Annealing processes of vacancy-type defects in electron-irradiated and as-grown 6*H*-SiC studied by positron lifetime spectroscopy

Atsuo Kawasuso,[a] Hisayoshi Itoh, and Sohei Okada
Japan Atomic Energy Research Institute, 1233 Watanuki, Takasaki 370-12, Japan

Hajime Okumura
Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba, Ibaraki 305, Japan

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Annealing processes of vacancy-type defects in 3 MeV electron-irradiated and as-grown 6*H*-SiC have been studied by positron lifetime spectroscopy. Vacancy-type defects giving rise to a positron lifetime of 183 ps were detected in as-grown *n*-type specimens. They were found to be annealed at around 1400 °C and were related to silicon vacancies, possibly complexes of silicon vacancies and nitrogen atoms. Defects related to carbon vacancies, silicon vacancies, and divacancies were found to be created by electron irradiation. The defects related to carbon vacancies and divacancies were found to be annealed up to 500 °C. The defects related to silicon vacancies were found to be annealed at around 750 and 1400 °C. The former annealing stage was inferred to be due to migration of silicon vacancies to internal sinks or nitrogen atoms to form complexes of silicon vacancies and nitrogen atoms. The latter annealing stage was explained as due to annihilations of the complexes as well as the case of as-grown specimens. © *1996 American Institute of Physics.*
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I. INTRODUCTION

Silicon carbide (SiC) has higher device performances than those of silicon (Si); wider band-gap width, higher saturated electron drift velocity, higher break down voltage.[1] This material also has a higher radiation resistance than Si owing to the higher atomic displacement energy. Thus, SiC is a promising material for power devices used in extreme conditions such as high temperature and radiation environments. Recently, large size of crystals, especially 6*H* and 4*H* polytype, are commercially supplied accompanying with the development of crystal-growth technique. However, various kinds of defects are frequently found even in as-grown state. To improve the quality of SiC crystals as device materials, harmful defects should be reduced. Clarification of the properties of intrinsic defects seems to be a primary importance since they are likely to be formed in crystal-growth processes due to a deviation from chemical stoichiometry. Properties of intrinsic defects in SiC have so far been studied with various methods, such as electron spin resonance (ESR), photoluminescence (PL), deep-level transient spectroscopy (DLTS), mainly combined with fast particle irradiation. Many works have suggested that silicon and carbon monovacancies and also the Frenkel pairs are stable at room temperature as mentioned below. This is quite different from the case of Si and intriguing from the view point of defect physics.

The results in the previous works on 6*H*-SiC were summarized as follows: Zhang *et al.*[23] found that acceptor-like levels at $E_C-0.62$ eV and $E_C-0.64$ eV, termed Z1/Z2, which remained even after the annealing at 1700 °C existed in as-grown Lely crystals. (Here, E_C denotes the energy of the bottom of the conduction band.) The concentrations of those levels were found to increase due to electron or ion irradiation. In addition to Z1/Z2 levels, three kinds of deep levels at $E_C-0.35$ eV, $E_C-0.57$ eV (or $E_C-0.60$ eV) and $E_C-1.10$ eV were found to be generated due to electron irradiation at room temperature.[2–4] Zhang *et al.* reported that each of former two levels was composed of close two levels which were termed E1/E2 and E3/E4, respectively. Ballandovich and Violina showed that above three levels annihilated due to the annealing up to 1100 °C.[4] Early PL studies[5–9] showed that a series of luminescence lines designated D_1 were observed in 3*C*, 4*H*, and 6*H*-SiC crystals due to the annealing at 1000–1300 °C following electron or ion irradiation. The D_1 luminescence was reported to persist even after the annealing at 1700 °C. Partick and Choyke[6] proposed that the D_1 luminescence was related to pure defect complexes, such as divacancies, since its intensity increased irrespective of irradiated ion species. To identify defect species introduced by irradiation, several ESR studies have been performed. Balona and Loubser[10] showed that six kinds of ESR active centers were generated due to 0.8 MeV electron irradiation at room temperature. They proposed that three of them were related to positively charged, neutral, and negatively charged carbon vacancies, the two of them were related to positively and negatively charged carbon divacancies and one of them was not identified. They also reported that the annealing temperatures of those centers depended on their charge states. Their defect identifications were based on an assumption that silicon vacancies were mobile at room temperature. It is, however, quite contrary to the case of 3*C*-SiC in which both silicon and carbon vacancies are stable at room temperature.[11,12] Vainer and II'in[13] found that ESR centers designated P12 were generated due to neutron irradiation in nitrogen doped 6*H*-SiC. They attributed the P12 center to complexes of silicon vacancies and nitrogen atoms. It was suggested that the centers could be correlated with the D_1 luminescence since the centers showed a similar thermal stability to that of the D_1 luminescence.[13] However,

