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Clustering of vacancy defects in high-purity semi-insulating SiC

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Positron lifetime spectroscopy was used to study native vacancy defects in semi-insulating silicon carbide. The material is shown to contain (i) vacancy clusters consisting of four to five missing atoms and (ii) Si-vacancy-related negatively charged defects. The total open volume bound to the clusters anticorrelates with the electrical resistivity in both as-grown and annealed materials. Our results suggest that Si-vacancy-related complexes electrically compensate the as-grown material, but migrate to increase the size of the clusters during annealing, leading to loss of resistivity.

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I. INTRODUCTION

Silicon carbide (SiC) is a promising semiconductor material for high-temperature, high-power, high-frequency, and radiation resistant applications. Semi-insulating SiC has shown great potential as a substrate material for SiC- and III-nitride microwave technology. SiC substrates can be made semi-insulating by introducing deep levels (either impurities or intrinsic defects) to the material. High-purity semi-insulating SiC can be grown by the high-temperature chemical vapor deposition (HTCVD) technique in which pure source gases are used.

Native vacancies have been observed in the material in electron paramagnetic resonance experiments, but their role in the electrical compensation is unclear. Positron lifetime spectroscopy is a method for studying vacancy defects in solid materials. Positrons are repelled by positive ion cores and tend to get trapped at vacancies. Since the electron density in the vacancies is lower than in the bulk, positron lifetime increases and its value indicates the open volume of the defect. Using the relative intensities of different lifetime components, one can determine the concentrations of different vacancy defects.

During the last few years, SiC has been extensively studied using positron spectroscopy (see, e.g., Refs. 8–24). These studies often involve irradiated materials. In this study we use positron lifetime spectroscopy to study as-grown bulk HTCVD 4H-SiC samples, grown under different conditions. We observe clusters of four to five vacancies, which grow in size even up to 30 missing atoms after high-temperature annealing. We also detect smaller open volume defects, which we attribute to negative V× related complexes. Comparison with the results of resistivity measurements shows that the presence of vacancy clusters anticorrelates with the semi-insulating properties of the material. We suggest that the clusters act as neutral agglomeration centers for the negative vacancy defects causing the high resistivity.

The paper is organized as follows. The details of the positron experiments and theoretical calculations are given in Sec. II. The positron results in the as-grown and high-temperature annealed SiC samples are given and interpreted in Sec. III. In Sec. IV, we present the identification of the vacancy defects in the light of theoretical calculations and earlier investigations, and discuss the vacancy concentrations and the effect of vacancy defects on the electrical compensation. Finally, Sec. V concludes the paper.

II. METHOD

A. Experimental details

We measured over 20 samples grown by the HTCVD method above 1900 °C in either hydrocarbon rich (type A) or poor (type B) conditions (examples shown in Table I). The studied samples are undoped and their impurity levels are ≲10¹⁶ cm⁻³ as measured by secondary-ion-mass spectrometry. Generally, all as-grown samples are insulating but sample A1 shows weak n-type conductivity. Postgrowth annealings were performed at 1600 °C in H₂ ambient in a CVD reactor. After annealing, the resistivity of A-type samples decreased and current-voltage measurements indicated that the samples became more n type. The type B samples remain semi-insulating also after annealing.

The samples were measured in darkness between 20 and 540 K with analog and digital positron lifetime spectrom-

