiation. The second possibility is the formation of the *A* center with a threshold energy which is above the migration energy of monovacancies. This process is possible at room-temperature irradiation. The vacancies are mobile, and combine with interstitial oxygen, and the *A* center concentration is increased. After low-temperature irradiation and following annealing, the monovacancies become mobile and interact with each other before the threshold energy of the *A* center formation is reached.

The IR-absorption measurements also show that in all electron irradiated Cz-Si samples neutral and negatively charged divacancies simultaneously exist. This was proved by the detection of the absorption band at 0.34 eV which is assigned to the negatively charged divacancy,[30] and the band at 0.73 eV which is attributed to the neutral divacancy.[31] The defect concentrations induced by room-temperature irradiation and by 4-K irradiation are in the same order of magnitude, and the maximum difference is a factor 3. The divacancy concentrations increase 2–3 orders of magnitude in the dose range from 10^{16} to 10^{19} cm^{-2}. The rise of the concentration of both the neutral and the negative divacancy increases by low-temperature irradiation. This result was also obtained from the fits of the positron lifetime according to the trapping model. It has to be noted that neutral divacancies were not taken into account in this model.

We can draw several conclusions from the correlated IR-absorption and positron-lifetime measurements. If the neutral *A* center acts as a shallow positron trap, the temperature dependence of the average positron lifetime in Cz silicon electron irradiated at room temperature can be explained. Both the concentration of the divacancy and the *A* center evenly increases in the dose range of $10^{16},\ldots,10^{19}$ cm^{-2}.

After low-temperature irradiation, the concentration of the *A* center is distinctly lower especially at weak doses. In order to explain the positron results, the concentration ratio of deep and shallow positron traps must be similar to that after room-temperature irradiation. This means that the neutral *A* center must not be the only shallow positron trap induced by 4-K irradiation. Other possible candidates for a shallow positron trap are modified *A* centers as complexes from an *A* center, and interstitial Si or impurities as carbon. Also, defects causing a lattice dilatation and acting like a dislocation are possible candidates. $\mathrm{O}_i\mathrm{Si}_i$ defects, being stable up to 300 °C were observed by IR absorption in Cz silizium.[32] However, the corresponding local vibrational mode[33] at 936 cm^{-1} was not observed in the samples under investigation.

In addition, the decrease in the *A* center concentration in the annealing range between 360 and 570 K (see Figs. 3 and 4, and the discussion in Sec. III A 2) points to the *A* center acting as a shallow trap. The annealing temperature of the *V*O complex was determined to be about 570 K by IR-absorption measurements.[29]

B. *p*-type silicon

The annealing behavior of five differently boron-doped samples after electron irradiation was studied at a measurement temperature of 90 K, or partly at room temperature. In addition, the sample-temperature dependence of the positron trapping was investigated for several examples.

1. Annealing behavior

The annealing behavior of differently boron-doped silicon after electron irradiation (2 MeV, 4 K, 10^{18} cm^{-2}) is shown in Fig. 7. The dependence of the average positron lifetime on the annealing temperature distinctly shows the influence of the oxygen content and doping concentration.

The weakly doped FZ sample ($\rho = 1.3\ \Omega$ cm, ●) was *p* conductive ($p = 8\times10^{15}$ cm^{-3}), and the Fermi level was at $E_v + 0.21$ eV. After irradiation and annealing up to room temperature, the position of the Fermi level was additionally determined to be $E_v + 0.26$ eV by Hall-effect measurements. This value differs only slightly from that of the unirradiated sample. An explanation is that the irradiation-induced defects anneal out below 300 K (see Fig. 7), and thus the shift of the Fermi level is also reversible.

The average positron lifetime is 235 ps at 90 K after irradiation, and this value is lower than $\bar{\tau}$ in irradiated *n*-type silicon. It can be caused by different charge states of the detected vacancies. In *p*-type material, the monovacancy is neutral and the trapping coefficient is 1–2 orders of magnitude smaller than for negatively charged monovacancies at low temperatures.[34] Assuming that the trapping coefficient of the neutral Si vacancy is 6.8×10^{14} s^{-1} as being determined for the neutral *V*P complex,[24] one can estimate the vacancy concentration to be 1.1×10^{17} cm^{-3} by using Eq. (1). This concentration is in a good agreement with the estimated vacancy concentrations in undoped and *n*-type silicon (see Secs. III A 1 and III C 1). This means that the introduction rate of vacancies is independent of the conduction type in silicon.

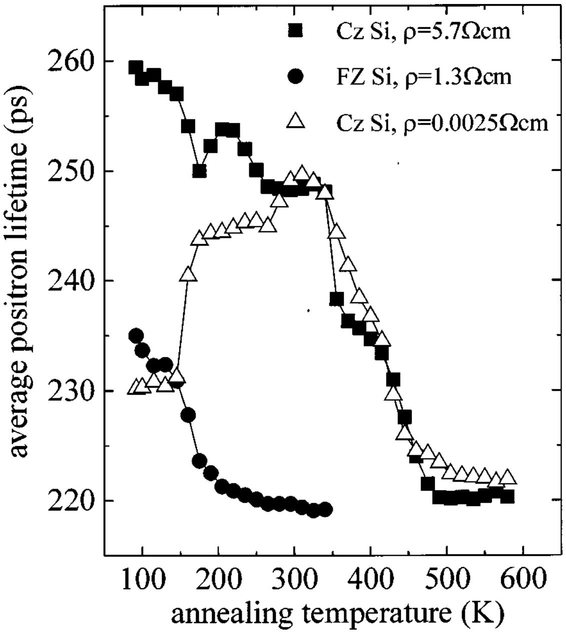

FIG. 7. The average positron lifetime measured at 90 K as a function of annealing temperature for differently boron-doped silicon after irradiation to a dose of 10^{18} cm^{-2} at 4 K with 2-MeV electrons.

