EPR identification of intrinsic defects in SiC

J. Isoya¹, T. Umeda¹, N. Mizuochi¹, N. T. Son², E. Janzén³, and T. Ohshima³

¹ University of Tsukuba, Tsukuba 305-8550, Japan
² Department of Physics, Chemistry and Biology, Linköping University, 581 83 Linköping, Sweden
³ Japan Atomic Energy Agency, Takasaki 370-1292, Japan

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The structure determination of intrinsic defects in 4H-SiC, 6H-SiC, and 3C-SiC by means of EPR is based on measuring the angular dependence of the $^{29}$Si/$^{13}$C hyperfine (HF) satellite lines, from which spin densities, sp-hybrid ratio, and p-orbital direction can be determined over major atoms comprising a defect. In most cases, not only the assignment of the variety due to the inequivalent sites ($h$- and $k$-sites in 4H-SiC) but also the identification of the defect species is accomplished through the comparison of the obtained HF parameters with those obtained from first principles calculations. Our works of identifying vacancy-related defects such as the monovacancies, divacancies, and antisite-vacancy pairs in 4H-SiC are reviewed. In addition, it is demonstrated that the observation of the central line of the $T_{V_{24}}$ center of $S = 3/2$ has been achieved by pulsed-ELDOR.

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1 University of Tsukuba, Tsukuba 305-8550, Japan
2 Department of Physics, Chemistry and Biology, Linköping University, 581 83 Linköping, Sweden
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1 Introduction

Electron paramagnetic resonance (EPR) has been proved to be the most successful technique in identifying deep centers in silicon. The abundance of isotopes with non-zero nuclear spin (29Si, I = 1/2, natural abundance 4.67%) is just right to keep the linewidth narrow enough for sufficient sensitivity and resolution and to observe the satellite lines due to hyperfine (HF) interactions easily. EPR has been also powerful in identifying point defects in diamond which supply smaller linewidth, although 13C (I = 1/2, 1.11%) enriched crystals were crucial for the identification in several cases [1–4]. As demonstrated typically by negatively charged vacancies [1, 5, 6] lattice relaxations involved in intrinsic defects are significantly different between silicon and diamond. The energy gap of SiC (Eg = 3.28 eV for 4H-SiC) is between that of silicon (Eg = 1.12 eV) and diamond (Eg = 5.47 eV). Thus, it is expected that the comparison of the same defect among silicon, diamond, and SiC should be useful for understanding the reconstruction of structure relaxations involved in intrinsic defects. Moreover, SiC is richer in the variety of intrinsic defects arising from two sublattices (Si and C), abundant polytypes (3C-, 4H-, and 6H-SiC), and the presence of defects specific in compound semiconductors such as antisites (SiC, C) and antisite-vacancy pairs. SiC is unique among compound semiconductors in having narrow EPR linewidths (∆Bpp ∼ 0.03 mT) and non-zero nuclear spin isotopes with reasonable (29Si, 4.7%) and tolerable (13C, 1.1%) natural abundance.

SiC is a promising semiconductor material for high-power, high-temperature, and radiation-tolerant devices. High-purity semi-insulating (SI) substrates are attained by utilizing intrinsic defects [7, 8]. To improve the efficiency of ion implantation doping, understanding the behavior of defects is critically important. The EPR spectrum of phosphorus-ion implanted 6H-SiC demonstrates the observation of residual defects after post-implantation annealing (Fig. 1).

In EPR spectra of intrinsic defects in SiC, several sets of 29Si and/or 13C HF lines are expected to appear as satellite lines of strong primary lines. The angular dependence of the line positions of primary lines are described by the spin-Hamiltonian for an electron spin$^S\cdot g\cdot B + [S\cdot D\cdot S]$.