TABLE I. Summary of samples studied in this paper. Annealings have been performed at 1600 °C in H₂ ambient. Type A samples are grown in hydrocarbon rich and type B samples in hydrocarbon poor environment. Resistivities are presented at 300 K.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C₂H₆</th>
<th>Annealing time (h)</th>
<th>Resistivity (Ω cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>Rich</td>
<td>0</td>
<td>n type</td>
</tr>
<tr>
<td>A1</td>
<td>Rich</td>
<td>0</td>
<td>n type</td>
</tr>
<tr>
<td>A2</td>
<td>Rich</td>
<td>0</td>
<td>2 × 10⁹</td>
</tr>
<tr>
<td>A2</td>
<td>Rich</td>
<td>1</td>
<td>1 × 10⁸</td>
</tr>
<tr>
<td>A2</td>
<td>Rich</td>
<td>2</td>
<td>4 × 10⁴ (n)</td>
</tr>
<tr>
<td>A2</td>
<td>Rich</td>
<td>3</td>
<td>5 × 10² (n)</td>
</tr>
<tr>
<td>B</td>
<td>Poor</td>
<td>0</td>
<td>&gt;10¹⁰</td>
</tr>
<tr>
<td>B</td>
<td>Poor</td>
<td>1</td>
<td>&gt;10¹⁰</td>
</tr>
</tbody>
</table>
eters. The time resolutions of the spectrometers were 240 and 215 ps full width at half maximum, respectively. The digital spectrometer was used for room-temperature measurements. The detectors were equipped with plastic scintillators and were positioned in face-to-face geometry in both cases. We used $10 \mu$Ci $^{22}$Na positron sources deposited on folded 1.5 $\mu$m Al foil. Typically, $(1-2) \times 10^6$ counts of annihilation events were collected for each lifetime spectrum. The lifetime spectrum was analyzed as the sum of exponential decay components, $\sum I_i \exp(-t/\tau_i)$, where the $\tau_i$ are the individual lifetime components and $I_i$ their intensities. The increase of the average positron lifetime $\tau_{\text{ave}} = \sum I_i \tau_i$, above the bulk lattice lifetime $\tau_0$, shows that vacancy defects are present in the material. The average lifetime $\tau_{\text{ave}}$ is insensitive to the de- composition procedure, and even a change as small as 1 ps can be reliably measured.

If the samples contain only one vacancy-type positron traps with positron lifetime $\tau_D$, the positrons have two different states from which to annihilate, i.e., bulk and defect. The longer experimental lifetime component will then be equal to that of the positron lifetime in the defect, i.e., $\tau_{\text{exp}}^D = \tau_D$. Because of the positrons trapping away from the bulk at rate $\kappa$, the shorter experimental lifetime component becomes $\tau_{\text{exp}} = (\tau_D^{-1} + \kappa)^{-1}$. This effect can be used to test whether the one-trap model is sufficient to explain the measured data. For more details on the analysis, see, e.g., Refs. 6 and 7.

B. Theoretical calculations

We theoretically calculated the positron lifetimes in vacancy clusters for the 4H polytype of SiC. For the positron states, we used the conventional scheme with the local density approximation for electron-positron correlation effects and the atomic superposition method in the numerical calculations. The positron annihilation rate $\lambda$ is

$$\lambda = \tau^{-1} = \pi r_s^2 c \int d |\psi_e(r)|^2 n_-(r) \gamma(n_-(r)), \quad (1)$$

where $n_-$ is the electron density, $\psi_e$ the positron wave function, $r_s$ the classical electron radius, $c$ the speed of light, and $\gamma$ the enhancement factor. We used a modified Boronski-Nieminen enhancement factor, which takes into account the lack of complete positron screening in semiconductors. The factor takes the form

$$\gamma(n_-(r)) = 1 + 1.23 r_s + 0.8295 r_s^{3/2} - 1.26 r_s^2 + 0.3286 r_s^{5/2} + (1 - 1/e_e) r_s^3 / 6, \quad (2)$$

where $r_s$ is calculated from the electron density as $r_s = \sqrt[3]{3/(4\pi n_-)}$. For the high-frequency dielectric constant in 4H polytype, we use the value $\varepsilon_e = 6.78$.30,31

We estimate the sizes of the observed vacancy clusters using these theoretical calculations. The calculated clusters are formed by removing Si-C pairs from the perfect lattice up to the size of 84 atoms. The atoms are removed according to their distance from the “origin” of the cluster (chosen to be the middle point between a Si-C bond, cubic position). The positron state is then solved in $480-2N$ atom supercells, where $N$ is the number of Si-C pairs removed.