The annealing curve of the weakly doped FZ sample shows the end of an annealing stage at 115 K and a main stage at 170 K. After a temperature treatment at 200 K, the positron lifetime of silicon bulk was measured. The main stage can be attributed to the annealing of monovacancies in agreement with electrical and EPR measurements.[35,36] An annealing stage at 100 K was also detected by electrical measurements. It was assigned to a defect complex with low thermal stability.[35] This defect should be connected with a divacancy produced as the primary irradiation-induced defect, because it was only observed after 2.5-MeV electron irradiation, and it was not detected after 1-MeV irradiation. The annealing shown by positrons at 115 K can be caused by these 2-MeV electron-induced complexes.

The annealing behavior of Cz-Si:B with a comparable doping concentration ($\rho = 5.7\ \Omega$ cm, ■) is completely different. Prior to irradiation, the sample was *p* type ($p = 2.5\times10^{15}$ cm^{-3}), and the Fermi level was located at $E_v + 0.22$ eV. The Fermi level was shifted toward midgap position by irradiation-induced defects, and then it was located at $E_v + 0.63$ eV. Monovacancies and divacancies are negatively charged in this sample state. The average positron lifetime is 260 ps after irradiation, and annealing up to the installation temperature of 90 K. This value was also observed in *n*-type Cz-Si after low-temperature electron irradiation with a fluence of 10^{18} cm^{-2} (see Sec. III C). The influence of shallow positron traps which reduce the average positron lifetime at low measurement temperatures will be discussed below.

The defect-related positron lifetime is constant 288 ps during the annealing in the temperature range between 90 and 350 K. This value can be considered to be an average of different defect types. The first annealing stage at 170 K shows the disappearance of monovacancies. A broad annealing was observed between 200 and 475 K, which can be subdivided into three weak annealing stages at 250, 350, and 450 K. In this B-doped, oxygen-rich sample various defect complexes were formed during the irradiation and annealing. A part of the monovacancies reacts with substitutional boron and produces E centers (VB) during the electron irradiation. These boron-vacancy complexes differ from other E centers, because the boron atom occupies the next-nearest-neighbor positron.[2] Therefore, no influence of boron can be expected on the defect-related positron lifetime compared to the specific lifetime of the monovacancy. EPR investigations showed the decomposition of VB complexes below room temperature.[2] In this temperature range, interstitial boron also becomes mobile. Thermally more stable defect complexes containing vacancies, boron, and oxygen (A center, divacancy, etc.) can be formed during these processes. After annealing at 475 K, no vacancylike defects can be detected by positrons. Therefore, the annealing of vacancylike defect complexes in boron-doped Cz-Si occurs at lower temperature compared to phosphorus-doped Cz-Si.

The very highly B-doped sample ($\rho = 0.0025\ \Omega$ cm, △) was strongly p conductive ($p = 4\times10^{19}$ cm^{-3}) before electron irradiation, and the Fermi level was located within the valence band. The irradiation caused no shift of the Fermi level, the sample remained in the degenerate state. In this sample state, the isolated monovacancies and divacancies are positively charged and cannot trap positrons. The average positron lifetime was 231 ps at 90 K, and the defect-related positron lifetime of $\tau_2 = 285$ ps is typical of a monovacancy. This component can be attributed to the VB complex which will be formed by low-temperature electron irradiation.[35,2]

The average positron lifetime is constant up to an annealing temperature of 150 K, and then it steeply increases to 245 ps in the range up to 170 K. The concentration of detectable vacancylike defects increases by the mobility of monovacancies and thus, by the formation of neutral or negatively charged vacancylike complexes. The average positron lifetime additionally increases above 250 K. In this temperature range, the E center disintegrates and then the free vacancies can agglomerate to defects with larger open volume.

A broad annealing stage between 340 and 475 K was then observed by analogy with the weakly B-doped sample ($\rho = 5.7\ \Omega$ cm, ■). The defect-related positron lifetime is constant 285 ps up to an annealing temperature of 400 K. Monovacancylike defects connected with boron and/or oxygen are the dominant positron traps. Above a temperature of 420 K, the defect-related positron lifetime increases to 305 ± 10 ps. The value is characteristic of a divacancy which anneals out between 450 and 620 K.[23,37] Isolated divacancies are positively charged in our sample. Therefore, the positron trapping center must be a divacancylike complex with boron and/or oxygen. This defect is less stable than the divacancy, because it is not observable after annealing at 500 K at a measurement temperature of 90 K.

Temperature-dependent positron-lifetime measurements, nevertheless, show the existence of shallow positron traps (see Fig. 10) which mask the signal of vacancy defects. Not all vacancylike defects are annealed after a treatment at 950 K (see also discussion below). Also, electrical measurements showed a broad annealing stage between 470 and 800 K.[35] This was interpreted as a combination of different annealing processes depending on electron energy during the low-temperature irradiation.

In addition, correlated IR-absorption measurements, positron-lifetime measurements, and measurements of the Doppler broadening of the annihilation line were carried out in Cz-Si:B with different boron content after low-temperature irradiation (4 K, 2 MeV, 10^{18} cm^{-2}) and following annealing at 300 K. Figures 8 and 9 show the dependences of the average positron lifetime and the line-shape parameter S on the annealing temperature for these samples determined at room temperature. In addition, Fig. 8 shows the annealing of the negatively charged divacancy observed by the decrease of the absorption band at 0.34 eV.[30]

The first annealing stage up to 500 K was also observed in Cz-Si:B by positrons at a measurement temperature of 90 K (see Fig. 7). This main stage above room temperature was assigned to the annealing of the divacancy, the E center, and other complexes containing vacancies, boron, and/or oxygen. For instance, the annealing of the negatively charged divacancy observed by IR spectroscopy occurs in the same temperature range. At annealing temperatures above 500 K, a positron lifetime near the bulk lifetime was measured at 90 K. In contrast, the investigations at room temperature show an increased average positron lifetime compared to the bulk value and, therefore, they prove a distinct positron trapping in deep traps at this state of the samples. This difference is due to the effectiveness of shallow positron traps (B acceptor and A center) at the low measurement temperature of 90 K (see the discussion in Sec. III B 2), accordingly the positron trapping in vacancylike defects is hidden.