[a]Electronic mail: ak@takamads.taka-jaeri.go.jp

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it is contrary to the proposal by Partick and Choyke as mentioned above. The photo-ESR study of quenched-in defects in $6H$-SiC by Vainer and Il'in[14] suggests that divacancies are introduced due to the quenching from 1900 to 2450 °C. Pensl and Choyke[15] proposed that the Z1/Z2 acceptor level is originating from the divacancies since the level and the divacancies have a series of correlations in their generation and properties. Thus, a number of extensive works have been performed to clarify the properties of radiation-induced defects in $6H$-SiC. Those works indicate that vacancy-type defects have important roles in irradiated and also in as-grown SiC.

Positron annihilation spectroscopy is a powerful tool to detect vacancy-type defects in crystalline solids.[16] Recently, this method has also been applied to the defect studies in SiC.[17] Puff *et al.*[18] reported that a lifetime component related to vacancy-type defects was found in $6H$- and $4H$-SiC grown by chemical vapor deposition. Girka *et al.*[19] and Rempel *et al.*[20,21] investigated the annealing behavior of average positron lifetime for electron-irradiated $6H$-SiC. Their work revealed three annealing stages at 150–500, 1400–1500, and 1700–2900 °C and one "negative" annealing stage at 1000–1100 °C. Girka *et al.* tentatively assigned the former stages to the annihilations of the Frenkel pairs and complexes of silicon vacancy and nitrogen atoms. The negative annealing stage was explained in terms of clustering of vacancies. Although their results indicate important information about annealing behaviors of vacancies, the identification of defects seems not to be complete since decomposition of lifetime spectra were not carried out.

In this work, to identify vacancy-type defects in electron-irradiated and as-grown $6H$-SiC in detail, we carried out positron lifetime measurements, which enabled to distinguish vacancy-related components, combined with isochronal annealing. We also performed PL measurements to reveal the correlation between the D_1 luminescence center and vacancy-type defects.

II. EXPERIMENT

Specimens used in this work were cut from modified Lely-grown n-type (nitrogen-doped) and p-type (aluminum-doped) $6H$-SiC wafers oriented to c axis with a thickness of 300 μm. All the wafers were commercially supplied by Cree Research Inc. The carrier densities at room temperature of each conduction type of specimen were 5.5×10^{17} and 1.8×10^{18} cm^{-3}, respectively. The specimens were irradiated with 3 MeV electrons at a fluence of 1×10^{17} e$^-$/cm^{-2} at around 60 °C using a dynamitron accelerator in Japan Atomic Energy Research Institute. Isochronal annealing was performed in the temperature range between 75 and 1500 °C for 5 min in a dry argon ambience.

About 6×10^5 Bq of ^{22}NaCl was deposited onto a titanium thin film with a thickness of 2 μm as a positron source. It was sandwiched by two specimens and positron lifetime measurement was carried out using a conventional fast-fast spectrometer with a time resolution of about 200 ps (FWHM) at room temperature. About 5×10^6 counts were accumulated in each spectrum. The source components were determined to be 140 and 520 ps with intensities of 14±4% and 0.5±0.3%, respectively, from a measurement of an unirradiated floating-zone grown Si crystal. Those components seem to come from the positron annihilation in the titanium film and in sodium, respectively. To check the validity of the source components we analyzed various semiconductors and metals using the source components and obtained the bulk lifetimes which agreed with those reported in the previous works.[16] After subtracting the source and background components, a lifetime spectrum $L(t)$ was decomposed into two lifetime components using a computer program named PATFIT-88:[22]

$$L(t)=(I_1/\tau_1)\exp(-t/\tau_1)+(I_2/\tau_2)\exp(-t/\tau_2). \quad (1)$$

Here, τ_i are the lifetimes and I_i are the intensities ($I_1+I_2=1$). Average positron lifetime is defined as

$$\langle\tau\rangle=I_1\tau_1+I_2\tau_2. \quad (2)$$

This quantity is sensitive to the change in positron lifetime. In the frame work of the two-state trapping model[16] in which positrons are assumed to annihilate through the bulk state or the trapped state at vacancy-type defects, the lifetimes τ_1 and τ_2 have following physical meanings:

$$\tau_1=\frac{1}{\tau_B^{-1}+\kappa}, \quad (3)$$

$$\tau_2=\tau_V. \quad (4)$$

Here, τ_B is the positron lifetime at the bulk which is determined to be 136±2 ps from a measurement of an unirradiated p-type specimen, τ_V the positron lifetime at vacancy-type defects, and κ the net positron trapping rate due to the defects:

$$\kappa=\frac{I_2}{I_1}(\tau_B^{-1}-\tau_2^{-1}). \quad (5)$$

The trapping rate is usually proportional to the concentration of defects (C_V) and specific trapping rate (μ):

$$\kappa=\mu C_V. \quad (6)$$

The validity of the analysis based on the two-state trapping model can be checked by the difference between τ_1 determined by Eq. (1) and that calculated by Eq. (3).