![FIG. 1. Positron lifetime spectra at 300 K. The solid lines are fits of sums of exponential decay components.](image)

Because the atoms are simply removed from their ideal positions, the calculated clusters are nonrelaxed. In general, the relaxation affects the open volume—and thus the positron lifetime of the clusters. Additionally, the presence of a trapped positron may alter the configuration of the surrounding atoms. According to calculations, lattice relaxations have been found to affect the positron lifetimes in the case of $V_{\text{Si}}$ in SiC by approximately 12–15 ps and in $V_2$ by 4–7 ps. Furthermore, the relative effect of relaxations in clusters has been found to diminish to an insignificant level in clusters bigger than $V_4$ in silicon (note that the open volume of $V_4$ in Si is larger than that of $V_4$ in SiC).

III. POSITRON LIFETIME RESULTS

Positron lifetime spectra are shown in Fig. 1. The reference sample, $p$-type bulk SiC, shows only a single lifetime of 150 ps, which we attribute to the positron lifetime $\tau_0$ in the SiC lattice. All HT-CVD samples have at least two lifetime components.

The lifetime spectra were decomposed into two components. Table II presents the average positron lifetime at 300 K and the two separated components. The intensity of the longer component is also shown. The longer lifetime is 260–290 ps in the as-grown state and increases up to 450 ps after annealing. These lifetime values are typically associated with a vacancy cluster consisting of more than two missing atoms.

The positron lifetime measurements as a function of temperature are shown in Fig. 2. We see that the average lifetime above 200 K is constant or decreases with temperature. This suggests that negative vacancies are present in the samples, since positron trapping to negative vacancies decreases with temperature, whereas trapping to neutral vacancies is temperature independent. Below 200 K, especially well seen in sample A1 Ann, the average lifetime starts to decrease, suggesting the presence of negative ions (residual impurities...
TABLE II. Samples, annealing times (at 1600 °C in H$_2$ ambient), resistivities (at 300 K), average positron lifetime $\tau_{\text{ave}}$, the fitted positron lifetime components $\tau_{1,2}$, and the intensity of the longer lifetime component $I_2$ (measured at 300 K). The positron trapping rates to monovacancies $\kappa_1$ and to vacancy clusters $\kappa_2$, vacancy defect concentrations for $V_{Si}$-related defects [$V_{Si}$], vacancy clusters [$V_N$], and cluster sizes $N$ have been determined by the positron annihilation measurements presented. Note that the change of Fermi level in type A2 sample evidently changes the charge state (and thus the positron trapping coefficient) of the defects (concentrations in boldface).

<table>
<thead>
<tr>
<th>Sample, annealing time</th>
<th>Resistivity (Ω cm)</th>
<th>$\tau_{\text{ave}}$ (ps)</th>
<th>$\tau_1$ (ps)</th>
<th>$\tau_2$ (ps)</th>
<th>$I_2$ (%</th>
<th>$\kappa_1$ (10$^9$ s$^{-1}$)</th>
<th>$\kappa_2$ (10$^{15}$ cm$^{-3}$)</th>
<th>$V_{Si}$</th>
<th>$V_N$</th>
<th>Cluster size $N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>$n$ type</td>
<td>191</td>
<td>168</td>
<td>284</td>
<td>20</td>
<td>7.5</td>
<td>2.6</td>
<td>120</td>
<td>50</td>
<td>5</td>
</tr>
<tr>
<td>A1, 1 h</td>
<td>$n$ type</td>
<td>208</td>
<td>138</td>
<td>350</td>
<td>33</td>
<td>2.1</td>
<td>2.9</td>
<td>30</td>
<td>28</td>
<td>10</td>
</tr>
<tr>
<td>A2</td>
<td>$2 \times 10^9$</td>
<td>163</td>
<td>152</td>
<td>283</td>
<td>8</td>
<td>1.3</td>
<td>0.4</td>
<td>61</td>
<td>8</td>
<td>5</td>
</tr>
<tr>
<td>A2, 1 h</td>
<td>$1 \times 10^8$</td>
<td>183</td>
<td>146</td>
<td>406</td>
<td>14</td>
<td>1.4</td>
<td>0.9</td>
<td>66</td>
<td>6</td>
<td>16</td>
</tr>
<tr>
<td>A2, 2 h</td>
<td>$4 \times 10^4$</td>
<td>206</td>
<td>144</td>
<td>440</td>
<td>21</td>
<td>2.0</td>
<td>1.7</td>
<td>33</td>
<td>6</td>
<td>27</td>
</tr>
<tr>
<td>A2, 3 h</td>
<td>$5 \times 10^2$</td>
<td>216</td>
<td>144</td>
<td>451</td>
<td>24</td>
<td>2.4</td>
<td>2.1</td>
<td>39</td>
<td>6</td>
<td>32</td>
</tr>
<tr>
<td>B</td>
<td>$&gt;10^{10}$</td>
<td>164</td>
<td>150</td>
<td>261</td>
<td>13</td>
<td>1.3</td>
<td>0.6</td>
<td>61</td>
<td>15</td>
<td>4</td>
</tr>
<tr>
<td>B, 1 h</td>
<td>$&gt;10^{10}$</td>
<td>179</td>
<td>146</td>
<td>342</td>
<td>17</td>
<td>1.4</td>
<td>1.0</td>
<td>69</td>
<td>11</td>
<td>9</td>
</tr>
</tbody>
</table>

