EPR studies of the isolated negatively charged silicon vacancies in n-type 4H- and 6H-SiC: Identification of C3v symmetry and silicon sites

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I. INTRODUCTION

The isolated lattice vacancy is one of the most fundamental intrinsic defects in semiconductor crystals. In the structure determination at the atomic level, for which electron paramagnetic resonance (EPR) is the principal experimental tool, a sufficient concentration of vacancies is produced as radiation damages by irradiation with high energy electrons. The vacancy usually introduces electrical levels into the forbidden gap, and can exist in different charge states. The vacancy usually introduces electrical levels into the forbidden gap, and can exist in different charge states. The ground state is the orbitally nondegenerate $4T_{2g}$ state which is not subject to a Jahn-Teller distortion. The negatively charged silicon vacancy ($V_{Si}^{-}$) in the hexagonal lattices of $4H$- and $6H$-SiC has been studied by electron paramagnetic resonance (EPR). The local structure was suggested to have $T_d$ symmetry from the isotropic $g$ value within the resolution of the conventional X-band measurements, from the isotropic $^{29}$Si hyperfine interaction of the nearest-neighbor silicon atoms and from the absence of the zero-field splitting with the high spin state of $S=3/2$. From the $^{13}$C hyperfine spectrum of the nearest-neighbor carbon atoms, the two kinds of $V_{Si}^{-}$, denoted $V_{Si}^{-}(I)$ and $V_{Si}^{-}(II)$, respectively have been distinguished. $V_{Si}^{-}(I)$ and $V_{Si}^{-}(II)$ are assigned to be arising from hexagonal site ($h$) and quasicubic sites ($k$ in $4H$-SiC, $k_1$ and $k_2$ in $6H$-SiC), respectively. In both $V_{Si}^{-}(I)$ and $V_{Si}^{-}(II)$, from the $^{13}$C hyperfine interactions, the symmetry has been revealed to be $C_{3v}$ with the arrangement of the four nearest-neighbor carbon atoms slightly distorted from a regular tetrahedron.

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Since the central line of the fine structure was hidden underneath the strong signal of $V_{Si}$, the spin multiplicity of $S=3/2$ was determined by the nutation method of the pulsed EPR technique. The measurement of the $^{13}$C hyperfine interactions of the nearest-neighbor (NN) carbon atoms identified that the $T_{\nu_2\sigma}$ center is an analog of a single silicon vacancy and revealed that the arrangement of the NN carbon atoms is slightly distorted from a regular tetrahedron. The concentration of the $T_{\nu_2\sigma}$ center is lower by $\sim 40$ times than that of $V_{Si}$ in $n$-4H-SiC irradiated with 3-MeV electrons at 330 K. The symmetry lowering which is manifested in the ZFS is likely to be caused by a perturbation of the crystal field, presumably by the presence of an accompanying impurity or defect. The triply degenerate $4T_2$ state of an electronic configuration $a_1^e e^2$ under $T_d$ symmetry splits into $a_1^e e^2$ and $e^2 a_1^e$ by the distortion to $C_{3v}$. The high spin configuration $[a_1^e e^2$ or $e^2 a_1^e]$ which reduces the electron repulsion energy is preferred rather than the low spin configuration expected from the symmetry-lowering crystal field alone. The orbitally nondegenerate $4A_2$ which is not subject to a Jahn-Teller distortion is derived from the configurations $a_1^e e^2$ and $e^2 a_1^e$.

A small deviation from an ideal tetrahedron in the atomic arrangements of the $\text{SiC}_4$ tetrahedron in 4H- and 6H-SiC was revealed from the high-precision x-ray structure determination. The example of the $T_{\nu_2\sigma}$ center indicates that the spin quartet state of $V_{Si}$ in the hexagonal polytypes might not necessarily require the $T_d$ symmetry. In our present work, we have measured the angular dependence of the $^{13}$C ($I=1/2$, natural abundance 1.1%) hyperfine lines of the four NN atoms of $V_{Si}$ in 4H-SiC and in 6H-SiC, since the $^{13}$C hyperfine interactions are most crucial in a structural determination of the silicon vacancy. Wimbauer et al. reported the $^{13}$C hyperfine splittings of the NN atoms of $V_{Si}$ in 4H-SiC when the magnetic field is parallel to the $c$ axis ([0001] axis). They measured the angular dependence of the $^{13}$C hyperfine lines of a NN atom which is located along [0001] (to be denoted the axial carbon atom); however, the angular dependence of the $^{13}$C hyperfine lines of the three NN atoms in the basal plane (to be denoted basal carbon atoms) was not reported. We have revealed that the symmetry of $V_{Si}$ in both 4H-SiC and 6H-SiC is indeed $C_{3v}$ from the detailed measurements of the $^{13}$C hyperfine interaction of the NN atoms.

$\text{SiC}$ has many polytypes differing in the stacking sequence of Si-C bilayers. Technologically important polytypes are $3C\text{-},$ 4H-,$^,$ and 6H-SiC. In the cubic lattice of $3C\text{-SiC}$, each silicon and carbon has one site. In performing a detailed local structure determination of defects and impurities in the hexagonal ($nH\text{-})$SiC crystals, we need to consider that there are $n/2$ inequivalent sites for each silicon and carbon sublattice. In 4H-SiC, each silicon and carbon has two inequivalent sites with either a hexagonal ($h$) or quasicubic ($k$) character as shown in Fig. 1(a). In 6H-SiC, each silicon and carbon has one hexagonal ($h$) site and two quasicubic ($k_1$ and $k_2$) sites, as shown in Fig. 1(b). The identification of impurities at the inequivalent lattice sites is important because the properties, such as their energy levels in the band

![FIG. 1. (a) The crystal structure of 4H-SiC with the positions of the hexagonal ($h$) site and the quasicubic ($k$) site for silicon. (b) The crystal structure of 6H-SiC with the positions of the hexagonal ($h$) site and the two quasicubic ($k_1$ and $k_2$) sites for silicon. (c) Two magnetically distinguishable orientations of tetrahedron consisting of NN carbon atoms. The coordinate system used for the principal directions of the spin-Hamiltonian parameters and the magnetic field directions is included. $\theta$ is the angle from the [0001] axis. $\phi$ is the angle from the [1100] axis in the (0001) plane.](image)
the hexagonal site and \(V_{Si}^{-}(II)\) from \(V_{Si}^{-}\) at the quasicubic sites.