The average positron lifetime measured at 300 K weakly increases in the annealing range between about 500 and 700 K for the two samples with the higher boron content (△ and ◆; see Fig. 8). Above 700 K, $\overline{\tau}$ decreases, and reaches the bulk value at about 950 K. The average positron lifetime is temperature independent in this annealed sample state. The defect component was determined to be 293 ± 3 ps above an annealing temperature of 500 K. This value points to monovacancylike and divacancylike defects, but an exact assignment to a defect type cannot be found from these results. We can assume that defects with an open volume similar to that of a monovacancy or divacancy anneal out in the temperature range between 700 and 950 K. These defects are thermally very stable. From EPR studies it is known that for instance V_3O_2 defects anneal at 870 K.[38]

The annealing of positron-sensitive defects is already completed at about 750 K for the weakly boron-doped sample (○; see Fig. 8). This can be a hint that boron is a part of the thermally more stable defects in higher doped silicon.

Moreover, Doppler broadening experiments were carried out for the annealing of identically treated samples as illus-

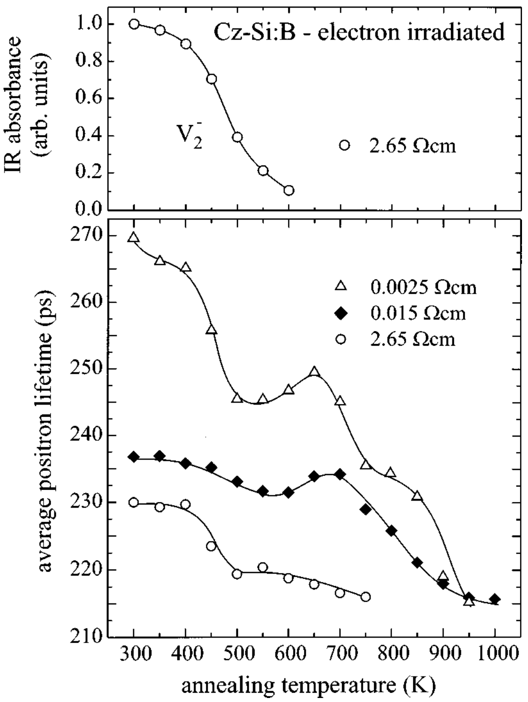

FIG. 8. The dependence of the intensity of the IR absorption band of the negatively charged divacancy (upper part) on the annealing temperature for *p*-type Si:B (2.65 Ω cm) after 2-MeV electron irradiation (10^{18} cm^{-2}) at 4 K. Change of the average positron lifetime with the annealing temperature in electron-irradiated differently doped Cz-Si:B. The measurement temperature was 300 K.

trated in Fig. 9. Here the annealing of divacancies and *E* centers up to 500 K can be seen for the different samples, analogous to the experiments using infrared-absorption and positron-lifetime spectroscopy (see Fig. 8). The increase of the average positron lifetime at higher annealing temperatures shows the formation of other vacancylike defects for the boron-doped samples. In general, the Doppler broadening parameter *S* should also increase for this samples. Contrary to expectation, the *S* parameter decreases below the bulk value for the boron-doped samples (△ and ◆; see Fig. 9). This low *S* parameter was already observed by many authors[39–41] for boron-doped or boron-implanted Cz material, and should be caused by the strong influence of the chemical environment of the open volume on its electron momentum distribution. However, the combination of our positron lifetime and Doppler broadening experiments and of results of other authors implies that defects containing one or two vacancies, oxygen atoms, and boron atoms, $V_xO_yB_z$, are formed between about 500 and 700 K. These defects vanish at about 950 K.

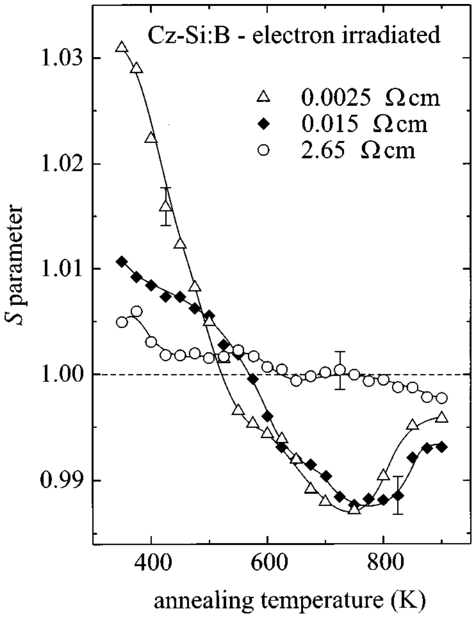

FIG. 9. The line-shape parameter *S* from the doppler experiment as functions of the annealing temperature for electron-irradiated *p*-type Si:B with different boron content. The results were obtained at 300 K.

To sum up, one may say that the annealing behavior of electron-irradiated boron-doped silicon strongly depends on the dopant and oxygen concentration. The dominant positron trapping center in FZ-Si with low boron and oxygen content is the monovacancy, which anneals up to 200 K. Four annealing stages were detected in the range between 90 and 470 K in Cz-Si with high oxygen concentration and comparable low boron content. These stages can be attributed to the annealing of the monovacancy, the *E* center, and other complexes containing vacancies, boron, and oxygen. The *E* center, its disintegration, and the formation of complexes of vacancies and impurities were observed in highly B-doped Cz-Si. In the temperature range above 340 K, the annealing is similar to that of weakly B-doped Cz silicon. At a temperature above 500 K, large defect complexes containing oxygen and boron are formed.

2. Temperature dependence of positron trapping

Highly B-doped Cz-Si with a carrier concentration of 4×10^{19} cm^{-3} remained of *p* type, with the Fermi level within the valence band, after irradiation with a dose of 10^{18} cm^{-2}. Isolated monovacancy and divacancies were thus positively charged in this state,[42,19] and, therefore, they were no positron traps. After irradiation, the defect-related lifetime was typical of monovacancies, 285 ps and we interpret this value as an average of defects involving vacancies, boron, and/or oxygen. The defect-related positron lifetime then increases due to the formation of more complex defects by further annealing (see the discussion in Sec. III B 1). Figure 10 shows the temperature dependence of the average positron lifetime in this electron-irradiated Cz-Si:B after different annealing steps.