or intrinsic defects), which act as shallow traps for positrons. Samples B and B Ann have oscillations in $\tau_{\text{ave}}$ around 100 K, which may reflect some charge transitions in the shallow traps. However, the concentrations of the shallow traps are low compared to those of the vacancy defects, as the decrease of the average lifetime is modest compared to the difference between the average and bulk lifetimes.

Figure 3 shows the temperature dependence of the positron lifetime components. The positron lifetime at vacancy clusters $\tau_2$ is approximately constant (350 or 270 ps), indicating positron annihilation in a well-defined defect state in each sample. On the other hand, the shorter lifetime $\tau_1$ has a clear tendency to decrease from 160–175 ps at 20 K to 140–150 ps at 500 K. If only the vacancy clusters corresponding to $\tau_2$ were present in the samples, the lifetime $\tau_1$ in the lattice would be related to $\tau_{\text{ave}}, \tau_b$, and $\tau_2$ as

$$\tau_1 = \frac{\tau_{\text{ave}} - \tau_b}{1 - \frac{\tau_{\text{ave}} - \tau_b}{\tau_2 - \tau_b}}.$$  (3)

The test lifetime $\tau_1^{\text{test}}$ calculated from the experimental values of $\tau_{\text{ave}}, \tau_b$, and $\tau_2$ varies between 95 and 137 ps, and thus it is well below the experimental $\tau_1$ in all samples at any temperature. This means that the vacancy clusters corresponding to $\tau_2$ are not the only defects. There also exist other smaller vacancy defects, which create a lifetime component mixed into the experimental $\tau_1$ lifetime. The smaller defects are especially prominent at low temperatures and their concentration in sample A1 grown under the hydrocarbon rich condition is high. The positron lifetime at the smaller vacancy defects is estimated to be above 170 ps from the low-temperature part of Fig. 3. On the other hand, the $\tau_{\text{ave}}$ vs. $T$ data in Fig. 2 indicate that the defect-specific lifetime is below 220 ps.

IV. DISCUSSION

A. Identification of the vacancy defects

1. Vacancy clusters

The measured lifetime $\tau_2$ is longer than that determined earlier (typical values reported in literature are shown in parentheses, see more discussion about lifetime values at the end of this section) for the carbon vacancy $V_C$ (≤160 ps), the silicon vacancy $V_{Si}$ (180–210 ps), or divacancy (<250 ps) in SiC. The electron density in the defect is thus lower, indicating that the observed defects are vacancy clusters.