PL measurements were performed at 4.2 K using He-Cd laser with lines at 325 nm. The spot size of the excitation laser light was about 100 μm.

III. RESULTS AND DISCUSSION

Figure 1 shows the positron lifetime spectra for as-grown p-type and n-type, and irradiated n-type specimens. The lifetime of the as-grown n-type specimen is found to be slightly longer than that of the as-grown p-type specimen. The lifetime of the n-type specimen increases after the electron irradiation. The lifetime spectrum for the irradiated p-type specimen was similar to that for the as-grown p-type specimen. Table I summarizes the results of the two-component analysis using Eq. (1). For the unirradiated p-type specimen, the two-component analysis was not available, and hence only one lifetime component was obtained. It allows us to conclude that the lifetime component is related

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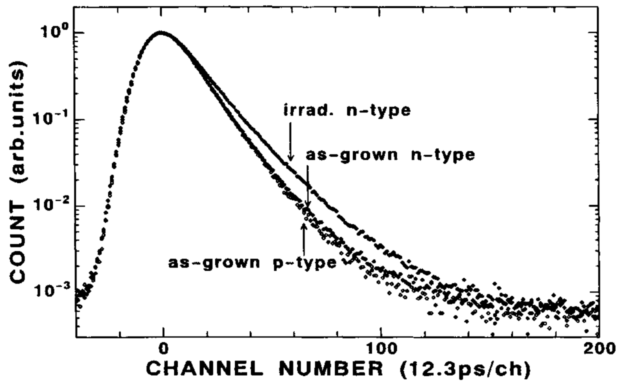

FIG. 1. Positron lifetime spectra for the as-grown p-type and n-type specimens, and the n-type specimen irradiated with 3 MeV electrons at a fluence of 1×10^{17} e^-/cm^2.

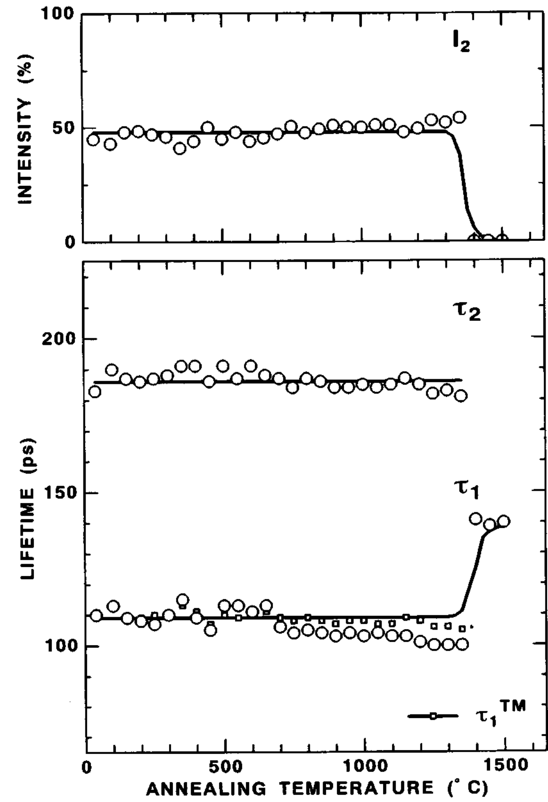

FIG. 2. Positron lifetimes τ_1 and τ_2, and intensity I_2 for as-grown n-type specimen as a function of annealing temperature. τ_1^{TM} denotes the lifetime calculated by Eq. (3).

to the positron annihilation at bulk. The lifetime of the p-type specimen does not increase significantly after the electron irradiation unlike to the case of the n-type specimen. The average lifetime of the as-grown n-type specimen is about 7 ps longer than that of the as-grown p-type specimen. For this specimen, the second lifetime component of 183 ps with an intensity of 45% is obtained. After the electron irradiation, the average lifetime of the n-type specimen is found to increase by about 35 ps. The lifetime and the intensity of the second component also increase to 210 ps and 65%, respectively, due to the irradiation. Thus, the positron lifetime depends on the conduction type of specimen. This will be discussed later. Now, we show the annealing behavior of the positron lifetime for the n-type specimens.