**II. EXPERIMENT**

The samples used in our experiments were single-crystalline \(n\)-type 4\(H\)- and 6\(H\)-SiC (Nippon Steel: nitrogen dopant) with the carrier concentrations of \(\sim 1 \times 10^{17}/\text{cm}^3\). The sample whose thickness is 1.5 mm was cut into the appropriate size (3 mm \(\times\) 15 mm) for our EPR measurements in the X band. The crystals of 4\(H\) - and 6\(H\)-SiC were irradiated by 3-MeV electrons with total fluencies of \(4 \times 10^{17}e/\text{cm}^2\) and \(1 \times 10^{19}e/\text{cm}^2\), respectively. The sample was placed on a water-cooled holder and was kept below 330 K during the electron irradiation. The samples of 4\(H\)-SiC were annealed at 573 K by a muffle furnace so as to decrease the interference with the unidentified signals. The line positions of the continuous wave (cw) EPR spectra were measured at room temperature on a Bruker Elexsys E500 X-band spectrometer by using the amplitude of 100-kHz field modulation of 0.01 mT. The \(^{13}\text{C}\) hyperfine lines of \(V_{Si}^{-}\) in 4\(H\)-SiC were measured with the microwave power of 0.2 \(\mu\text{W}\) by using the spherical cavity (Bruker ER4122SHQ, \(Q_L = 8600\), \(TE_{011}\) mode). The \(^{13}\text{C}\) hyperfine lines of \(V_{Si}^{-}\) in 6\(H\)-SiC were measured with the microwave power of 2 \(\mu\text{W}\) by using the optical transmission cavity (Bruker ER4104OR, \(Q_L = 4000\), \(TE_{102}\) mode). The calibration of the magnetic field was carried out by measuring simultaneously at room temperature the sample and the perylene cation in conc. \(\text{H}_2\text{SO}_4\) (\(g = 2.002569 \pm 0.000006\)) (Refs. 26 and 27) sealed in the capillary which was co-mounted with the sample. In estimating the spin concentration of \(V_{Si}^{-}\), the signal intensity obtained by double integration of the first derivative signal was compared with that of the EPR signal of \(^{3}\text{Cr}\) in the two magnetically distinguishable \(^{29}\text{Si}\) nuclei in 6\(H\)-SiC. In estimating the \(^{13}\text{C}\) hyperfine lines, two sets of four carbon atoms C1–C4 and C2–C4 were measured with an intensity ratio 1:1:1. Upon rotation with \(B_0\parallel [1\overline{1}00]\), the \(^{13}\text{C}\) hyperfine line of the basal carbon atoms splits into, at most, three lines with the intensity ratio 1:1:1. Upon rotation with \(B_0\parallel [1\overline{1}20]\), the \(^{13}\text{C}\) hyperfine line of the basal carbon atoms splits into four lines with an intensity ratio 1:2:2:1 at an arbitrary orientation. These patterns of the rotational plots of the line positions of the basal carbon atoms are similar whether the local arrangement of each of two sets of four carbon atoms C1–C4 and C1’–C4’ is an ideal tetrahedron or a slightly distorted tetrahedron with \(C_{3v}\) symmetry. In \(C_{3v}\) symmetry, the \(^{13}\text{C}\) hyperfine line of the axial carbon atoms and the basal carbon atoms are not symmetry related, it is expected that the principal values of \(A^{13}\text{C}\) should be different between the axial and basal carbon atoms. In the \(C_{3v}\) symmetry, the \(A^{13}\text{C}\) of the basal carbon atoms is nearly uniaxial. The principal axis with the largest principal value is, herein, termed the unique axis. In the \(C_{3v}\) symmetry, the unique axis is in a (1\overline{1}20) plane. An orientation which exhibits the maximum hyperfine splitting with the unique axis parallel to \(B_0\) is included in the rotation with \(B_0\parallel [1\overline{1}20]\). The minimum hyperfine splitting of the basal carbon atoms occurs either with \(B_0\) perpendicular to the unique axis in a (1\overline{1}20) plane or with \(B_0\parallel [1\overline{1}20]\). In the pattern of the rotational plots of the line positions, it is expected that the \(C_{3v}\) symmetry should be revealed by the difference in both the maximum hyperfine splitting and the minimum hyperfine splitting between the axial and the basal carbon atoms. The deviation from an ideal tetrahedron might be also evidenced by the deviation of the angle between the unique axis of \(A^{13}\text{C}\) of the basal atoms and the \(c\) axis ([0001]) from an ideal tetrahedral angle.

**I. 4\(H\)-SiC**

The EPR spectrum of the electron irradiated \(n\)-4\(H\)-SiC when the magnetic field is parallel to the \(c\) axis (\(B_0\parallel [0001]\)) is shown in Fig. 2. In the central part of the spectrum, the strong primary line labeled \(a\) with the linewidth \(\Delta B_{pp} = 0.022\text{ mT}\) of \(V_{Si}^{-}\) (\(g = 2.0028\)) (Ref. 13) is observed. The satellite lines labeled \(b\) and \(c\) arise from \(^{29}\text{Si}\) \((I = 1/2, \text{natural abundance } 4.6832\%)\) hyperfine interactions of NN nitrogen atoms, \(^{28}\text{Si}\) \((I = 1/2, \text{natural abundance } 98.96\%)\) hyperfine interactions of NNN nitrogen atoms, and \(c\) lines from the configurations with one \(^{29}\text{Si}\) nucleus in 12 silicon atoms of the NNN shell, and the \(c\) lines from the configurations with two \(^{28}\text{Si}\) nuclei in the NNN shell. The hyperfine splitting of 0.298 mT agrees with that was
reported. The relative intensity ratios of \( \frac{b}{a} \) and \( \frac{c}{a} \), 0.252 and 0.038, respectively, agree with those \( \approx 0.273 \) and \( \approx 0.037 \), respectively, calculated from the natural abundance of silicon isotopes. The spin concentration of \( \text{V}_{\text{Si}} \) was estimated to be \( 5 \times 10^{17} / \text{cm}^3 \).