The calculated positron lifetimes in vacancy clusters are presented in Fig. 4. The results obtained are similar to those reported earlier for 3C- and 6H-SiC. Our calculations give for the positron lifetime in bulk SiC a value of $\tau_p$ =143.7 ps, in agreement with the measured value $\tau_b$ =149.6 ps. When using the theoretical calculations to determine the measured cluster sizes, we compare the differences between the bulk and defect lifetimes.
According to the theoretical calculations, a measured positron lifetime of 260 ps observed in as-grown samples corresponds to a vacancy cluster $V_{4}/H_{20849}$ two Si-C molecules removed. The lifetime of 350 ps, detected after annealing, is expected for an open volume of a cluster $V_{10}$. The estimated cluster sizes in different samples are presented in Table II. We observe that the cluster sizes increase in the annealings from the size of roughly five missing Si-C pairs in the as-grown material up to 30 missing Si-C pairs in the sample annealed for 3 h. These approximate values represent the averages of the open volume distribution of vacancy clusters. This may mean various different cluster sizes or possibly a “magic” cluster size, in which the number of dangling bonds is minimized, as shown in, e.g., Si and GaAs.$^{32,33}$ Clustering of vacancies due to annealing has been previously reported in n-type 6H-SiC after neutron and ion irradiations.$^{19,34,35}$

### 2. Si-vacancy-related defects

The estimated lifetime of the positrons trapped at the smaller observed vacancy defects is $\tau_{v}=195\pm 25$ ps range, i.e., $\tau_{v}-\tau_{b}=20–70$ ps. In order to identify this defect, we need to consider the different lifetime values that have been associated with different aspects of SiC. Reported positron lifetimes (both experimental and theoretical) for bulk material range between 134 and 150 ps. The lifetime values associated with different vacancy defects vary clearly more.

For 4H polytype, bulk lifetime values including 141 ps,$^{36}$ 145 ps,$^{9}$ 150 ps,$^{21}$ and, for 3C-SiC, 140 ps have been reported.$^{17}$ The most common polytype encountered in recent positron studies for SiC is 6H, for which several values for bulk lifetime have been proposed, in the range of 136–150 ps.$^{8,14–16,18,20–22}$ The theoretical calculations give lifetimes of 134 ps for 4H-SiC,$^{23}$ 141 ps for 6H-SiC, and 138 ps for 3C-SiC.$^{11}$ It should be noted that different calculation schemes (especially different enhancement factors) cause differences in the resulting absolute lifetimes, which become evident when comparing results from different studies.$^{23}$ A somewhat similar situation applies to experimental values (e.g., due to differences in measurement geometry, energy windows, or source corrections). Thus, in comparisons between different lifetime values obtained from different studies, we preferably compare the differences between determined lifetime values in defects and bulk ($\tau_{v}-\tau_{b}$) rather than focus solely on the absolute values of the lifetimes.

The studies of positron trapping in vacancy-type defects are typically performed by making use of irradiation, and the identification of the defects is often based on comparing the measured and the theoretical positron lifetime values. The reported values for positron lifetimes in $V_{Si}$ based on irradiation experiments are typically around $\tau_{v}=200$ ps in the range $\tau_{v}-\tau_{b}=14–116$ ps.$^{8,14,15,17,22,37}$ Theoretical calculations reported in the literature predict $\tau_{v}-\tau_{b}=47–64$ ps in 4H- and 6H-SiC (Refs. 11 and 23) for $V_{Si}$. For $V_{C}$, values of $\tau_{v}-\tau_{b}$ =8 and 16 ps have been reported$^{14,37}$ and theory gives $\tau_{v}-\tau_{b}=6–12$ ps.$^{11,23}$

In addition to the previous values, lifetime differences in the range $\tau_{v}-\tau_{b}=65–94$ ps have been reported in irradiated samples.$^{12,20,22,24}$ The experimental values reported,$^{8,15}$ $\tau_{v}-\tau_{b}=80–83$ ps, for the divacancy ($V_{Si}V_{C}$) are in good agree-
ment with the reported theoretical predictions $\tau_V - \tau_b = 73–75$ ps for 4H-SiC (Ref. 23) and 6H-SiC (Ref. 11).