The average positron lifetime decreases with decreasing sample temperature, and this behavior indicates the competitive trapping of a neutral vacancy defect and shallow positron traps. Fits according to the trapping model taking into account these two defect types yield parameters summarized in Table IV. The mean binding energy of positrons to shallow traps is about 18 meV, and the mean trapping coefficient at 25 K was determined to be 5.8×10^{15} s^{-1}. These values are both lower compared to those for undoped Cz and FZ material. On the assumption that negatively charged vacancies without open volume act as shallow traps, one can conclude that the boron acceptor is this shallow trap. A further indication to the boron acceptor acting as dominant shallow trap is the unchanged concentration of shallow traps within

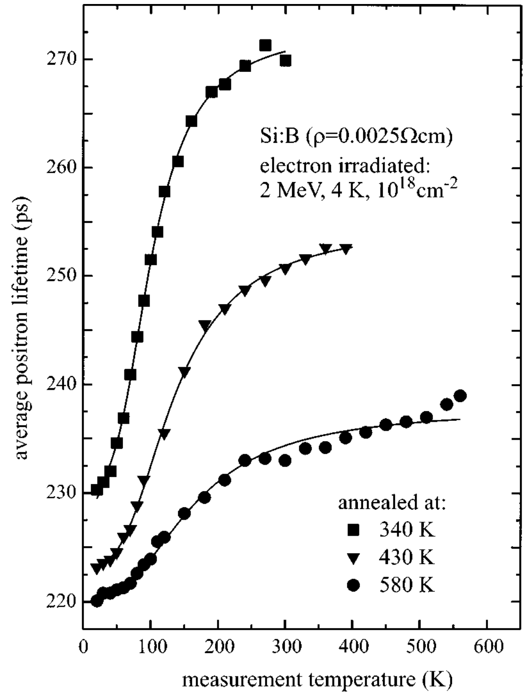

FIG. 10. Average positron lifetime vs sample temperature in electron-irradiated ($E = 2$ MeV, $\Phi = 10^{18}$ cm^{-2}, $T = 4$ K) Cz-Si:B ($\rho = 0.0025\ \Omega$ cm) at different annealing states. Solid lines are fits according to the trapping model taking into account a neutral vacancy defect and shallow positron traps.

the margin of error during the annealing in the temperature range between 340 and 580 K. An annealing of shallow traps was detected in this temperature range for undoped and *n*-type samples. The *A* center anneals out at about 570 K.[29] The positron trapping at the irradiation induced *A* centers is covered by the competitive trapping at the boron acceptors which exist in a high concentration ($p = 4 \times 10^{19}$ cm^{-3}). Therefore, the *A* centers cannot be detected by positrons in these samples.

The trapping rate of the neutral vacancy defect decreases in this annealing range. The corresponding defect concentration varies between 1.4×10^{18} and 1.3×10^{17} cm^{-3} taking into account a trapping coefficient of 7×10^{14} s^{-1}.[34] After treatment at 900 K, the annealing of the vacancy defects was completed. In the whole range between 340 and 900 K, different annealing stages (see Fig. 7) were observed, supporting our assumption that the defect-related lifetime is an average of different vacancy defects. The trapping rate of vacancylike defects was also determined at a measurement temperature of 300 K from the average positron lifetime. The one-defect trapping model[13] was used and, therefore, the influence of shallow traps was neglected at this temperature. A comparison between the fitted trapping rate κ_V and trapping rate $\kappa_{V_{\mathrm{cal}}}$ calculated from the experimental values of average and defect-related positron lifetimes is shown in Table IV. There is a good agreement and the small difference is due to the shallow traps still acting at room temperature. This can be concluded because no saturation of positron trapping was reached at a sample temperature of 300 K (see Fig. 10).

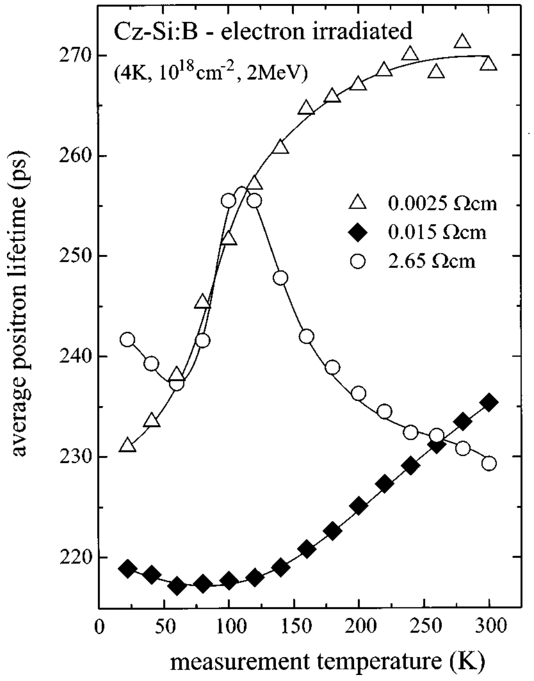

FIG. 11. Temperature dependence of the average positron lifetime in electron-irradiated (4 K, 10^{18} cm^{-2}, 2 MeV), differently doped Cz-Si:B after annealing at room temperature.

Figure 11 shows the temperature dependence of the average positron lifetime in electron-irradiated (4 K, 10^{18} cm^{-2}, 2 MeV), differently doped Cz-Si:B after annealing at room temperature. It is clear that the boron content decisively influences the dominant defect structure in the sample and, therefore, also the temperature-dependent behavior of the average positron lifetime. For the highly doped sample (△), the temperature behavior of $\overline{\tau}$ is determined by the positron trapping in shallow traps which were attributed to the boron acceptor, and in several neutral defects containing vacancies, boron, and/or oxygen (see the discussion above).