In our spectrum shown in Fig. 2, the \( d \) and \( e \) lines correspond to the \( ^{13}\text{C} \) hyperfine lines from basal carbon atoms and axial carbon atoms, respectively. In our spectrum taken with a high resolution, we note that the \( d \) lines consist of two sets of lines labeled \( d_I \) and \( d_{II} \). Thus, we could resolve two kinds of \( \text{V}_{\text{Si}} \), to be denoted \( \text{V}_{\text{Si}}(I) \) and \( \text{V}_{\text{Si}}(II) \), respectively. At some orientations where the interfering signals did not overlap, it is noticeable that these \( ^{13}\text{C} \) hyperfine lines accompany weak satellite lines arising from the configurations with one \( ^{13}\text{C} \) atom in the NN shell and one \( ^{29}\text{Si} \) atom in the NNN shell, at the line positions of the same hyperfine splitting \( \approx 0.298 \text{ mT} \) and with the same relative intensity ratio \( \frac{b}{a} \) as the primary line \( a \).

Upon rotation with \( \theta = 112^\circ \), each of \( d_1 \) and \( d_{II} \) lines at \( \text{B}_{||}[0001] \) splits into three lines with the intensity ratio 1:1:1. (labeled \( f_1, g_1, \) and \( h_1 \) for the three lines from \( d_1 \), and \( f_{II}, g_{II}, \) and \( h_{II} \) for the three lines from \( d_{II} \), respectively). In the spectrum with the rotation angle \( 75^\circ \) from [0001] shown in Fig. 3, the low field components of the satellite lines (labeled \( f'_1 \) and \( f'_{II} \), respectively) corresponding to \( b \) lines of the primary line \( a \) are noticed in both \( f_1 \) and \( f_{II} \) lines. This orientation is a typical example that has been used to estimate...
with filled triangles shown in Fig. 6. In Figs. 5 and 6, each of the points marked corresponding to intensity ratio 2:4. The sets with the larger intensity are large hyperfine lines measured upon rotation with line does consist of two lines denoted unidentified centers.

The angular dependence of the line positions of \( ^{13} \text{C} \) hyperfine line of axial carbon atoms labeled \( e \) exhibit the minimum hyperfine splitting and the basal carbon atoms labeled \( g \) exhibit the minimum one of the rotation with \( \mathbf{B}_{0}[1\overline{1}00] \), their line positions do not superimpose (Fig. 5). Both the number of equivalent carbon atoms at special orientations and the pattern of the roadmap obtained by the angular dependence of the line positions indicate that both \( V_{S_i}(I) \) and \( V_{S_i}(I) \) do have \( C_{3v} \) symmetry.

The signal intensity ratios of the axial (the \( e \) line at \( \mathbf{B}_{0}[0001] \)) and the basal (the \( d_{1} \) and \( d_{II} \) lines at \( \mathbf{B}_{0}[0001] \) \( ^{13} \text{C} \) hyperfine lines with respect to the primary line (a) are shown in Table I. The values listed as the observed ratios were obtained as the average among the ratios measured at several orientations where the \( ^{13} \text{C} \) hyperfine lines were relatively free from the interference of the unidentified signals.

2. 6H-SiC

The EPR spectrum of \( V_{S_i} \) in the electron irradiated \( n \)-type 6H-SiC when the magnetic field is parallel to the \( c \) axis (\( \mathbf{B}_{0}[0001] \)) is shown in Fig. 7. The spin concentration of \( V_{S_i} \) was estimated to be \( 1 \times 10^{18} \text{cm}^{-3} \). In the central part of the spectrum, the strong primary line labeled (a) (the linewidth \( \Delta B_{pp} = 0.030 \text{ mT} \) accompanied with the characteristic satellite lines labeled \( b \) and \( c \) arising from the \( ^{29} \text{Si} \) hyperfine interactions of NNN atoms is observed. The \( g \) value was determined to be \( 2.0028 \pm 0.0001 \), that is the same as that of \( V_{S_i} \) in 4H-SiC.
As for the $^{13}$C hyperfine lines of the NN carbon atoms, Schneider et al. reported the $c$ axis splitting for the axial and the basal carbon atoms. In Fig. 7, the $^{13}$C hyperfine lines arising from the axial carbon atoms are labeled $e$. Likewise, in $4H$-SiC, the $^{13}$C hyperfine lines arising from the basal carbon atoms are resolved into two sets labeled $d_{I}$ and $d_{II}$, respectively. Thus, our high resolution $^{13}$C hyperfine spectra taken with the magnetic field modulation of 0.01 mT could distinguish two kinds of $V_{Si}^{2}$, to be denoted $V_{Si}^{2}(I)$ and $V_{Si}^{2}(II)$, respectively.

The EPR spectra were recorded at 2.5° intervals with the crystal rotated around $\theta$, $\phi=90^\circ$, $\theta=0^\circ$ for $B_0||[001]$ and $\theta=90^\circ$ for $B_0||[1120]$. The filled triangles and the filled squares represent the resonant primary lines and the axial $^{13}$C hyperfine lines, respectively. The filled and open circles represent the $^{13}$C hyperfine lines of the basal carbon atoms of $V_{Si}^{2}(I)$ and those of $V_{Si}^{2}(II)$, respectively.