Figure 2 shows the annealing behaviors of the lifetimes τ_1 and τ_2 and intensity I_2 for the as-grown n-type specimen. Here, τ_1^{TM} denotes the lifetime τ_1 calculated from Eq. (3). The lifetime τ_1 agrees well with the lifetime τ_1^{TM} assuring the validity of the analysis based on the two-state trapping model. Thus, the lifetimes τ_1 and τ_2 are related to the positron annihilations at the bulk and vacancy-type defects, respectively. The lifetime τ_2 seems to be nearly independent of annealing temperature. The intensity I_2 is found to decrease to the detection limit at around 1400 °C. Figure 3 shows the annealing behavior of the trapping rate calculated using Eq. (1). The trapping rate is also found to decrease to the detection limit at around 1400 °C. (This is a consequence of $I_2\rightarrow0$.) Above results show that only one kind of vacancy-type defects acting as positron trapping centers is present in the as-grown n-type specimen and the defects disappear at around 1400 °C.

Theoretical positron lifetimes at a carbon vacancy, a silicon vacancy, and a divacancy in 6H-SiC were calculated to be 150, 183, and 214 ps, respectively, by Brouer *et al.*[23] The lifetime τ_2 observed for the as-grown n-type specimen coincides with the theoretical lifetime at a silicon vacancy. This suggests that defects related to silicon vacancies are present in this type of specimen. The ESR study by Itoh *et al.*[11,12] showed that pure silicon vacancies in 3C-SiC became mo-

TABLE I. The lifetime and intensity obtained from the two-component analysis and average lifetime calculated by Eq. (2) for as-grown and as-irradiated specimens.

Specimen	τ_1 (ps)	τ_2 (ps)	I_2 (%)	$\langle\tau\rangle$ (ps)
As-grown p type	136	⋯	⋯	136
Irradiated p type	138	⋯	⋯	138
As-grown n type	110	183	45	143
Irradiated n type	118	210	65	178

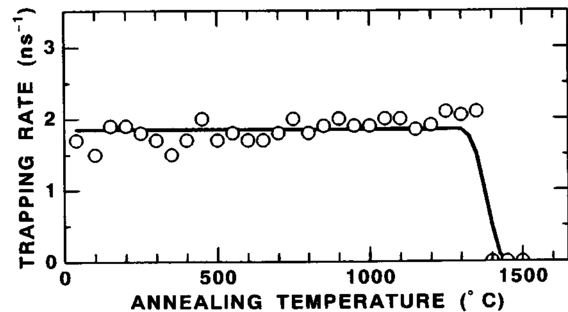

FIG. 3. Trapping rate κ responsible for the defect component (second lifetime) for the as-grown n-type specimen as a function of annealing temperature.

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bile at around 750 °C. Balona and Loubser[10] showed that an ESR spectrum designated F in $6H$-SiC disappeared due to the annealing at 750 °C. Although the F spectrum was originally attributed to carbon divacancies, Itoh *et al.*[11] proposed that the center was related to pure silicon vacancies since the spectrum showed similar g-tensor and hyperfine coupling constant to those of the silicon vacancies in $3C$-SiC. The positron annihilation centers observed for the as-grown n-type specimen have considerably high thermal stability as compared to that of pure silicon vacancies. Thus, we propose that the positron annihilation centers are not related to pure silicon vacancies but related to silicon vacancies combined with impurity atoms, possibly complexes of silicon vacancies and nitrogen atoms. Probably, mobile silicon vacancies which are thermally formed in crystal-growth process combine with high content of nitrogen atoms to form the complexes. The complexes may be frozen into crystal during cool down process.

The complex is analogous with E center in Si (complex of a vacancy and a phosphorus atom) which acts as a deep single acceptor.[24] If we simply assume that the complex of a silicon vacancy and a nitrogen atom also has an acceptor level within the band gap and hence charges as single negative in n-type specimen, the specific trapping rate of the complex for a positron may be of similar order to that of the E center (i.e., $10^{16}\ \mathrm{s}^{-1}$)[25] since the dielectric constants of Si (11.9) and $6H$-SiC (10.0) is similar to each other. The concentration of the complexes at as-grown state is estimated to be of the order of $10^{16}\ \mathrm{cm}^{-3}$ using the trapping rate shown in Fig. 3 and Eq. (6). This indicates that high content of vacancies exist at high temperature where crystal growth is taken place.