The first term represents the electron Zeeman interaction. The second term, representing the fine structure interaction,
Although the effects of n-type, p-type, and Si donors at silicon sites by using 6H-SiC doped during neutron-transmutation-doped 6H-SiC [11] and are assigned to the spectra of P-ion implanted 6H-SiC (1–2) are indicated. Figure 1 (online colour at: www.pss-b.com) Echo-detected EPR spectra of P-ion implanted 6H-SiC (1 × 10¹⁸ cm⁻² at each of 9 steps between 9 and 21 MeV at 800 °C, annealed at 1650 °C). Intensity of 2-pulse Hahn echo was measured as a function of the magnetic field strength, P₂, P₃ which were originally observed in neutron-transmutation-doped 6H-SiC [9] are assigned by theoretical studies to be P donors at carbon sites [10]. At low temperatures, signals from carbon sites with a long spin-lattice relaxation time are suppressed by using a fast repetition rate of the pulse sequence in accumulation. In addition to P and N donors (in the substrate), the signals from residual defects are noticed. The line positions of P(i), P(j), which were originally observed in neutron-transmutation-doped 6H-SiC [11] and are assigned to the shallow P donors at silicon sites by using 6H-SiC doped during CVD growth [12], are indicated. which splits the primary lines into 2S lines and splits the energy levels even at zero-magnetic field (zero-field splitting, ZFS), is included for a case with S ≥ 1. Based on the g-values and hence the resonant line positions specific for each EPR center, different EPR spectra arising from different defects can be distinguished (Fig. 2).

The primary lines with high intensities are used to investigate how the concentration of defects varying upon different processing conditions, such as electron irradiation conditions (electron energy, dose and temperature), heat treatment, and light illumination. Before the microscopic structure is established, the EPR spectra are often tentatively referred by the labels such as T₁, P₁, K₁, (n = 1, 2, 3, …) by using the initials of the research group, Eln, HEIn, Sln for those found in samples irradiated by electrons at room temperature or high temperatures and in Si samples, respectively, whereas IDn indicating intrinsic defects.

Although the g and D tensors are useful parameters for determination of the local symmetry and the spin multiplicity and hence the charge state, the primary lines lack definite chemical identity (Si or C). The detailed geometric and electronic structure identification comes from the HF interaction. For deep-level intrinsic defects in SiC, the wave function of the unpaired electron is extended to several atoms, Si₁, Si₂, … and C₁, C₂, … It is naturally expected that several major atoms comprising the defect such as four nearest-neighbors of vacancies and six nearest-neighbors of divacancies should have a HF splitting large enough to be resolved from the primary lines. Since the natural abundance of ²⁹Si and ³¹C is low and the number of major atoms of deep intrinsic defects is not large, each set of satellite lines arises from the case that one and only one of the major atoms is occupied by ²⁹Si/³¹C. The line positions of the i-th satellite lines are described by the spin-Hamiltonian

\[ \mathcal{H} = \beta \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{B} + [\mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S}] + [\mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I} - g_n \mathbf{g} \cdot \beta I_z \cdot \mathbf{B}] \]

where nuclear spin I = 1/2 for both ²⁹Si and ³¹C and gₚ(²⁹Si) = −1.1106, gₚ(³¹C) = 1.40483 [13]. The third and fourth terms represent the HF interaction with the nucleus of the i-th atom and the nuclear Zeeman interaction, respectively. For structure determination of intrinsic defects, the observation of ²⁹Si/³¹C HF satellite lines from all of the major-component atoms of the defect is desired. Although the wave function of the unpaired electron extends to further atoms, their HF interactions are often too weak resulting in unresolvable HF structures which contribute only to the linewidth of the primary and satellite lines. The primary lines are usually arising from a combination that all of major-component atoms are occupied by isotopes with zero nuclear spin. The intensity ratio between the satellite lines and the primary lines is important to determine the chemical identity (which gives the HF interaction, ²⁹Si or ³¹C) and the number of equivalent atoms.