As for the $^{13}$C hyperfine lines of the NN carbon atoms, Schneider et al. reported the $c$ axis splitting for the axial and the basal carbon atoms. In Fig. 7, the $^{13}$C hyperfine lines arising from the axial carbon atoms are labeled $e$. Likewise, in $4H$-SiC, the $^{13}$C hyperfine lines arising from the basal carbon atoms are resolved into two sets labeled $d_{I}$ and $d_{II}$, respectively. Thus, our high resolution $^{13}$C hyperfine spectra taken with the magnetic field modulation of 0.01 mT could distinguish two kinds of $V_{Si}^{2}$, to be denoted $V_{Si}^{2}(I)$ and $V_{Si}^{2}(II)$, respectively.

The EPR spectra were recorded at 2.5° intervals with the crystal rotated around [1 $\bar{1}$00], with $B_0\perp[1 0 0]$ at room temperature. The angular dependence of the line positions of the $^{13}$C hyperfine lines is shown in Fig. 8. Each point represents the line position observed. In the rotation with $B_0\perp[1 0 0]$, each of $d_{I}$ and $d_{II}$ line at $B_0||[001]$ splits into three lines at an arbitrary angle. In the rotation with $B_0\perp[1 0 0]$, the $e$ line could not be resolved into two lines corresponding to $V_{Si}^{2}(I)$ and $V_{Si}^{2}(II)$. In obtaining the EPR parameters from the fitting of the line positions, we assumed that the $e_{I}$ and $e_{II}$ lines superimposed. The signal intensity ratios of the axial and the basal $^{13}$C hyperfine lines with respect to the primary line are included in Table I.

### Table I. The signal intensity ratio of the $^{13}$C hyperfine lines of the NN carbon atoms compared to the primary line.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Carbons</th>
<th>Axial $^{13}$C</th>
<th>Basal $^{13}$C</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$4H$-SiC</td>
<td>$V_{Si}^{2}$</td>
<td>0.005</td>
<td>0.015</td>
<td>Ref. 8</td>
</tr>
<tr>
<td></td>
<td>$V_{Si}^{2}(I, II)$</td>
<td>0.005</td>
<td>0.015</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>I</td>
<td>0.002±0.001</td>
<td>0.005±0.002</td>
<td></td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>0.002±0.001</td>
<td>0.007±0.002</td>
<td></td>
</tr>
<tr>
<td>$3C$-SiC</td>
<td>$V_{Si}^{2}$</td>
<td>0.022</td>
<td>0.018±0.005</td>
<td>Ref. 5</td>
</tr>
<tr>
<td>$6H$-SiC</td>
<td>$V_{Si}^{2}(I, II)$</td>
<td>0.005</td>
<td>0.004±0.002</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>I</td>
<td>0.003±0.002</td>
<td>0.009±0.002</td>
<td></td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>0.007±0.002</td>
<td>0.007±0.002</td>
<td></td>
</tr>
</tbody>
</table>

FIG. 7. The EPR spectrum of the electron-irradiated $n$-type $6H$-SiC taken with the magnetic field along the [0001] axis at room temperature. The microwave frequency, the microwave power, and the amplitude of the 100-kHz field modulation were 9.424 GHz, 2 $\mu W$, and 0.01 mT, respectively. The lower spectrum is the expanded spectrum.

FIG. 8. Angular dependence of the line positions of $V_{Si}^{2}$ in $6H$-SiC. The crystal was rotated with the magnetic field in the ($\bar{1}100$) plane. In the magnetic field direction ($\theta, \phi=90^\circ$), $\theta=0^\circ$ for $B_0||[001]$ and $\theta=90^\circ$ for $B_0||[1120]$. The filled triangles and the filled squares represent the resonant primary lines and the axial $^{13}$C hyperfine lines, respectively. The filled and open circles represent the $^{13}$C hyperfine lines of the basal carbon atoms of $V_{Si}^{2}(I)$ and those of $V_{Si}^{2}(II)$, respectively.

B. EPR parameters

The spin Hamiltonian parameters were obtained by fitting observed field strengths and microwave frequencies to the spin Hamiltonian,

$$H_S = \beta_e \tilde{S} \cdot g \cdot B + \tilde{S} \cdot D \cdot S + \tilde{S} \cdot A_{I}^{13C} I - g_{\alpha^{13C}} \beta_\alpha I \cdot B. \quad (1)$$
where electron spin $S = 3/2$ and $^{13}$C nuclear spin $I = 1/2$. $\beta_v$ is the Bohr magneton and $\beta_n$ is the nuclear magneton. The nuclear Zeeman matrix was taken as isotropic ($g_{n^{13}C} \approx 1.40483$). $g$, $D$, and $A$ denote the $g$ matrix, the ZFS tensor, and the hyperfine matrix, respectively. The ZFS matrix $D$ was set to zero matrix $O$. The least squares fitting was carried out by using computer program EPR.FOR in which the resonant magnetic fields are calculated by the exact diagonalization of the spin Hamiltonian matrix. The spin Hamiltonian parameters were obtained by using a crystal coordinate system in which the $z$ axis is $[0001]$ and the $x$ axis is $[1\bar{1}00]$. It should be noted that one rotation with $B_0$ in the $(1\bar{1}00)$ plane or in the $(1\bar{1}20)$ plane is sufficient to determine $A^{13}$C of the axial carbon atom C1 when the symmetry of the vacancy belongs to the $C_{3v}$ point group. In the case of the basal carbon atoms, $A^{13}$C of C2 which is one particular carbon atom located on $(1\bar{1}20)$ plane can be determined by applying the appropriate symmetry transformations to utilize the line positions of other carbon atoms as the line positions of C2 that should be obtained by the rotation in different planes. Thus, $A^{13}$C of the basal carbon atom C2 can be determined from one rotation with $B_0$ in the $(1\bar{1}00)$ plane or in the $(1\bar{1}20)$ plane. By applying the appropriate symmetry transformations, the parameters belonging to other basal carbon atoms can be obtained. For obtaining $A^{13}$C(C1) and $A^{13}$C(C2) of both $V_{\bar{S}1}(I)$ and $V_{\bar{S}1}(II)$ in 4$H$-SiC, we used the line positions of both the rotation with $B_{0\parallel}[1\bar{1}00]$ and that with $B_{0\perp}[1\bar{1}20]$. For obtaining $A^{13}$C(C1) and $A^{13}$C(C2) of both $V_{\bar{S}1}(I)$ and $V_{\bar{S}1}(II)$ in 6$H$-SiC, we used the line positions of the rotation with $B_{0\parallel}[1\bar{1}00]$. For the least squares fitting, the line positions read from the spectra taken at every 2.5° were used.