The weakly doped sample ($p \approx 5 \times 10^{15}$ cm^{-3}, ○) shows the typical behavior which was found for competitive positron trapping in shallow traps (boron acceptor and irradiation-induced *A* centers) and in negatively charged vacancy defects. After irradiation with an electron dose of 10^{18} cm^{-2}, this sample is compensated for, and the diva-

TABLE IV. Annealing temperature T_a and fitted values for positron binding energy at shallow traps E_{st}, concentration C_{st}, and trapping coefficient μ_{st} of shallow traps, and trapping rate of vacancy defects κ_V in electron-irradiated Cz-Si-B ($\rho = 0.0025\ \Omega$ cm).

T_a (K)	E_{st} (meV)	C_{st} (10^{18} cm^{-3})	μ_{st} (10^{15} s^{-1})	κ_V (10^{10} s^{-1})	$\kappa_{V\,\mathrm{cal}}$ (300 K) (10^{10} s^{-1})
340	18.0±1.6	4.2±1.0	6.3±1.1	2.0 ±0.1	1.5
430	17.2±1.8	4.9±0.9	5.2±0.7	0.54±0.02	0.41
580	17.7±5.3	5.8±2.5	5.9±2.2	0.18±0.01	0.14

cancy is negatively charged. The defect-related positron lifetime was determined to be 308±5 ps, and this value is in a good agreement with experimental and theoretical lifetimes for the divacancy.[37,18] The concentration of the dominant divacancy at 300 K can be estimated from the trapping rate $\kappa = 6.3\times10^{8}\ \mathrm{s}^{-1}$ and the trapping coefficient $\mu = 1.9\times10^{15}\ \mathrm{s}^{-1}$ according to Eq. (1) to be $C_V = 1.7\times10^{16}\ \mathrm{cm}^{-3}$. The positron annihilation in shallow traps can be neglected at this measurement temperature.

The course of the temperature dependence of $\overline{\tau}$ for the moderately doped Si:B sample ($p\approx1.5\times10^{18}\ \mathrm{cm}^{-3}$, ◆) shows a saturation behavior at the bulk value τ_b at low temperature and an increase in the average lifetime for sample temperatures above 150 K (see Fig. 11). The defect-related positron lifetime was determined to be 299±3 ps, and this value is equal to that of the neutral divacancy.[37] The sample was partly compensated for by the electron irradiation, so that the Fermi level was shifted toward the midgap and was located above the ionization level (+/0) of the divacancy. The shallow positron traps act in this sample up to 300 K and, therefore, the divacancy concentration cannot be accurately determined. The effect of shallow traps of a very high concentration up to 550 K was also detected in electron-irradiated GaAs.[14] We still see from the temperature dependence that the dominant vacancy defect is neutral and the defect-related positron lifetime points to a divacancylike defect.

For the latter three boron-doped Cz samples, the courses of the temperature dependence of average positron lifetime (see Fig. 11) remain unchanged during the annealing on principle. $\overline{\tau}$ decreases by the annealing and, after an annealing at 750 (○) or 950 K (△ and ◆), respectively, it is temperature independent and equal to τ_b.

C. *n*-type silicon

Silicon *n*-type samples differently doped with P, As, and Sb were available for positron-lifetime measurements. In addition to the annealing experiments, temperature-dependent investigations were performed in phosphorus-doped silicon.

1. Si:P

Figure 12 shows the annealing behavior of *n*-type silicon with different phosphorus concentration. The behavior of the very weakly doped sample ($\rho = 5000\ \Omega$ cm, ■) was already discussed in Sec. III A 1. The P concentration is too low to influence the positron-lifetime results.

The highly doped Cz-Si sample with $\rho = 0.001\ \Omega$ cm (△) was strongly *n* conductive prior to irradiation. The Fermi level was located in the conduction band. The semiconductor remained *n* type after electron irradiation with a fluence of $10^{18}\ \mathrm{cm}^{-2}$, i.e., the Fermi level was not shifted significantly.

The average positron lifetime was measured to be 259 ps at 90 K after irradiation. A defect component could only be separated after annealing at 260 K. The defect-related lifetime was constant 255±5 ps up to a treatment at 500 K. This value corresponds to the defect-related positron lifetime of the *E* center (VP^-).[8] We conclude that the *E* center is the dominant defect detectable by positrons in electron-irradiated silicon with a very high P concentration. The average positron lifetime is higher compared to the defect-related lifetime when annealing starts. Therefore, other defects with higher defect-related positron lifetimes, such as isolated monovacancy, divacancy, and/or vacancylike complexes containing oxygen, exist besides the *E* center. The temperature-dependent positron-lifetime measurements show also the presence of shallow positron traps (see the discussion below).

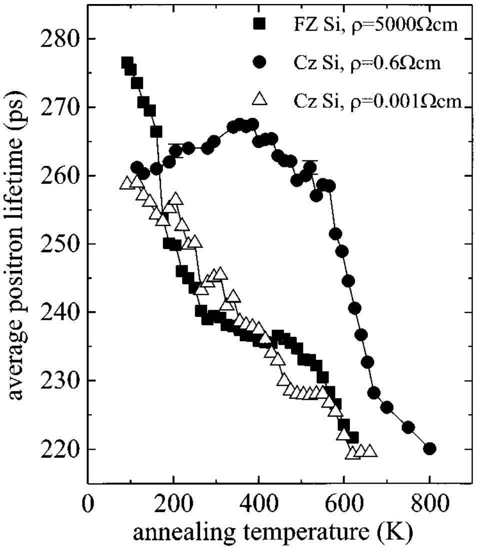

FIG. 12. Average positron lifetime as function of annealing temperature for electron-irradiated *n*-Si:P with different doping concentrations. The irradiations were performed with 2-MeV electrons at 4 K to a dose of $10^{18}\ \mathrm{cm}^{-2}$. The positron lifetime was determined at 90 K.

The average positron lifetime continuously decreases in the annealing range between 90 and 470 K. Individual annealing stages cannot be separated in this range. We conclude that the annealing of the *VP* complex takes place in this temperature range. This is in a good agreement with EPR and IR results, which prove an annealing temperature of 400 K for the *E* center.[43,44]

The average positron lifetime is then constant in the temperature range from 470 to 570 K. This plateau is followed by an annealing stage that goes up to 620 K. This annealing stage corresponds to that found in undoped material, and is attributed to the divacancy. The defect-related lifetime could not be determined in this range for Si:P due to the very low intensity of the component. The positron lifetime of the bulk was measured after 620-K treatment. The annealing of vacancylike defects was then completed.