Vacancies are also often detected in as-grown materials. In many cases, the lifetime values are somewhat longer than the values found after irradiation. Lifetime values mainly in the range of 250–350 ps ($\tau_V - \tau_b = 100–200$ ps) have been observed in as-grown SiC samples.\textsuperscript{13,14,16,21} Also, smaller values of $\tau_V - \tau_b = 50–75$ ps have been reported\textsuperscript{18} and attributed to $V_{Si}$ and $V_{Si}C$. According both to our and earlier reported\textsuperscript{10} theoretical calculations, a lifetime of 250 ps corresponds to an open volume of at least similar size to that of $V_d$, i.e., $(V_{Si}V_C)^{1/2}$.

In the light of the lifetime values discussed above, the possible candidates for the smaller vacancy defects observed here are thus monovacancies or monovacancy-related complexes in the Si and C sublattices and small clusters with at most two to three missing atoms. Several arguments point in the direction that the observed defects are related to $V_{Si}$ rather than $V_C$. The main point is that, as shown above, the lifetime of the smaller vacancy defect is $\approx 170$ ps, i.e., above all presented estimates for the carbon vacancy $V_C$. In addition, the C vacancy in semi-insulating SiC could be positively charged according to theoretical calculations\textsuperscript{38} and electron paramagnetic resonance (EPR) experiments\textsuperscript{5} and thus repulsive to positrons. Hence, we attribute the defect responsible for the increase of $\tau_V$ at low temperature to the Si vacancy or a complex involving $V_{Si}$.

It is interesting that the Si-vacancy-related defects are prominent at low temperatures, whereas the larger vacancy clusters dominate the positron lifetime spectrum at high measurement temperatures. Positron trapping at neutral defects is independent of temperature, whereas the negative defects become stronger positron traps at lower temperatures.\textsuperscript{6,7} Hence, the temperature dependence of the lifetime components suggests that the observed Si-vacancy-related defects act as acceptors in semi-insulating HT-CVD SiC, but the vacancy clusters are electrically neutral. In the annealed A1-type sample, however, the average positron lifetime decreases with the increasing temperature. This evidently means that a part of the clusters in the $n$-type material is negatively charged.

### B. Vacancy defect concentrations

The vacancy defect concentrations can be estimated from the positron trapping model using the decomposed lifetimes and intensities. In the calculation, we assume that both vacancy clusters (CL) and vacancies in Si sublattice (V) are present and the positron lifetimes at the vacancies in the Si sublattice and in the bulk SiC are intermixed with the component $\tau_d$. The positron trapping rates $\kappa$ are\textsuperscript{6,7}

$$\kappa_V = \frac{\tau_d(\tau_V^{-1} - \tau_{\text{CL}}^{-1}) - \tau_d^{-1}}{(\tau_V - \tau_d)}, \quad (4)$$

$$\kappa_{\text{CL}} = \frac{I_2}{I_1}(\tau_b^{-1} - \tau_{\text{CL}}^{-1} + \kappa_V). \quad (5)$$

The positron lifetime for the vacancy cluster is taken directly from the decomposition as $\tau_{\text{CL}} = \tau_d$. For the positron lifetime at the Si-vacancy-related defects, we use $\tau_b = 195$ ps, which is in the middle of our range determined for the lifetime of the smaller defect. Values close to this are also often attributed to the positron lifetime in $V_{Si}$ (see Sec. IV A 2). The defect concentrations can be obtained from the trapping rates $\kappa$ as $c = \kappa N_{\text{def}}$. Here, $N_{\text{def}} = 9.64 \times 10^{12}$ cm$^{-3}$ is the atomic density of SiC.