The $g$ matrix was obtained from the fitting of the primary lines. In both $V_{\bar{S}1}(I)$ and $V_{\bar{S}1}(II)$ in both 4$H$-SiC and 6$H$-SiC, the $g$ matrix was isotropic within a relative accuracy of 0.0001. Recently, the difference in $g$ value between $V_{\bar{S}1}$ at the quasicubic site ($g(k) = 2.0032$, isotropic) and $V_{\bar{S}1}$ at the hexagonal site ($g(h) - g(\bar{h}) = 0.00002$) in 4$H$-SiC was resolved by the measurement at the $W$ band (95 GHz). The maximum difference in the line positions ($g(k) - g(\bar{h}) = 0.00004$) is estimated to be 0.0066 mT at the $X$ band which is much smaller than the linewidth ($\Delta B_{pp} = 0.022$ mT at $B_0[0001]$).

The EPR parameters obtained from the fitting of the line positions of 4$H$- and 6$H$-SiC are summarized in Table II. The root-mean-square (rms) error estimates for principal values and principal directions are included. The solid curves in Figs. 5, 6, and 8 are calculated by using the parameters obtained. In Table II, the number of measured line positions used and the rms field deviations (mT) achieved are listed for each fitting of the axial $^{13}$C hyperfine lines of $V_{\bar{S}1}(I)$, the basal $^{13}$C hyperfine lines of $V_{\bar{S}1}^-(I)$, the axial $^{13}$C hyperfine lines of $V_{\bar{S}1}(II)$, and the basal $^{13}$C hyperfine lines of $V_{\bar{S}1}(II)$.

In Table II, the reported values of $A^{13}$C of $V_{\bar{S}1}$ in 4$H$-SiC (Ref. 8) are included. It should be noted that the averaged value ($A^{13}$C$_{\parallel} = 80.1$ MHz and $A^{13}$C$_{\perp} = 34.0$ MHz) of $A^{13}$C(C1) of $V_{\bar{S}1}(I)$ and $A^{13}$C(C1) of $V_{\bar{S}1}(II)$ obtained in this work is in good agreement with the reported values ($A^{13}$C$_{\parallel} = 80.1$ MHz and $A^{13}$C$_{\perp} = 33.9$ MHz).

C. Structure and silicon sites of $V_{\bar{S}1}$

The wave function of the unpaired electron is described by a linear combination of atomic orbitals (LCAO) approximation

$$\Psi = \sum_i \eta_i (\alpha_i \varphi_{nx} + \beta_i \varphi_{np}),$$

where the summation is over the surrounding carbon ($ns, np$: $2s, 2p$) and silicon ($ns, np$: $3s, 3p$) atoms on which the unpaired electrons are delocalized. The fractional unpaired electron population ($\eta^2_i$) on the atom concerned and the hybrid ratio ($\beta_i^2/\alpha_i^2$, where $\alpha_i^2 + \beta_i^2 = 1$) are estimated from the hyperfine parameters. In the estimation ($\eta^2_i \alpha_i^2 \alpha_0 = A_{iso}$, $\eta_i^2 \beta_i^2 \beta_0 = A_{aniso}$), we used $\alpha_0 = 3776.92$ MHz, and $\beta_0 = 107.39$ MHz for $^{13}$C. The results are listed in Table III. In the wave function of the unpaired electron of $V_{\bar{S}1}$ of 4$H$-SiC, the fraction which localizes on the four NN carbon atoms is 63.4% and 66.3% for $V_{\bar{S}1}(I)$ and $V_{\bar{S}1}(II)$, respectively. In the wave function of the unpaired electron of $V_{\bar{S}1}$ of 6$H$-SiC, the fraction which localizes on the four NN carbon atoms is 63.6% and 65.1% for $V_{\bar{S}1}(I)$ and $V_{\bar{S}1}(II)$, respectively. As for the 12 NNN silicon atoms, the hyperfine splitting observed as the satellite lines of the primary line was isotropic within the resolution of our measurements and the anisotropic part which is arising from the contribution of $3p$ orbital could not be measured. In $V_{\bar{S}1}$ of both 4$H$-SiC and 6$H$-SiC, the sum of the contribution of the $3s$ orbital of 12 NNN silicon atoms is estimated to be 2.3% by using $a_0 = -4594.12$ MHz for $^{29}$Si.

From the pattern of the rotational plots, it is determined that both $V_{\bar{S}1}(I)$ and $V_{\bar{S}1}(II)$ in both 4$H$-SiC and 6$H$-SiC have a $C_{3v}$ symmetry. With a $C_{3v}$ symmetry, the axial carbon atom and basal carbon atom are not symmetry related. The deviation from an ideal tetrahedral symmetry is confirmed by the fact that, as seen from Table II, the principal values of $A^{13}$C(C1) are not the same as the principal values of $A^{13}$C(C2). From the small difference of the principal values of $A^{13}$C between the axial carbon atoms and the basal carbon atoms, it is inferred that the distortion of the structure from $T_d$ to $C_{3v}$ is considered to be very small. The polar angle $\theta$ of the unique axis of the $^{13}$C hyperfine matrix of basal carbon atoms, 110.0°, 110.0°, 109.2°, and 109.1° for $V_{\bar{S}1}(I)$ in 4$H$-SiC and in 6$H$-SiC and $V_{\bar{S}1}(II)$ in 4$H$-SiC and in 6$H$-SiC, respectively, is deviated from an ideal tetrahedral angle (109.47°). The $^{13}$C hyperfine spectra confirm that the NN atoms are four carbon atoms arranged in a configuration close to regular tetrahedron and that these carbon atoms have a relatively large spin density. We note that the contribution to the wave function of the unpaired electron from the atomic orbital of carbon is almost purely $p$, as shown in Table III. The dominant structure relaxation in $V_{\bar{S}1}$ is likely to be outward displacements of the NN atoms.
TABLE II. EPR parameters of the negatively charged silicon vacancies in SiC.