The sample with the low doping level ($\approx10^{16}\ \mathrm{cm}^{-3}$, $\rho = 0.6\ \Omega$ cm, ●) was of *n*-type conductivity prior to irradiation. The Fermi level was located at $E_v + 0.67$ eV, and was shifted in a midgap position ($E_v + 0.56$ eV) by electron irradiation (2 MeV, 4 K, $10^{18}\ \mathrm{cm}^{-2}$). In this case, monovacancies and divacancies are negatively charged and, therefore, they can act as deep positron traps just like in weakly doped Si:P (■). The average positron lifetime was determined to be ≈260 ps after irradiation and annealing up to 90 K. This value corresponds with that measured for highly doped Cz silicon (△). However, the annealing behavior and so the dominant vacancylike defects distinctly differ.

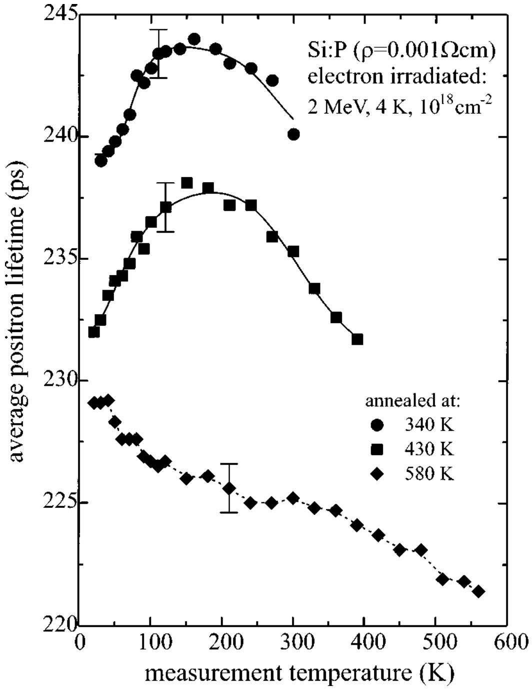

FIG. 13. Average positron lifetime as a function of the measurement temperature in electron-irradiated ($E=2\,\mathrm{MeV}$, $\Phi=10^{18}\,\mathrm{cm}^{-2}$, $T=4\,\mathrm{K}$) Cz-Si:P ($\rho=0.001\,\Omega\,\mathrm{cm}$) after different annealing steps. The solid lines correspond to fits according to the trapping model taking into account a negative vacancy defect and a shallow positron trap.

Here the average positron lifetime is nearly constant up to an annealing temperature of 580 K. The defect-related positron lifetime is typical of a monovacancylike defect, and it amounts to 280 ps. The isolated monovacancy and the *E* center are no candidates for this defect due to its high thermal stability. The dominant defects must be complexes of oxygen and vacancies. The annealing temperatures of V_2O, V_3O, and V_2O_2 were determined to be in the range between 620 und 670 K by EPR measurements.[38] The main annealing appears between annealing temperatures of 550 and 700 K in our sample. An exact and free separation of the defect components is not possible. Kawasuso *et al.* found annealing temperatures of V_2O and V_3O at 650 K by fixing the defect-related lifetimes.[9] But we have to take into account that results obtained by fixing components cannot be safely interpreted. The annealing of vacancylike defects of the low-doped Cz-Si:P (●) was completed after a temperature treatment at 800 K.

To summarize the annealing experiments for phosphorus-doped silicon, it may be said that the impurity (oxygen) and the dopant atoms distinctly influence the formation and annealing behavior of electron-irradiated Si:P. The annealing of monovacancies and divacancies was observed at 170 and 550 K in very weakly doped Si:P. The *E* center is the dominant defect in very highly doped Si:P (degenerated), and this *V*P complex disappears at about 400 K. Oxygen atoms thermally stabilize the vacancies up to 800 K in weakly P-doped Cz silicon.

Figure 13 shows the temperature-dependent positron lifetime in the electron-irradiated Cz-Si:P ($\rho=0.001\,\Omega$ cm) with a carrier concentration of $8\times10^{19}\,\mathrm{cm}^{-3}$ after different annealing steps. This sample is degenerated and also of *n*-type conductivity, with the Fermi level located in the conduction band after electron irradiation (4 K, $10^{18}\,\mathrm{cm}^{-2}$). The dominant deep positron trapping center is the *E* center with a defect-related lifetime of 255 ps (see the discussion above). This is in a good agreement with results from other authors.[7,4] The *V*-P complex introduces a single acceptor level at $E_c-0.43\,\mathrm{eV}$,[45] and in highly *n*-type material it is therefore negatively charged.

The behavior observed after annealing at 340 and 430 K shows the presence of shallow and deep (*E* center) positron traps. The decrease in average positron lifetime with increasing measurement temperature above 150 K is typical of a negative vacancylike defect, the *V*P defect. Below 150 K, the positron lifetime decreases with decreasing temperature due to the reduced detrapping from shallow traps. The solid lines in Fig. 13 correspond to the trapping model taking into account a negative vacancy defect and shallow traps. The fitting parameters have large errors, but it is distinct that the binding energy of the Rydberg state of the vacancylike defect E_R ($\approx$200 meV) is larger compared to the undoped Cz-Si. This can be explained by the different dominant deep positron trapping centers in highly *n*-doped Cz-Si (*E* center) and in undoped Cz material (divacancy).

The positron binding energy of the shallow trap E_{st} ($\approx$20 meV) is lower than in undoped Cz-Si, and this points to the influence of the position of the Fermi level and/or of the P dopant on the shallow trap. After electron irradiation, the Fermi level is located in midgap position for undoped Cz-Si, and into the conduction band in degenerated P-doped silicon. In the latter sample, the *A* center is negatively charged, and another binding energy of the shallow trap can be expected.