Among major Si/C atoms of a defect, some are symmetry-related as in the case of three basal silicon atoms Si₂, in the positively charged carbon vacancy (S = 1/2, Cᵥ symmetry at 150 K) in 4H-SiC (Fig. 3) [14]. For the magnetic field B[][0001], these three atoms are equivalent and their ²⁹Si satellite lines are superimposed as shown in Fig. 3. From the fit of the angular dependence of the line
Both centers exhibit four \(^{29}\)Si HF satellite lines originating from four Si neighbors (\(\text{Si}_{1}\) and \(\text{Si}_{2}\)) of a V\(_{\text{Si}}\) (c). Angular dependency of line positions of the other HF satellite lines originating from four Si neighbors (\(\text{Si}_{3}\)) of a V\(_{\text{Si}}\). The wave function of the unpaired electron is satisfactorily described by linear combination of atomic orbitals (LCAO)

\[
\Psi = \sum_i \eta_i (\alpha_i \psi_{\alpha i} + \beta_i \psi_{\beta i}),
\]

where \(\alpha_i\) and \(\beta_i\) (\(\alpha_i^2 + \beta_i^2 = 1\)) are the s- and p-orbital contributions of the \(i\)-th atom and the total spin density \(\eta_i^2\) indicates the degree of the spin localization on the \(i\)-th atom. The HF tensor of the \(i\)-th atom \(A_i\) has usually axial symmetry with the principal values \(A_{i\alpha}\) and \(A_{i\beta}\) or nearly uniaxial. The HF interaction is divided into isotropic part \(A_{i\text{iso}}\) and anisotropic part \(A_{i\text{aniso}}\)

\[
A_{i\text{iso}} = \frac{[A_i(i) + 2 A_i(i)\hat{Z}]}{3} = \eta_i^2 \alpha_i^2 A_0, \\
A_{i\text{aniso}} = \frac{[A_i(i) - A_i(i)\hat{Z}]}{3} = \eta_i^2 \beta_i^2 b_0,
\]

where we use \(A_0 = 134.77\) mT, \(b_0 = 3.83\) mT for \(^{1}\)C and \(A_0 = -163.93\) mT, \(b_0 = -4.075\) mT for \(^{28}\)Si [13]. In addition to the spin density \(\eta_i^2\) and sp-hybrid ratio \(\beta_i^2/\alpha_i^2\), the direction of the p-orbital is determined from the principal axes of \(A_i\). Thus, the observation of the HF structure, which gives the orbital parameters, is crucial for the structure identification of defects.

As typically demonstrated in the case of the neutral divacancy, \([V_{\text{Si}}V_{\text{Si}}]_0^0\), in which the unpaired electrons are mostly localized on three nearest neighbors of \(V_{\text{Si}}\) among the six nearest-neighbors [15], the wave function of unpaired electrons might extend quite unevenly among the major atoms comprising the intrinsic defects. In such a case, the identification of the defect from EPR data is not straightforward, since a part of the major atoms which do not give the \(^{28}\)Si\(^{13}\)C satellite lines are invisible in the EPR spectra. Now, the first principles calculations provide not only the predicted structure of intrinsic defects but also the expected HF parameters [16]. Thus, the comparison of HF parameters obtained by experiments and theoretical studies is often crucial for the defect identification (see Fig. 4).

For some of major-component atoms which exhibit a weak isotropic HF splitting with the anisotropy hidden underneath the linewidth, only the number of equivalent atoms and \(\eta_i^2\alpha_i^2\) are obtainable. Nevertheless, such information is still important in comparison with that obtained by theoretical studies. To extract the HF interactions hidden underneath the linewidth, we have applied pulsed ENDOR (electron nuclear double resonance) of pulsed EPR techniques which have much higher resolutions than that of the conventional EPR. The first-order ENDOR frequencies are determined as

\[h_{\text{ENDOR}} = |M_A A_{\text{eff}} - g_\beta B|\]

here \(h\) is the Planck constant, \(g_\beta\) the nuclear magneton and \(A_{\text{eff}}\) the effective HF splitting. Since the nucleus is unambiguously determined from the observed nuclear Zeeman frequency \((g_\beta B/h)\), ENDOR is useful for identifying the nucleus (\(^{28}\)Si or \(^{13}\)C) giving rise to the resolved HF satellite