Figure 4 shows the annealing behaviors of the lifetimes τ_1 and τ_2, and intensity I_2 for the irradiated n-type specimen. It is found that the lifetime τ_2 shortens as 210 ps→200 ps→189 ps→183 ps due to the annealing at around 100, 200, 450, and 750 °C, respectively. The intensity I_2 is found to decrease to the detection limit at around 1400 °C. This annealing behavior is similar to that observed in the as-grown n-type specimen.

The atomic displacement energy for $6H$-SiC was determined to be 21.8 eV by Barry *et al.*[26] The value of atomic displacement energy was reported to be almost the same for both Si and C sublattice.[27] Thus, from an elemental theory of radiation damage,[28] the mean energy of primary knock-on atom (PKA) is estimated to be approximately 100 eV in the case of 3 MeV electron irradiation and hence at most one or two atoms will be displaced by PKA. Total number of displacement atom is estimated to be of the order of $10^{17}\ \mathrm{cm}^{-3}$ in the present electron fluence ($1\times10^{17}\ \mathrm{e/cm}^2$). The above arguments allow us to think that silicon vacancies, carbon vacancies, Frenkel pairs, and small amount of divacancies are directly created by the irradiation. The lifetime τ_2 seems to be a weighted average between defects related to silicon vacancies and divacancies since the lifetime varies between the theoretical lifetimes at a silicon vacancy and a divacancy as mentioned above. Here, it should be noted that the lifetime τ_1 deviates from that expected from the two-state trapping model below 500 °C. This shows that another component, which gives a lifetime close to the bulk lifetime, mixes to the first lifetime component. Probably, the component comes from defects related to carbon vacancies since the theoretical positron lifetime at a carbon vacancy (150 ps) is close to the bulk lifetime (136 ps). In the case that an additional component mixes to the first component, the trapping rates responsible for the mixed component and the second component, respectively, are given by

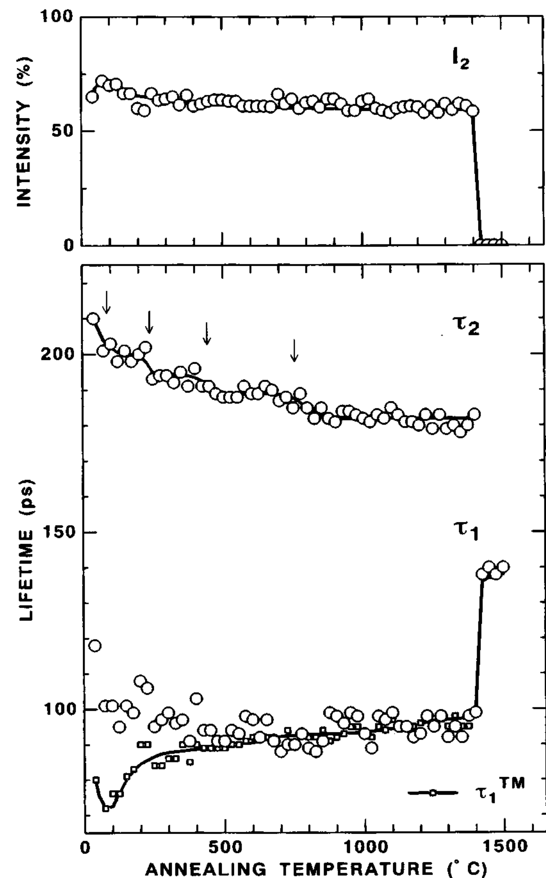

FIG. 4. Positron lifetimes τ_1 and τ_2, and intensity I_2 for the n-type specimen irradiated with 3 MeV electrons at a fluence of $1\times10^{17}\ \mathrm{e^-/cm^2}$ as a function of annealing temperature. τ_1^{TM} denotes the lifetime calculated by Eq. (3).

$$\kappa_1=\frac{\tau_1(\tau_B^{-1}-I_2\tau_2^{-1})-I_1}{\tau_S-\tau_1}, \tag{7}$$

$$\kappa_2=\frac{I_2}{I_1}\cdot\frac{\tau_B^{-1}-\tau_2^{-1}-I_1\tau_S^{-1}(1-\tau_1\tau_2^{-1})}{1-\tau_1\tau_S^{-1}}, \tag{8}$$

instead of Eq. (3).[16] Here, κ_1 and τ_S are the trapping rate and the lifetime, respectively, responsible for the mixed component. Figure 5 shows the annealing behavior of the trapping rates κ_1 and κ_2 calculated under the assumption that the mixed component is caused by defects related to carbon vacancies (τ_S=150 ps). It is found that the trapping rate κ_1 decreases at around 75 and 300 °C and reach the detection limit at higher temperature. This result shows that defects related to carbon vacancies are annealed at those temperatures. Such an annealing behavior is similar to the previous results by ESR[29] for p-type $3C$-SiC in which carbon vacan-