After annealing at 580 K, the average positron lifetime increases with decreasing measurement temperature in the whole range, the influence of shallow traps is disappeared. This is an indication that the *A* center acts as shallow trap, because this defect anneals above a temperature of 570 K.[29] The concentration of *V*P defects is about $3.6\times10^{16}\,\mathrm{cm}^{-3}$, determined at a measurement temperature of 300 K by the one-defect trapping model [Eq. (1)].[13] The trapping coefficient for negatively charged vacancies at room temperature of $1\times10^{15}\,\mathrm{s}^{-1}$ was used.[34] The annealing of the vacancy defect is completed after a treatment at about 650 K (compare the discussion of Fig. 12).

2. Si:As

Figure 14 shows the dependence of the average positron lifetime on the annealing temperature for electron-irradiated *n*-Si:As with different doping concentrations. Cz samples with specific resistivities of 1.2 and 0.0016 Ω cm were studied in the temperature range from 90 to 1100 K.

The weakly doped sample ($\rho=1.2\,\Omega$ cm, □) was of *n*-type conductivity ($n=3\times10^{15}\,\mathrm{cm}^{-3}$), and the Fermi level was located 0.91 eV above the valence band before irradiation. The Fermi level was then shifted in the direction of midgap by electron irradiation, and was pinned at $E_v+0.78\,\mathrm{eV}$ at room temperature. The monovacancies and divacancies are negatively charged, and can trap positrons in this case.

The average positron lifetime of 275 ps was measured at 90 K after electron irradiation. The defect-related positron

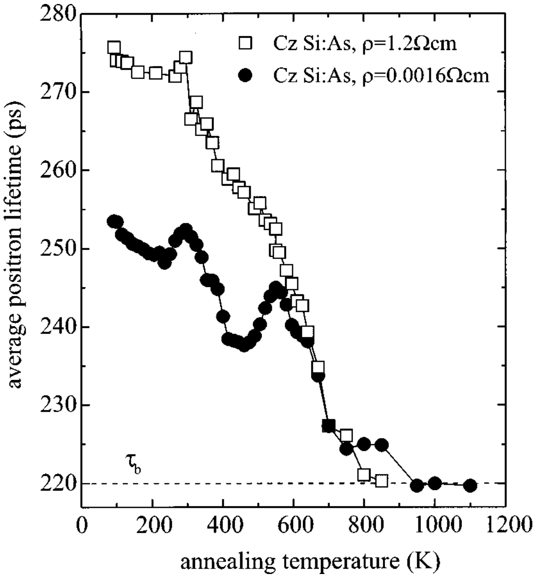

FIG. 14. Change of the average positron lifetime with the annealing temperature for differently arsenic-doped silicon after 2-MeV electron irradiation (10^{18} cm^{-2}) at 4 K. The measurement temperature was 90 K. The bulk lifetime τ_b is indicated by the dashed line.

lifetime was determined to be 290 ps. This component can be considered as an average value of different vacancylike defects existing in this sample state. Since the positron lifetime of the monovacancy is between 270 and 280 ps, we conclude that divacancies or complexes containing divacancies also exist at 90 K. Furthermore, one can assume that *E* centers (*V*As) are also induced in arsenic-doped silicon by the low-temperature irradiation.[35]

The average positron lifetime is nearly unchanged up to an annealing temperature of 300 K. This behavior was also proved in arsenic-doped silicon by electrical measurements.[35] The monovacancies becoming mobile below 170 K cannot play an important part in this material, but can cause the weak decrease of $\overline{\tau}$ between 90 and 200 K. Then, a wide annealing stage was observed in the temperature range between 300 and 800 K. The defect-related lifetime decreases in this range and reaches a value of 260 ps at 700 K. The vacancylike positron traps cannot be attributed to microscopic structures without further assumptions. A continuous annealing of irradiation-induced defects between 400 and 800 K was also observed by electrical measurements.[35] The annealing of the *E* center in Si:As was shown at about 450 K by EPR studies. Divacancies and V_xO_y complexes anneal out above 450 K. The observed annealing stage proves the annealing of all detectable vacancy defects.

The highly doped Si:As sample ($\rho = 0.0016\ \Omega$ cm, ●) was degenerated, and the Fermi level was also located in the conduction band after electron irradiation. The monovacancy and divacancy are double negatively charged, and can act as positron traps in this sample state.[5] The average positron lifetime was measured to be 253 ps at 90 K after electron irradiation. This value is distinctly lower than the average positron lifetime determined in weakly doped Si:As. A two-component fit was not satisfactory due to the nearly complete positron trapping at defects. A defect with a specific positron lifetime of 248 ps dominates the trapping behavior. This defect can be assigned to the *E* center. This conclusion is supported by the high doping concentration of the investigated sample ($n = 3.5\times10^{19}$ cm^{-3}), by the fact that *E* centers are formed by low-temperature irradiation,[35] and by the defect-related lifetime being typical of a complex consisting of a vacancy and a doping atom of the fifth group.[8]

No distinct annealing was observed up to 300 K. The weak decrease of $\overline{\tau}$ in this range can also be attributed to the monovacancy becoming mobile at about 170 K. The average positron lifetime distinctly decreases above room temperature, and then it increases again between the annealing temperatures 450 and 550 K. This increase can be attributed to the dissociation of the *E* center. The released vacancies react to thermally more stable defects with a larger open volume. The defect-related positron lifetime also increases to a value of $\tau_2 > 290$ ps above an annealing temperature of 570 K. This value is again an average of lifetimes of several vacancy defects. The further annealing of divacancies and V_xO_y complexes proceeds up to 950 K. The annealing behavior above 570 K is similar to that of the weakly arsenic-doped sample.

The annealing studies of electron-irradiated Si:As show, in accordance with electrical investigations, that no defects anneal in the temperature range between 90 and 300 K. The *E* center (*V*As) with a defect-related positron lifetime of 248 ps is the dominant defect up to an annealing temperature of 450 K in highly doped material. Divacancies and complexes with vacancies and oxygen are formed after dissociation of the *V*As complexes, and then they anneal up to 900 K. A wide annealing stage between room temperature and 800 K was observed in weakly doped Si:As, but no assignment to vacancy defects is possible.