**Figure 3** (online colour at: www.pss-b.com) (a) EPR spectrum of carbon vacancies (\(V_c\)) in p-type 4H-SiC (3 MeV electron irradiation at 800 \(^\circ\)C with \(2 \times 10^{15}\) e/cm\(^2\)) measured at 150 K. The E15 and E16 centers arise from \(V_c\) at \(k\)- and \(b\)-sites, respectively [14]. Both centers exhibit four \(^{29}\)Si HF satellite lines originating from four Si neighbors (\(\text{Si}_{1}\) and \(\text{Si}_{2}\)) of a V\(_{\text{Si}}\). (b) Angular dependency of line positions of \(^{29}\)Si satellite lines, when magnetic field is rotating from \([0001]\) to \([1120]\). (Umeda et al., Phys. Rev. B 69, 121201(R) (2004). Copyright 2004 by the American Physical Society) [14].

**Figure 4** (online colour at: www.pss-b.com) Scheme of procedures of identification of intrinsic defects in SiC.
lines. Since the ENDOR frequencies depend on $M_e$ (±1/2 for $S = 1/2$, ±1 and 0 for $S = 1$, ±1/2 and ±3/2 for $S = 3/2$), the spin multiplicity ($S$) can be determined. Actually, this technique was employed for the case of silicon vacancies ($V_{\text{Si}}$ and $V_{\text{Si}}^\text{+}$, $S = 3/2$) [17, 18]. The intensities of the $^{29}\text{Si}^{13}\text{C}$ HF lines, which do lead to the decisive structure determination, are severely limited by their low natural abundances. To produce the defect of interest selectively at sufficient concentrations, we performed electron irradiation at various temperatures (−160 °C to 800 °C), with different doses (1 × 10$^{17}$−1 × 10$^{19}$ e/cm$^2$), and post-irradiation heat-treatment processes (100−1500 °C) and used thick single-crystal samples (typically 3 × 10 × 1.5 mm) of both n- and p-type of different concentrations.

2 Isolated vacancy The lattice vacancy which is one of most fundamental intrinsic defects is also the primary defect produced upon irradiation with energetic particles. The mobility of isolated vacancy is remarkably different among diamond, SiC, and silicon. In SiC and diamond isolated vacancies are observable after electron irradiation at room temperature, at which divacancies and impurity-vacancy complexes are formed in silicon.

A variety of isolated vacancies arising from different sublattices (Si and C), inequivalent sites (hexagonal site $h$ and cubic site $k$), and having different charge states is expected in 4H-SiC. The difference in the electron negativity (2.55 for C and 1.9 for Si on the Pauling scale) favors the negative charge state (−1) for the silicon vacancy ($V_{\text{Si}}$), and the positive charge state (+1) for the carbon vacancy ($V_{\text{C}}$). So far, several $V_{\text{Si}}$, $V_{\text{C}}$, and $V_{\text{C}}$ centers have been identified by EPR in 3C-, 4H- and 6H-SiC.

First, let us consider the isolated vacancies in silicon. Features of the EPR spectra of $V^+$ ($D_{2}$, $S = 1/2$) labeled Si-G1 and $V^-$ ($C_{\text{av}}$, $S = 1/2$) labeled Si-G2 [5, 6, 19] were successfully explained with a dominant Jahn–Teller distortion by using simple one-electron LCAO models illustrated in Fig. 5. Tetrahedral crystal field splits the defect molecular orbitals into a singlet $a_1$ and a triplet $t_2$. In the positively charged vacancy ($V^+$), under undistorted $T_d$ symmetry, two electrons enter into $a_1$ and the third electron enters into $t_2$.