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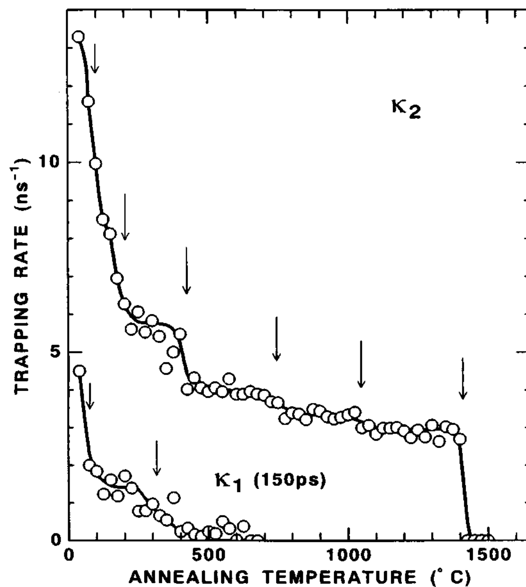

FIG. 5. Trapping rates κ_1 and κ_2 responsible for the one defect component (mixed into the first lifetime) and the other defect component (second lifetime), respectively, for irradiated n-type specimen as a function of annealing temperature.

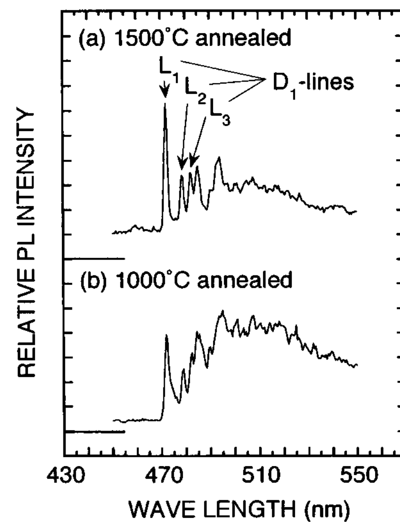

FIG. 6. PL spectra for the n-type specimen irradiated with 3 MeV electrons at a fluence of 1×10^{17} e^-/cm^2 after the annealing at (a) 1500 °C and (b) 1000 °C for 5 min.

cies were suggested to annihilate between 100 and 300 °C. The above annealing stages may be explained by recombination between carbon vacancies and mobile interstitials, recombination of the close Frenkel pairs and/or migration of carbon vacancies to internal sinks. Possibly, the low-temperature stage is responsible for the recombination processes, and the high-temperature stage for the migration process.

The trapping rate κ_2 is found to drastically decrease at around 100, 200, and 450 °C. As shown in Fig. 4, the lifetime τ_2 approaches the lifetime at silicon vacancies accompanying with the annealings. These results show that defects related to divacancies annihilate up to 450 °C, and the remaining component is caused by defects related to silicon vacancies. This seems to be somewhat peculiar since divacancies is thought to be more stable than silicon vacancies. Defects related to divacancies are considered to promptly reach the detection limit through recombination with interstitials at low temperature. It is probably due to the following reasons: (i) The concentration of divacancies is lower than that of silicon vacancies and/or (ii) most divacancies involve interstitials at fairly close site. Those arguments are based on the fact that the energy of PKA is too low to cause large cascade damage in the case of 3 MeV electron irradiation as mentioned above. Although the former explanation seems to be contradict to the drastic decrease in the trapping rate κ_2 up to 500 °C, it may be explained as the large specific trapping rate of divacancies due to the Coulomb attraction as discussed later.

The trapping rate κ_2 slightly decreases at around 750 and 1050 °C, and ultimately reaches to the detection limit at around 1400 °C. Considering the ESR studies where pure silicon vacancies become mobile at around 750 °C as mentioned above, the annealing stage is concluded to be due to the migration of pure silicon vacancies. Mobile silicon vacancies seem to annihilate at sinks or to form complexes of silicon vacancies and nitrogen atoms. After the annealing at 750 °C, the trapping rate κ_2 is higher than the trapping rate κ for the as-grown n-type specimen which was attributed to complexes of silicon vacancies and nitrogen atoms. This also supports that excess complexes of silicon vacancies and nitrogen atoms are formed due to the annealing at around 750 °C following irradiation. Accompanying with the annealing at 750 °C, the lifetime τ_2 decreases from 189 to 183 ps. Probably, this reflects the fact that the size of effective open volume of complexes of silicon vacancies and nitrogen atoms is slightly smaller than that of pure silicon vacancies. The weak annealing stage at around 1050 °C may be correlated with that for the DLTS levels observed by Ballandovich and Violina as mentioned above.[4] Present result suggests that a small part of complexes of silicon vacancies and nitrogen atoms disappear at the stage. However, the detailed process for the annealing stage is not clear at present moment. The annealing stage at around 1400 °C shows that the residual complexes of silicon vacancies and nitrogen atoms diminish at the stage. It is consistent with the conclusion for the as-grown n-type specimen. Girka *et al.*[19] also reported that complexes of silicon vacancies and nitrogen atoms were annealed at around 1400 °C. Probably, the complexes dissociate to silicon vacancies and nitrogen atoms. The mobile silicon vacancies will disappear at internal sinks or at surface of specimen. Present result shows that no vacancy clustering occur even when the complexes dissociate. Probably, this is because silicon vacancies disappear with repeating dissociation and association with nitrogen atoms due to the high content of nitrogen atoms.