Positron trapping coefficients for negative vacancies at 300 K range typically between $0.5 \times 10^{15}$ and $5 \times 10^{15}$ s$^{-1}$ in semiconductors.\textsuperscript{6} For instance, a value of $\mu_{VSi} = 1.1 \times 10^{15}$ s$^{-1}$ has been reported for $V_{Si}V_{C}$ (Ref. 15) in SiC at room temperature. Also, coefficients as high as $6 \times 10^{16}$ s$^{-1}$ have been reported for $V_{Si}$ in SiC.\textsuperscript{17} We consider the latter value to be much too high, as the typical coefficients reported for semiconductors are an order-of-magnitude less. It should be noted, however, that determining the values for the trapping coefficient $\mu$ is not an easy task and thus one should consider the possibility of the coefficient differing even by a factor of 2–3 from the physically proper value. Using an inaccurate trapping coefficient would thus affect the determined absolute defect concentrations (linearly). Still, the error would be similar in all samples and the comparison of the concentrations between different samples is possible.

Due to the high uncertainties associated with the value of $\mu_V$, we use positron trapping coefficient at 300 K, $\mu_{VSi} = 2 \times 10^{15}$ s$^{-1}$, for singly negative vacancies in Si sublattice, which is a typical value in wide band-gap semiconductors.\textsuperscript{6} For neutral vacancies, we use $\mu_{VSi}^0 = 1 \times 10^{15}$ s$^{-1}$, since the trapping coefficients of the neutral and negative mono- and divacancies in Si have been found to differ by a factor of 1.5–3.5.\textsuperscript{3,39,40} In $n$-type samples, we use a value of $3\mu_{VSi}$, since theoretical calculations predict that $V_{Si}$ changes it charge state from $1^-$ to $2^-$ and eventually to $3^-$ when the Fermi level approaches the conduction band.\textsuperscript{38} This change of charge state of $V_{Si}$ is likely to occur in sample A2, where the conductivity of the sample changes from semi-insulating to $n$ type, indicating the movement of the Fermi level. No change in the conductivity of samples A1 and B was observed. For small vacancy clusters (transition limited positron trapping), the positron trapping coefficient for vacancy clusters of $n$ vacancies can be approximated as $\mu_{\text{CL}} = n\mu_V$.\textsuperscript{41} As can be observed in Fig. 2, a part of the vacancy clusters in the annealed sample A1 are likely to be negative, which increases the overall trapping coefficient of the clusters. Hence, the concentration of the vacancy clusters in the annealed sample A1 is probably a bit overestimated. The determined vacancy defect concentrations are summarized in Table II.
being in the mid-10^{16} \text{ cm}^{-3} for the Si-vacancy-related defects and 10^{15}–10^{16} \text{ cm}^{-3} for the vacancy clusters.

The experimental vacancy defect concentrations and sizes (Table II) suggest the following interpretation: Annealings of the samples of type A, grown under hydrocarbon rich conditions, increase the sizes of the vacancy clusters from approximately 5 to about 30 vacancies, with a simultaneous decrease of the cluster concentration. The Si vacancy complex concentration is also lowered by the annealing of the n-type sample A1. Thus, we suggest that annealing causes \( V_{Si} \) to (partly) agglomerate to the vacancy clusters by migration.

In the originally semi-insulating sample A2, the trapping rate \( \kappa_1 \) of positrons to the \( V_{Si} \)-related defects increases roughly by a factor of 2. However, the annealing decreases the resistivity of the sample (towards \( n \)-type conductivity), which indicates that the Fermi level moves towards the conduction band. This is likely to induce an increase of the negativity of the \( V_{Si} \), which would increase the trapping coefficient to these vacancies by a factor of 2–3, depending on the initial and final charge states. Hence, the concentration of the \( V_{Si} \)-related defects decreases during the annealing. However, it is worth noting that the estimation of the concentration of the \( V_{Si} \)-related defects is less accurate than in sample A1 due to the likely change in the charge state of the defects. Interestingly, the total open volume increases in the annealing of the A-type sample. Based on these observations, we suggest that the annealing causes \( V_{Si} \) to agglomerate to the clusters.

Annealing also increases the average size of the vacancy clusters in the sample of type B, grown under hydrocarbon poor conditions. The concentration of the \( V_{Si} \)-related defects is not significantly changed in the annealing.