Thus, $V^+$ in silicon, which is subjected to a Jahn–Teller distortion, undergoes a tetragonal distortion and the resulting symmetry is $D_{2h}$ (Fig. 5(b)). The orbital occupied by the unpaired electron ($b_2$) spreads equally over the four nearest-neighbors with the spin density $\gamma^2 = 14.6\%$ and the sp-hybrid ratio $\beta^2/\alpha^2 = 5.5$ on each silicon. In the (100), axial symmetry, the two atoms in two pairs (b, c and a, d) are pulled together [19]. Since the $b_2$ orbital can accommodate one more electron, the neutral vacancy with four electrons has $D_{2h}$ symmetry and $S = 0$. Under $D_{2h}$ symmetry, the fifth electron of the negatively charged vacancy ($V^-$) goes into a degenerate $e$ level. Thus, further Jahn–Teller distortion lowers the symmetry to $C_{\text{av}}$, resulting in the effective spin $S = 1/2$ (Fig. 6(a)). The distortion is pulling one pair of atoms (b and c) together toward each other and separating the other pair of atoms (a and d) slightly. The unpaired electron is localized mainly on two (a and d) of the four nearest-neighbors with the spin density $\gamma^2 = 27.3\%$ and the sp-hybrid ratio $\beta^2/\alpha^2 = 2.52$ [5, 6]. In both $V^+$ and $V^-$, the sum of the spin densities of the nearest-neighbors is similar between $V^+$ (58.4%) and $V^-$ (54.6%).

$V^+$ in diamond has $T_d$ symmetry with the effective spin $S = 3/2$ (three electrons in the triply degenerate $t_2$ level) as shown in Fig. 6(b) left. The orbitally nondegenerate $a_1$ state is not subjected to a Jahn–Teller distortion. The large fraction (~83%) of the unpaired electron is localized on the four nearest-neighbors [1]. The electron–electron repulsion due to the strong localization favors the high spin state in which three electrons occupy three different orbitals. In silicon, the energy gain is obtained by Jahn–Teller distortion, while the electron–electron repulsion is lowered by a large delocalization. The extent of the wave function of the unpaired electron was confirmed by ENDOR measure-
ments up to the 17-th atom along the (110) zigzag chain [6]. Thus, important factors which govern the geometric and electronic structures are the degree of structure relaxation and the electron–electron repulsion.

### 2.1 Silicon vacancy in SiC

In SiC, negatively charged silicon vacancies (V\(_{\text{V}}\)) are found in 3C-, 4H-, and 6H-SiC [17, 18, 22]. Basically, they are similar to V\(^-\) in diamond in that the ground state of high spin state (S = 3/2). The T\(_d\) symmetry of V\(_{\text{V}}\) in 3C-SiC (the T1 center) was confirmed by the angular dependence of \(^1\text{C}\) HF lines of the nearest-neighbors [20, 21]. In the T\(_d\) symmetry, all three \(\Delta E = \pm 1\) transitions of \(S = 3/2\) are superimposed since the ZFS vanishes. The effective spin \(S = 3/2\) of V\(_{\text{V}}\) in 4H-SiC was confirmed by the ENDOR measurements [17]. This high spin state has been ascribed to predominant tetrahedral character of the local structure which is indicated by isotropic g-value, isotropic \(^{29}\text{Si}\) HF interactions of next-nearest-neighbors, and the absence of ZFS. By measuring the angular dependence of \(^1\text{C}\) HF lines of the nearest-neighbors, two spectra labeled V\(_{\text{V}}\)(I) and V\(_{\text{V}}\)(II) are distinguished (Fig. 7) [22]. It is emphasized that the V\(_{\text{V}}\) centers are very similar between 6H-SiC and 4H-SiC (Figs. 8(a) and (b)). From the intensity ratio of the corresponding spectra in 6H-SiC, V\(_{\text{V}}\)(I) and V\(_{\text{V}}\)(II) are assigned to be arising from V\(_{\text{V}}\)(h) and V\(_{\text{V}}\)(k), respectively. In both types, the C\(_s\) symmetry is demonstrated by the inequivalence in \(\eta^2\) and \(\beta_i^2/\alpha_i^2\) between C\(_1\) and C\(_{3v}\) (Table 1, Fig. 9). Thus, the arrangement of nearest-neighbors of V\(_{\text{V}}\) in 4H-SiC is slightly distorted from regular tetrahedron.