Temperature-dependent positron-lifetime measurements also detect, for arsenic-doped silicon the existence of shallow positron traps (no figure). Analogous to the results on highly doped Si:P (see Fig. 13), the average positron lifetime decreases with decreasing sample temperature below 200 K and, after annealing at 580 K, the influence of shallow traps cannot be observed in highly arsenic-doped Si. The negatively charged *A* center can be assigned to this defect type in this degenerated *n*-type Si:As sample. The temperature behavior of $\overline{\tau}$ for the weakly doped sample is similar to that for undoped Cz silicon (see Fig. 3). In this case the neutral *A* center can act as shallow trap.

3. *Si:Sb*

The annealing behavior of two differently Sb-doped Cz-Si samples ($\rho = 0.025$ and 0.0089 Ω cm) which were irradiated with 2-MeV electrons and with a fluence of 10^{18} cm^{-2} at 4 K was also investigated. Both samples were strongly *n* conductive, and the Fermi level was located within the conduction band before and after electron irradiation. Monovacancies and divacancies should be detectable in these samples. The annealing behavior is similar for both samples, and the following discussion applies to all.

The average positron lifetime was determined to be 267.5 ± 1 ps at 90 K after irradiation. The temperature-dependent measurements show that the positron annihilation in shallow traps only occurs below a sample temperature of 80 K (no figure). The trapping at shallow positron traps is therefore negligible at a measurement temperature of 90 K,

TABLE V. Defect-related positron lifetimes and annealing ranges of the different *E* centers in electron-irradiated silicon.

	VB	VP	VAs	VSb
defect-related lifetime (ps)	285	255	248	252
annealing range (K)	200, . . . ,250	300, . . . ,470	450, . . . ,550	400, . . . ,500

and the concentration of vacancy defects can be calculated by Eq. (1). The defect-related positron lifetime was determined to be 280 ps, and this value is the average of irradiation-induced vacancylike defects (also see the discussion above). The determined defect concentration is then $C_V = 4.8\times10^{16}\ \mathrm{cm}^{-3}$ by using the trapping coefficient of negatively charged VP centers, $\mu = 1.8\times10^{16}\ \mathrm{s}^{-1}$.[24] This result corresponds to an introduction rate of 0.05 cm^{-1} determined at 90 K for vacancy defects in low-temperature electron-irradiated Si:Sb.

A continuous decrease in the average positron lifetime, and thus in the vacancy concentration, was observed in the annealing range between 90 and 240 K. The defect-related positron lifetime is constant up to 190 K (280 ps), and decreases then to 267 ± 5 ps. The monovacancy anneals in this range and after that the dominant defect-type changes to a defect with a lower open volume compared to a monovacancy.

The average positron lifetime is constant in the temperature range from 240 to 400 K. The next annealing stage follows above 400 K. Both, the average and the defect-related positron lifetime decrease, and τ_2 reaches a value of 252 ps. This stage can be attributed to the annealing of *V*Sb complexes. The defect component of 252 ps is similar to that decomposed for the *E* center in Si:P, and the annealing temperature corresponds to that determined to be 470 K by EPR experiments in Si:Sb.[46] An annealing temperature of 500 K measured by positron lifetime spectroscopy is also known in literature.[9] In this case, the defect-related lifetime of 240 ps was fixed as an average of *V*O, $V\mathrm{O}_2$, and *V*Sb.

The bulk value of the positron lifetime is reached at an annealing temperature of about 650 K, and $\overline{\tau}$ is then temperature independent (not shown). The sample with the higher Sb concentration ($\rho = 0.0089\ \Omega$ cm) shows an additional annealing stage above 600 K. The defect-related positron lifetime cannot be separated due to the too low intensity of the defect component. It is known from EPR measurements that $V_x\mathrm{O}_y$ complexes anneal above 600 K.[38] These defects definitely exist in electron-irradiated undoped Cz silicon.

IV. CONCLUSIONS

The introduction rate of vacancy defects after 4-K irradiation was determined at 90 K to be $0.10\pm0.05\ \mathrm{cm}^{-1}$. This value is independent of dopant in silicon.

The annealing behavior of electron-irradiated silicon (2 MeV, $10^{18}\ \mathrm{cm}^{-2}$, 4 K) observed by positron lifetime spectroscopy is distinctly dependent on the doping and oxygen concentrations of the sample. The annealing of the isolated monovacancy and divacancy was observed in pure FZ-Si at 170, and between 450 and 650 K, respectively. The stabilization of vacancy defects by oxygen was proved in undoped Cz silicon.

Irradiation-induced vacancylike defects in boron doped FZ material completely anneal below room temperature due to the disappearance of the dominant *E* center (*V*B) at 260 K. In oxygen-rich Cz-Si:B, the vacancies and also the *E* center are stabilized by oxygen and boron atoms, and the annealing of these defects is finished up to 950 K depending on the boron concentration.

Vacancylike defects in highly doped Cz-Si:P and *V*P complexes, in addition to monovacancies and divacancies, anneal out up to 600 K. In Cz-Si with a low phosphorus content, vacancylike defects are thermally stabilized up to 800 K because the dominant defects are combined with oxygen. The *E* center in Si:Sb anneals out at about 400 K, and in Si:As above 450 K. The annealing of irradiation-induced vacancy defects containing oxygen occurs up to about 800 K in these samples. Table V summarizes the defect-related positron lifetimes and the annealing ranges for the different *E* centers in electron-irradiated doped silicon.

The temperature-dependent behavior of the average positron lifetime is typical of the competitive positron trapping in shallow and deep positron traps for all electron-irradiated silicon samples. In highly *p*-type Si:B, the dominant shallow positron trap can be attributed to the boron acceptor. It was shown that the boron acceptor in silicon acts as a shallow positron trap. The concentration of shallow traps depends on the oxygen concentration in undoped and *n*-type material. The negatively charged *A* center can be assigned to the shallow positron trap in highly *n*-doped silicon. On the assumption that the neutral *A* center can act as shallow trap due to its small open volume, we attribute the temperature dependence of the average positron lifetime in undoped and weakly *n*-doped Si to this defect in addition to vacancy defects. However, it cannot be excluded that the *A* center is modified by impurities for example.

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