**C. Electrical compensation**

The positron results lead to several important conclusions regarding the origin of the semi-insulating properties of the material. The temperature dependence of the average positron lifetime (Fig. 2) shows that the samples of both types A and B do not contain significant concentrations of negative ions, such as impurities or negative interstitials or antisite defects. These types of defects thus contribute little to the electrical compensation, at maximum at the level of their detection limit; their concentration is at most in the mid-10^{15} \text{ cm}^{-3} range. This observation also correlates with low concentrations of B and Al acceptors (<5 \times 10^{15} and <5 \times 10^{14} \text{ cm}^{-3}, respectively) measured with secondary-ion-mass spectrometry.

The samples grown in hydrocarbon rich conditions (type A) are either slightly \( n \) type already after the growth or lose their high resistivity after annealing. The detected negative \( V_{Si} \)-related complex is an obvious candidate for the compensating intrinsic defect in as-grown material. Hence, the \( n \)-type character of the annealed samples can be explained by the loss of compensation due to the migration of negative \( V_{Si} \) to primarily neutral vacancy clusters. It is worth noting that a part of the vacancy clusters turn negative in the annealing of sample A1. This does not affect the interpretation that the compensation is weakened due to the migration of \( V_{Si} \) to the clusters, however, as the negativity implies that the cluster concentration presented in Table II overestimates the “proper” value.

The concentration of the vacancy clusters should thus increase with the decreasing resistivity of HTCVD SiC. To verify this relation in the as-grown samples, we measured positron lifetime and resistivity as a function of position in a striplike sample, cut diagonally across a wafer grown in hydrocarbon rich growth conditions (type A). The lifetime component \( \tau_2=247\pm10 \text{ ps} \) remained constant over the sample, indicating constant vacancy cluster size (\( \approx 4 \) atoms). As can be seen in Fig. 5, the average positron lifetime and the resistivity of the sample anticorrelate. The change of \( \tau_{ave} \) is caused by the variation in the intensity \( I_2 \) and thus the positron trapping rate at the vacancy clusters. The concentration of the clusters thus decreases with increasing resistivity of the material, most likely since less compensating \( V_{Si} \)-related complexes have migrated to the neutral vacancy clusters during the growth. Unfortunately, the direct analysis of the concentrations of \( V_{Si} \)-related defects using Eqs. (4) and (5) is not possible in the case of the data of Fig. 5 since (i) the changes of the average lifetime are small, only about 6 ps, (ii) the single-trap model is almost valid (i.e., the concentration of the \( V_{Si} \)-related defects is barely above the density limit of 10^{16} \text{ cm}^{-3}), and (iii) the differing position of the Fermi level may have an influence on the charge state of \( V_{Si} \)-related defects.

The annealing of samples grown under hydrocarbon poor conditions (type B) leads to the growth of the vacancy clusters, but the concentration of the smaller defects is not substantially changed. This suggests that in B-type material, the Si vacancies have transformed (or belong to) to more stable complexes, such as the \( V_{C}C_{Si} \), or divacancies, which remain as compensating centers after the annealing. It is also possible that the high resistivity of type B samples could also be dominated by the C vacancy, which is more stable than \( V_{Si} \) according to calculations.
V. CONCLUSIONS

Positron lifetime measurements in semi-insulating HTCVD SiC samples reveal vacancy clusters of the size of four to five missing atoms. Their charge state in the semi-insulating material is neutral. The clusters grow in size to about 30 missing atoms in postgrowth annealings at 1600 °C. Positron experiments also identify Si-vacancy-related smaller complexes, which are negatively charged. They partly disappear during annealing in materials grown under hydrocarbon rich conditions. After annealing, the materials become more n type, as part of the compensation is lost by the migration of Si-vacancy-related defects to (partially) increase the size of the open volume of clusters. Hence, our results suggest that the Si vacancy complexes act as compensating centers partly responsible for the insulating properties of high-purity HTCVD SiC. This conclusion is supported by the measurement of resistivity variations across a SiC wafer, which shows that concentration of the vacancy clusters anticorrelates with the resistivity.

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