The T\(_{\text{V}_{2a}}\) center can be observed by photoluminescence (PL), which is called the V2 line (1.352 eV). The correspondence between T\(_{\text{V}_{2a}}\) and V2 was demonstrated by optically detected magnetic resonance (ODMR) [23].

<table>
<thead>
<tr>
<th>center, symmetry</th>
<th>atom</th>
<th>(\eta_i^2) (%)</th>
<th>(\beta_i^2/\alpha_i^2)</th>
<th>(\theta)</th>
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<tr>
<td>V(_{\text{V}})(h) (C(_s))</td>
<td>C(_1)</td>
<td>15.9</td>
<td>11.3</td>
<td>0°</td>
</tr>
<tr>
<td>C(_{3v})</td>
<td>16.1</td>
<td>12.7</td>
<td>110.0°</td>
<td></td>
</tr>
<tr>
<td>total</td>
<td>64.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V(_{\text{V}})(k) (C(_s))</td>
<td>C(_1)</td>
<td>15.9</td>
<td>11.2</td>
<td>0°</td>
</tr>
<tr>
<td>C(_{3v})</td>
<td>16.2</td>
<td>11.9</td>
<td>109.2°</td>
<td></td>
</tr>
<tr>
<td>total</td>
<td>64.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T(<em>{\text{V}</em>{2a}}) (C(_{3v}))</td>
<td>C(_1)</td>
<td>15.4</td>
<td>10.7</td>
<td>0°</td>
</tr>
<tr>
<td>C(_{3v})</td>
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<td>12.2</td>
<td>107.5°</td>
<td></td>
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<tr>
<td>total</td>
<td>62.2</td>
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</tr>
</tbody>
</table>
in Fig. 9. In both $V_{Si}^-$ and $T_{V_{2a}}^-$, the $^{29}Si$ HF splitting is isotropic within the resolution of cw-EPR and the satellite lines arising from two $^{29}Si$ nuclei on among these twelve silicon atoms are also observed. The angular dependence of three primary lines and the $^{13}C$ satellites of four nearest-neighbors (C$_{1a}$) is shown in Fig. 8(c). The complete analysis of the $T_{V_{2a}}$ spectrum was achieved by utilizing the enhancement of the signal intensity due to electron spin polarization by light illumination [24, 25]. However, the central primary line of $T_{V_{2a}}$ was often missing, because it was not enhanced by illumination and was usually hidden underneath the $V_{Si}^-$ signal. This misled to that $T_{V_{2a}}$ originates from $V_{Si}^-$ with $S = 1$ [25]. The observation of the central primary line can be achieved by a pulsed-ELDOR technique shown in Section 3. The spin multiplicity of $T_{V_{2a}}$ has been determined to be $S = 3/2$ by the nutation method of pulsed-EPR [24] and by pulsed ENDOR [18]. The $C_{3v}$ symmetry of $T_{V_{2a}}$, which was already manifested by the ZFS, has been supported by the larger deviation from a regular tetrahedral angle (109.5°→107.5°, see Table 1).

The defect wave function is rather delocalized for $V_{Si}^-$ in SiC (62–65% on C$_{1a}$ atoms, see Table 1) than for V$^-$ in diamond (83%). The sp-hybrid ratio is larger than that (~7) of V$^-$ in diamond. Four carbon dangling bonds of $V_{Si}^-$ are well separated in SiC [26, 27], preserving the high spin state of $V_{Si}^-$. This situation is strikingly contrastive to the case of carbon vacancies explained in the next section.

2.2 Carbon vacancy in SiC Positively charged carbon vacancies ($V_{C}^+$, $S = 1/2$) have been found in 4H- and 6H-SiC but not in 3C-SiC. In 4H-SiC, a negatively charged carbon vacancy ($V_{C}^-$, $S = 1/2$) was also found.