Figure 6 shows the PL spectra for the irradiated n-type specimen after the annealing at 1000 and 1500 °C, respectively, for 5 min. As seen in the figure, the D_1 luminescence lines at 472.0, 479.0, and 482.5 nm (denoted by L_1, L_2 and L_3) were observed. Those lines were related to no-phonon

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transitions corresponding to the three inequivalent sites of $6H$-SiC.[6] The luminescence was not observed in as-irradiated state. It is also found that the intensity of the luminescence increases with increasing annealing temperature. The D_1 luminescence is proposed to be related to divacancies as shown above. However, no evidence for the formation of divacancies was found after the annealing above 1000 °C as mentioned above. Present results also show that the luminescence could not be correlated to defects related to silicon vacancies since they annihilate up to 1400 °C. Further, it may also be pointed out that the Z1/Z2 DLTS levels could be correlated to neither divacancies nor defects related to silicon vacancies since the levels are reported to be stable even at 1700 °C.[23]

Present results indicate that complexes of silicon vacancies and nitrogen atoms giving rise to a lifetime of 183 ps exist in the as-grown n-type specimen, while no such defects which act as positron trapping centers are present in the as-grown p-type specimen. One possible explanation for the result is that in the p-type specimen silicon vacancies hardly form complexes with aluminum atoms since aluminum atoms occupy silicon sublattice. Alternatively, it is interpreted in terms of the effect of charge state of the vacancies as mentioned below. In addition to complexes of silicon vacancies and nitrogen atoms, silicon vacancies and divacancies were found in the n-type specimen after electron irradiation, while no such defects were found in the p-type specimen even after the irradiation. This feature may be explained as an amphoteric nature of vacancies: Probably, vacancies have both donor and acceptor levels within the band gap. In the p-type specimen, vacancies may act as donors and compensate free holes to charge as positive and hence a positron is hardly trapped by them due to the Coulomb repulsion. On the contrary, in the n-type specimen, vacancies act as acceptors and compensate electrons to charge as negative and hence a positron can be trapped by them due to the Coulomb attraction. Vainer and Il'in[14] proposed that a divacancy charges as double negative in n-type specimen, namely it acts as a double acceptor. This suggests that divacancies work as strong positron trapping centers in the n-type specimen. It could also explain the drastic decrease in the trapping rate k_2 due to the annealing up to 500 °C where divacancies seem to annihilate as shown above. Although present results suggest that a divacancy also has a donor level, it has not yet been shown. The DLTS study[4] also shows that the E1/E2 and E3/E4 levels are acceptors and the level at $E_C - 0.11$ eV is donor. If these levels are originating from defects related to silicon vacancies, it could explain the fact that defects related to silicon vacancies were not observed for the p-type specimen.

IV. SUMMARY

Annealing behavior of vacancy-type defects in as-grown and electron-irradiated $6H$-SiC have been studied using positron lifetime spectroscopy. The results of this work are summarized as follows: The defects related to silicon vacancies, possibly complexes of silicon vacancies and nitrogen atoms were found to be present in as-grown n-type specimen. They were found to be annealed at around 1400 °C. The defects related to carbon vacancies, divacancies and silicon vacancies were found to be introduced by 3 MeV electron irradiation in n-type specimen. The former two types of defects were found to disappear up to 500 °C. Probably these are mainly due to the recombination with mobile interstitials. Some part of defects related to silicon vacancies were found to disappear due to the annealing above 750 °C and to ultimately diminish at around 1400 °C. The former annealing stage was attributed to migration of silicon vacancies to internal sinks or to nitrogen atoms forming complexes of silicon vacancies and nitrogen atoms. The latter one was attributed to the disappearance of the complexes. No vacancy-type defects were detected in the p-type specimen even after the electron irradiation. This may be interpreted in terms of the positively charged defects. PL measurements have also been performed to elucidate the correlation between vacancy-type defects and the D_1 luminescence which was attributed to divacancies in the previous works. However, present results show that the luminescence center is not related to vacancy-type defects, such as divacancies, silicon vacancies, and complexes of vacancies and impurities.