<table>
<thead>
<tr>
<th>Polytype</th>
<th>g</th>
<th>Principal values (MHz)</th>
<th>Principal directions</th>
<th>N(^a)</th>
<th>rms(^b) (mT)</th>
<th>Comment</th>
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<tbody>
<tr>
<td>4H-SiC</td>
<td></td>
<td>(V_{\text{Si}})</td>
<td>(A_1C(1)=80.1) (A_1C(1)=33.9)</td>
<td></td>
<td></td>
<td>Ref. 8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(V_{\text{Si}}(I))</td>
<td>(A_1C(1)=80.2\pm0.1) (A_1C(1)=33.2\pm0.1)</td>
<td></td>
<td></td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(V_{\text{Si}}(II))</td>
<td>(A_1C(1)=76.3\pm0.1) (A_1C(1)=28.3\pm0.1)</td>
<td></td>
<td></td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(T_{\nu2\sigma})</td>
<td>(A_1C(1)=80.3\pm0.1) (A_1C(1)=34.8\pm0.2)</td>
<td></td>
<td></td>
<td>Ref. 13</td>
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<tr>
<td>6H-SiC</td>
<td></td>
<td>(V_{\text{Si}}(I))</td>
<td>(A_1C(1)=80.0\pm0.1) (A_1C(1)=32.8\pm0.1)</td>
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<tr>
<td></td>
<td></td>
<td>(V_{\text{Si}}(II))</td>
<td>(A_1C(1)=75.8\pm0.1) (A_1C(1)=28.4\pm0.1)</td>
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<tr>
<td>3C-SiC</td>
<td></td>
<td>(V_{\text{Si}})</td>
<td>(A_1C(1)=80.4) (A_1C(1)=33.0)</td>
<td></td>
<td></td>
<td>Ref. 5</td>
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\(a\)The number of the measured line positions.  
\(b\)Root-mean-square field deviation.  
\(c\)In our work, the \(g\) value was determined by measuring simultaneously with the reference sample.

While the \(C_{3v}\) symmetry is revealed by the \(^{13}\)C hyperfine interactions of the NN atoms, the ZFS has not been observed by conventional, cw EPR technique. By using the nutation method of pulsed EPR technique, the presence of ZFS in \(V_{\text{Si}}\) in 4H-SiC was revealed.\(^{13}\) We showed that the primary line of \(V_{\text{Si}}\) in 4H-SiC consists of all three \(\Delta M_S=\pm1\) transitions of \(S=3/2\) of non-distorted configuration and \(|S,M_S|=|3/2, 1/2\rangle\leftrightarrow|3/2, -1/2\rangle\) transition of slightly distorted configuration. The nutation frequency of non-distorted configuration of which three \(\Delta M_S=\pm1\) transitions are superimposed or are located within the extent of the excitation bandwidth of the microwave pulse (\(B_1\approx0.3\) mT) is \(\omega_1=g\beta_eB_1/h\). The nutation frequency of slightly distorted configuration is \(2\omega_1\) since only \(|3/2, 1/2\rangle\leftrightarrow|3/2, -1/2\rangle\) transition is excited by the microwave pulse with the \(|3/2, \pm3/2\rangle\leftrightarrow|3/2, \pm1/2\rangle\) transitions being located away from the \(|3/2, 1/2\rangle\leftrightarrow|3/2, -1/2\rangle\) transition by at least \(\sim B_1\) due to the ZFS. In slightly distorted configuration, the \(|3/2, \pm3/2\rangle\leftrightarrow|3/2, \pm1/2\rangle\) transitions which are likely to be broadened by a distribution of ZFS presumably due to local strains are too broad to be observed as separate signals. Thus, the magnitude of ZFS is distributed from a value smaller than \(B_1\) to one larger than \(B_1\). The criterion of whether configurations are nondistorted or distorted in the nutation experiments depends on the relative magnitude between \(|D|\) and \(B_1\).

In 4H-SiC, there are two types of silicon sites, one with
TABLE III. Hyperfine and orbital parameters of $V_{Si}$

<table>
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<tr>
<th></th>
<th>$A_{iso}$ (MHz)</th>
<th>$A_{aniso}$ (MHz)</th>
<th>$\eta^2$</th>
<th>$\beta^2\alpha'^2$</th>
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<tr>
<td>4H-SiC</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>$^{13}$C(C1):I</td>
<td>48.9±0.4</td>
<td>15.7±0.4</td>
<td>0.159</td>
<td>11.3</td>
</tr>
<tr>
<td>$^{13}$C(C1):II</td>
<td>49.2±0.4</td>
<td>15.7±0.4</td>
<td>0.159</td>
<td>11.2</td>
</tr>
<tr>
<td>$^{13}$C(C2):I</td>
<td>44.3±0.4</td>
<td>16.0±0.4</td>
<td>0.161</td>
<td>12.7</td>
</tr>
<tr>
<td>$^{13}$C(C2):II</td>
<td>47.3±0.4</td>
<td>16.0±0.4</td>
<td>0.162</td>
<td>11.9</td>
</tr>
<tr>
<td>6H-SiC</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{13}$C(C1)</td>
<td>48.5±0.2</td>
<td>15.7±0.2</td>
<td>0.159</td>
<td>11.4</td>
</tr>
<tr>
<td>$^{13}$C(C2)</td>
<td>44.2±0.2</td>
<td>15.8±0.2</td>
<td>0.159</td>
<td>12.6</td>
</tr>
<tr>
<td>$^{13}$C(C2):II</td>
<td>47.8±0.2</td>
<td>16.3±0.2</td>
<td>0.164</td>
<td>12.0</td>
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</table>