The E15 [28] and E16 [29] centers in 4H-SiC have been established to be $V_C^+$ at cubic (h) and hexagonal (k) sites, respectively [14, 30]. Similarly, the Ky1/2 and Ky3 centers in 6H-SiC have been identified as $V_C^-$ at two cubic ($k_1$, $k_2$) and one hexagonal sites, respectively [31]. All of these spectra exhibit $^{28}Si$ HF satellite lines arising from four Si neighbors of a $V_C^-$. Angular dependences of the primary and $^{28}Si$ HF lines are summarized in Fig. 10(a) to (d).

Again we can find a close similarity between the EPR spectra in 6H-SiC (Fig. 10(a)) and 4H-SiC (Fig. 10(b)). The $V_C^-$ centers are typical examples in which the structure relaxation is remarkably different between the inequivalent sites (Fig. 11) and the assignment of EPR spectra has been achieved by agreement between the observed
Figure 12 (online colour at: www.pss-b.com) Angular-dependence measurement on $^{29}$Si HF lines of $V_c(k)$ with C$_{ih}$ symmetry at 5 K. These spectra were measured using 2-pulse Hahn echo ($\pi/2$ pulse – $\pi$ pulse – $\pi$ – echo, $\tau = 1.2$ $\mu$s, repetition time = 10 ms) of pulsed EPR.

$^{29}$Si HF tensors and those obtained by the first principles calculations [16, 30]. As shown in Table 2, the HF parameters obtained from the first principles calculation are consistent with those from EPR measurements at low temperatures. We owe to the contributions of theoretical groups that two EPR spectra EI5/EI6 significantly different in the temperature spectrum were observed as a function of temperature. From the analysis of the reorientation time, the motionally narrowed of the high-temperature spectrum were observed as a function of temperature. From the analysis of the reorientation time, the activation energy of the reorientation was estimated to be 0.015 eV [30].

At high temperatures, rapid thermally-activated reorientations (bond switching [Si$_1$–Si$_3$, Si$_1$–Si$_4$, Si$_2$–Si$_3$, Si$_2$–Si$_4$] ↔ [Si$_1$–Si$_2$, Si$_3$–Si$_4$] ↔ [Si$_1$–Si$_2$, Si$_3$–Si$_4$]) results in C$_{3v}$ symmetry. Features characteristic of reorientation effects, such as the lifetime broadening of the low-temperature spectrum and the motionally narrowing of the high-temperature spectrum were observed as a function of temperature. From the analysis of the reorientation time, the activation energy of the reorientation was estimated to be 0.015 eV [30].

Table 2 Principal values (in unit of mT) and directions of $^{29}$Si HF tensors of carbon vacancy centers in 4H-SiC. $\theta$ or ($\theta$, $\phi$) represents the principal axis of $A_{zz}$ with respect to the Cartesian coordinate defined in Fig. 11.

<table>
<thead>
<tr>
<th>center</th>
<th>symmetry</th>
<th>atom</th>
<th>first-principles calculation</th>
<th>experiment (EPR, 5K)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
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<td>$V_c(k)$</td>
<td>C$_{ih}$</td>
<td>Si$_1$</td>
<td>$A_{xx}$, $A_{yy}$, $A_{zz}$ (5.4°, 90°)</td>
<td>$A_{xx}$, $A_{yy}$, $A_{zz}$ (7.7°, 90°)</td>
<td>[30]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Si$_2$</td>
<td>$A_{xx}$, $A_{yy}$, $A_{zz}$ (117.0°, 270°)</td>
<td>$A_{xx}$, $A_{yy}$, $A_{zz}$ (121.5°, 270°)</td>
<td>[30]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Si$_3$</td>
<td>$A_{xx}$, $A_{yy}$, $A_{zz}$ (105.7°, 61°)</td>
<td>$A_{xx}$, $A_{yy}$, $A_{zz}$ (103.2°, 67.4°)</td>
<td>[32]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Si$_4$</td>
<td>$A_{xx}$, $A_{yy}$, $A_{zz}$ (105.7°, 119°)</td>
<td>$A_{xx}$, $A_{yy}$, $A_{zz}$ (103.2°, 112.6°)</td>
<td></td>
</tr>
<tr>
<td>$V_c(h)$</td>
<td>C$_{3v}$</td>
<td>Si$_1$</td>
<td>$A_{xx}$, $A_{yy}$, $A_{zz}$ (15.2°, 90°)</td>
<td>$A_{xx}$, $A_{yy}$, $A_{zz}$ (15.2°, 90°)</td>
<td>[30]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Si$_2$</td>
<td>$A_{xx}$, $A_{yy}$, $A_{zz}$ (18.2°)</td>
<td>$A_{xx}$, $A_{yy}$, $A_{zz}$ (18.2°)</td>
<td>[30]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Si$_3$</td>
<td>$A_{xx}$, $A_{yy}$, $A_{zz}$ (98.8°)</td>
<td>$A_{xx}$, $A_{yy}$, $A_{zz}$ (98.8°)</td>
<td>[30]</td>
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<tr>
<td></td>
<td></td>
<td>Si$_4$</td>
<td>$A_{xx}$, $A_{yy}$, $A_{zz}$ (21.1°, 112°)</td>
<td>$A_{xx}$, $A_{yy}$, $A_{zz}$ (21.1°, 112°)</td>
<td>[30]</td>
</tr>
</tbody>
</table>