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[1] G. Pensl and R. Helbig, Festkörperprobleme **30**, 133 (1990).
[2] H. Zhang, G. Pensl, A. Dömen, and S. Leibenzeder, The Electrochemical Society, Extended Abstracts **89-2**, 699 (1989).
[3] H. Zhang, G. Pensl, P. Glasow, and S. Leibenzeder, The Electrochemical Society, Extended Abstract **89-2**, 714 (1989).
[4] V. S. Ballandovich and G. N. Violina, Cryst. Lattice Defects Amorphous Mater. **13**, 189 (1987).
[5] W. J. Choyke and L. Patrick, Phys. Rev. B **4**, 1843 (1971).
[6] L. Patrick and W. J. Choyke, Phys. Rev. B **5**, 3253 (1972).
[7] L. Patrick and W. J. Choyke, J. Phys. Chem. Solids **34**, 565 (1973).
[8] V. V. Makarov, Sov. Phys. Solid State **13**, 1974 (1972).
[9] W. J. Choyke, Inst. Phys. Conf. Ser. **31**, 58 (1977).
[10] L. A. de S. Balona, and J. H. N. Loubser, J. Phys. C **3**, 2344 (1970).
[11] H. Itoh, N. Hayakawa, I. Nashiyama, and E. Sakuma, J. Appl. Phys. **66**, 4529 (1989).
[12] H. Itoh, M. Yoshikawa, I. Nashiyama, S. Misawa, H. Okumura, and S. Yoshida, Inst. Phys. Conf. Ser. **137**, 255 (1994).
[13] V. S. Vainer and V. A. Il'in, Sov. Phys. Solid State **23**, 1432 (1981).
[14] V. S. Vainer and V. A. Il'in, Sov. Phys. Solid State **23**, 2126 (1981).
[15] G. Pensl and W. J. Choyke, Physica B **185**, 264 (1993).
[16] For example, W. Brandt, and A. Dupasquier, *Positron Solid-State Physics* (North Holland, Amsterdam, 1989).
[17] For a general review, Yu. A. Vodakov and E. N. Mokhov, Inst. Phys. Conf. Ser. **137**, 197 (1994).
[18] W. Puff, M. Boumerzoug, J. Brown, P. Mascher, D. Macdonald, P. J. Simpson, A. G. Balogh, H. Hahn, W. Chang, and M. Rose, Appl. Phys. A **61**, 55 (1995).
[19] A. I. Girka, V. A. Kuleshin, A. D. Mokrushin, E. N. Mokhov, S. V. Svirida, and A. V. Shishkin, Sov. Phys. Semicond. **23**, 1337 (1989).
[20] A. A. Rempel and H.-E. Schaefer, Appl. Phys. A **61**, 51 (1995).
[21] A. A. Rempel, H.-E. Schaefer, M. Forster, and A. I. Girka, Mater. Res. Soc. Symp. Proc. **327**, 299 (1994).
[22] P. Kirkegaard, N. Pederson, and M. Eldrup, PATFIT-88, Riso-M-2704, 1989.
[23] G. Brauer, W. Anwand, Y. Pacaud, W. Skorupa, F. Plazaola, P. G. Coleman, A. P. Knights, J. Störmer, and P. Willutzki, Inst. Phys. Conf. Ser. (to be published).
[24] G. D. Watkins and J. W. Corbett, Phys. Rev. **134**, 1359 (1964).

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[25] A. Kawasuso, M. Hasegawa, M. Suezawa, S. Yamaguchi, and K. Sumino, Jpn. J. Appl. Phys. **34**, 2197 (1995).
[26] A. L. Barry, B. Lehmann, D. Fritsch, and D. Bräunig, IEEE Trans. Nucl. Sci. **NS-30**, 1111 (1991).
[27] K. W. Böer, *Survey of Semiconductor Physics* (Van Nostrand Reinhold, New York, 1990), Chap. 23, p. 629.
[28] D. S. Billington and J. H. Crawford, Jr., *Radiation Damage in Solids* (Princeton University, New Jersey, 1961), Chap. 2, pp. 12–54.
[29] H. Itoh, M. Yoshikawa, I. Nashiyama, S. Misawa, H. Okumura, and S. Yoshida, J. Electron. Mater. **21**, 707 (1992).

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