hexagonal character ($h$) and the other with cubic character ($k$), with the population ratio of 1:1. In 6H-SiC, there are three types of silicon sites, one with a hexagonal character ($h$) and the other two with a cubic character ($k_1$, $k_2$), with the population ratio of 1:1:1. Now, we assign the $V_{Si}$ spectra to these inequivalent silicon sites. In both 4H-SiC and 6H-SiC, the difference in the principal values between $^{13}$C(C1) and $^{13}$C(C2) is smaller in $V_{Si}(II)$ than in $V_{Si}(I)$. The polar angle $\theta$ of the unique axis of $^{13}$C(C2) is closer to tetrahedral angle (109.47°) in $V_{Si}(II)$ (109.2° in 4H-SiC and 109.1° in 6H-SiC) than in $V_{Si}(I)$ (110.0° in 4H-SiC and 110.0° in 6H-SiC). Therefore, the deviation from an ideal tetrahedron is smaller in $V_{Si}(II)$ than in $V_{Si}(I)$. It is likely that the vacancy at the hexagonal silicon site should be more distorted than the vacancy at the quasicubic silicon site. As seen from Figs. 2–4, the concentration ratio $[V_{Si}(II)]/[V_{Si}(I)]$ in 4H-SiC obtained from the intensity ratio between the corresponding!$^{13}$C hyperfine lines ($d_H/d_1$, $e_H/e_1$, $f_H/f_1$, $g_H/g_1$, and $j_H/j_1$) is ~1.4. The concentration ratio $[V_{Si}(II)]/[V_{Si}(I)]$ in 6H-SiC obtained from the intensity ratio between the corresponding $^{13}$C hyperfine lines of the basal carbon atoms ($d_H/d_1$ in the case of the c axis spectrum shown in Fig. 7) is ~3.0. Since the deviation from an ideal tetrahedron of $V_{Si}(I)$ is larger than that of $V_{Si}(II)$, and since the concentration ratio $[V_{Si}(II)]/[V_{Si}(I)]$ in 6H-SiC is nearly twelve as large as that in 4H-SiC, we assume that $V_{Si}(I)$ and $V_{Si}(II)$ are vacancies at the hexagonal silicon site and at quasicubic site(s), respectively. In the case that the EPR spectra of impurities at all three different sites of 6H-SiC are resolved, the difference of the EPR parameters between the hexagonal and quasicubic sites is much larger than that between two quasicubic sites.9,16–24 In our case of $V_{Si}$ in 6H-SiC, the difference of the EPR parameters between the two quasicubic sites was too small to be resolved by cw EPR method. In Table II, $^{13}$C of $V_{Si}$ in 3C-SiC5 and $^{13}$C(C1) and $^{13}$C(C2) of $T_{V_{Si}}$ in 4H-SiC (Ref. 13) are included. The $^{13}$C hyperfine matrix of the basal carbon atoms $^{13}$C(C2) of $V_{Si}(II)$ in 4H- and 6H-SiC is closer to that of $V_{Si}$ in 3C-SiC than that of $V_{Si}(I)$ in 4H- and 6H-SiC. This fact supports the assignment that $V_{Si}(I)$ is at hexagonal silicon site and $V_{Si}(II)$ is at quasicubic site(s). The $^{13}$C hyperfine matrices of the axial carbon atoms $^{13}$C(C1) are similar among $V_{Si}$ in 3C-SiC, $V_{Si}(I, II)$ in 4H- SiC, $V_{Si}(I, II)$ in 6H-SiC, and $T_{V_{Si}}$ in 4H-SiC. From the similarity of $^{13}$C(C1) and $^{13}$C(C2) between $T_{V_{Si}}$ and $V_{Si}(I, II)$, the arrangement of four carbon atoms around the vacancy in $T_{V_{Si}}$ is similar to that of the isolated negatively charged vacancy $V_{Si}(I, II)$. Thus, the small ZFS of $T_{V_{Si}}$ is ascribed to additional symmetry-lowering crystal field caused by possible presence of an accompanying nonparamagnetic impurity or defect located at some distance along [0001].13

From the $^{13}$C hyperfine interaction of the NN carbon atoms, the symmetries of $V_{Si}(I)$ and $V_{Si}(II)$ both in 4H-SiC and in 6H-SiC are determined to be $C_{3v}$. Under $T_d$ symmetry, the high spin ground state $^4A_2$ ($S=3/2$) arises from electronic configuration $a_1^2e^2$. Under the $C_{3v}$ symmetry, the $t_2$ triplet splits into $a_1^2$ and a doublet $e$. The high spin ground state $^4A_2$ ($S=3/2$) is an orbitally non-degenerated state free from Jahn-Teller distortion is derived from the configurations ($a_1^2$) $e^2$ and $e^2$ ($a_1^2$).13,32 So far, the single vacancies which have $S=3/2$ ground state are limited to those having $T_d$ symmetry except $T_{V_{Si}}$ in 4H-SiC.13 The lowering of the crystal field in $T_{V_{Si}}$ was ascribed to the possible presence of an impurity or defect at some distance along [0001]. In our present work, it is revealed that isolated vacancy $V_{Si}$ in the hexagonal lattices of 4H-SiC and 6H-SiC does have $S=3/2$ ground state although with $C_{3v}$ symmetry. Thus, threefold degenerate $t_2$ state under tetrahedral symmetry is not necessarily required to attain the high spin configuration of $S=3/2$. Our example in which three parallel spins are occupied in $a_1^2$ and $e$ under $C_{3v}$ symmetry demonstrates the important role of electron-electron interaction in determining the electronic state of vacancies of wide-gap semiconductor crystals such as SiC.

The intensity ratio of the $^{13}$C hyperfine line relative to the primary line listed in Table I is slightly smaller than that is calculated from the natural abundance of $^{13}$C. In $V_{Si}(I, II)$ in 4H-SiC, the ratio $[V_{Si}(II)]/[V_{Si}(I)]$ obtained from the $^{13}$C hyperfine lines of the axial carbon atoms is slightly smaller than that obtained from the $^{13}$C hyperfine lines of the basal carbon atoms. The concentration ratio $[V_{Si}(II)]/[V_{Si}(I)]$ was obtained as the average among the peak height ratios at several orientations. For the axial carbon atoms of $V_{Si}(I, II)$ in 4H-SiC, the number of orientations where the $^{13}$C hyperfine lines of $V_{Si}(I)$ and $V_{Si}(II)$ are resolved is limited. Since the signals from non-identified centers interfered with the weak $^{13}$C hyperfine lines at several orientations and moreover the splitting of the line positions between $V_{Si}(I)$ and $V_{Si}(II)$ is small, measuring the $^{13}$C hyperfine lines accurately was not easy. The fact that the ratio $[V_{Si}(II)]/[V_{Si}(I)]$ obtained from the $^{13}$C hyperfine lines of the basal carbon atoms in 4H-SiC (1.4) is larger than that is calculated from the population ratio of silicon atoms between hexagonal and cubic sites (1.0) might suggest the difference in thermal stability between $V_{Si}(I)$ and $V_{Si}(II)$. Even if the ZFS is vanishing, the high spin state might be detected by the splitting of hyperfine lines in the cw EPR measurements. From the second order perturbation treatment, the line position $B$ of the $[S, M_S\rightarrow 1, m_1] \leftrightarrow [S, M_S, m_1]$ transition is given as.

165206-9
$$\begin{align*}
g \beta_B &= h \nu + K m_1 + \frac{1}{2h \nu} \left( |A_1|^2 m_1^2 + A_2 m_1 (2M_S - 1) + \frac{1}{2} A_3 (m_1 I_1 - m_1^2) \right).
\end{align*}$$

Details of the coefficients in Eq. (3) are given in the Appendix. In the case of $S = 3/2$, it is expected that the hyperfine line should split into three lines. However, in our case, the maximum magnitude of the splitting is estimated to be 0.005 mT which is smaller than the linewidth (0.022 mT in 4H-SiC and 0.030 mT in 6H-SiC).

**IV. SUMMARY**

The angular dependence of the $^{13}$C hyperfine lines of the isolated negatively charged vacancy ($V_{Si}^-$) in electron-irradiated 4H-SiC and 6H-SiC has been measured by the X-band cw EPR method. In both 4H-SiC and 6H-SiC, two kinds of $V_{Si}^-$, denoted $V_{Si}^-(I)$ and $V_{Si}^-(II)$, respectively, have been distinguished. The $C_{3v}$ symmetry with the arrangement of the four nearest-neighbor carbon atoms slightly distorted from a regular tetrahedron has been revealed in both $V_{Si}^-(I)$ and $V_{Si}^-(II)$.

From the difference in the degree of distortion from an ideal regular tetrahedron between $V_{Si}^-(I)$ and $V_{Si}^-(II)$ and from the difference in the concentration ratio [$V_{Si}^-(II)$]/[$V_{Si}^-(I)$] between 4H-SiC and 6H-SiC, $V_{Si}^-(I)$ and $V_{Si}^-(II)$ are assigned to be arising from hexagonal site ($h$) and quasicubic site(s) ($k$ in 4H-SiC, $k_1$ and $k_2$ in 6H-SiC), respectively. By revealing the $C_{3v}$ symmetry of the isolated vacancy with $S=3/2$, the important role of electron-electron interaction to attain the high spin configuration is demonstrated.

**ACKNOWLEDGMENTS**

This work was performed under the management of FED as a part of the METI Project (R&D of Ultra-Low-Loss Power Device Technologies) supported by NEDO.

**APPENDIX**

The coefficients in Eq. (3) are given as follows:

$$|A_1|^2 = (\mathbf{k} \cdot \mathbf{A} \cdot \mathbf{A}\cdot \mathbf{k}) - K^2, \quad (A1)$$

$$A_2 = \text{det} \mathbf{A}/K, \quad (A2)$$

$$A_3 = \text{Tr} \mathbf{A} \cdot \mathbf{A} - (\mathbf{k} \cdot \mathbf{A} \cdot \mathbf{A} \cdot \mathbf{k}), \quad (A3)$$

$$k = \mathbf{A} \cdot \mathbf{g} \cdot \mathbf{h}/gK, \quad (A4)$$

$$K^2 = \mathbf{h} \cdot \mathbf{g} \cdot \mathbf{A} \cdot \mathbf{g} \cdot \mathbf{h}/g^2, \quad (A5)$$

$$g = \mathbf{h} \cdot \mathbf{g} \cdot \mathbf{A} \cdot \mathbf{h}. \quad (A6)$$

The symbols $\mathbf{A}$, $\mathbf{g}$, and $\mathbf{h}$ represent the hyperfine matrix, the $g$ matrix, and the unit vector that is parallel to the static field $\mathbf{B}$, respectively. The $\text{det} \mathbf{A}$ in Eq. (A2) and the $\text{Tr} \mathbf{A}$ in Eq. (A3) indicate the determinant of $\mathbf{A}$ and the trace of $\mathbf{A}$, respectively.

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*To whom correspondence should be addressed.
10 Among the terms which induce the zero-field splitting (ZFS), $S^4$ terms are not allowed in the spin Hamiltonian of $S=3/2$. Since each term must be invariant under the point symmetry operations, there are no $S^2$ terms for cubic symmetry. Thus, ZFS vanishes for $S=3/2$ in the tetrahedral symmetry, see The Physical Principles of Electron Paramagnetic Resonance (Ref. 11).
21 A.V. Duijn-Arnold, R. Zondervan, J. Schmidt, P.G. Baranov,