Figure 11, the p-orbital directions of Si$_{1}$ and Si$_{2}$ are tilted to approach each other to form a Si$_{1}$–Si$_{2}$ bond. A similar reconstructed bond between Si$_{1}$ and Si$_{2}$ is formed by tilting of Si$_{1}$ and Si$_{2}$ dangling bonds.

Table 3 Tetrahedron composed of the nearest-neighbors [Si$_{1}$,Si$_{2}$,Si$_{3}$,Si$_{4}$], where Si$_{1}$, Si$_{2}$, Si$_{3}$, and Si$_{4}$ are not symmetrically equivalent. Upon rotation with $B$ $\perp$ [0001], the primary line and the set of $^{29}$Si$_{3}$, the set of Si$_{3}$ split into three lines. The set of Si$_{3}$ splits into six lines. These behaviors are shown in Fig. 10(b).

From the obtained HF parameters (Table 2), the spin density ($\rho^s$), sp-hybrid ratio ($\beta^s/\alpha^s$), and the direction of p-orbital (polar angles of $\theta$, $\phi$) of nearest-neighbor silicon atoms are estimated (Table 3). As is drawn in Fig. 11, the tetrahedron composed of Si$_{1}$, Si$_{2}$, Si$_{3}$, and Si$_{4}$ is classified into two symmetry-related sets, C$_{3v}$ and C$_{4v}$. In the first place, Si$_{1}$, Si$_{2}$, and Si$_{3}$ are tilted to approach each other to form a Si$_{1}$–Si$_{2}$ bond. A similar reconstructed bond between Si$_{1}$ and Si$_{2}$ is formed by tilting of Si$_{1}$ and Si$_{2}$ dangling bonds.

In 4H-SiC, for both C(h) and C(k) sites, there are two magnetically distinguishable orientations of [CSi$_{3}$] tetrahedron, [Si$_{1}$,C(h/k)Si$_{2}$,Si$_{3}$] and [Si$_{1}$,C(h/k′)Si$_{2}$,Si$_{3}$,Si$_{4}$]. In analyzing the angular dependence of the $^{29}$Si HF lines of $V_C$, the presence of two orientations needs to be considered. However, instead of going into these technical details, we discuss the structure relaxation by using one tetrahedron of the principal axis of $V_C$, with respect to the Cartesian coordinate defined in Fig. 11.
The spin density distribution on Si is temperature dependent. As temperature increases, the spin relaxation takes place as to form a Si–Si bond (or Si–Si or Si–Si) pair. Likewise, the case of V\(_2\)\(_h\) (the thermally activated reorientation results in C\(_{3v}\) symmetry at high temperatures). Furthermore, the \(^2\)Si EPR signal (a.u.) does not appear at low temperatures (see Fig. 11) can be also observed. Using a pulsed ENDOR technique, the anisotropy of the Si HF tensors of the nearest-neighbors (Si\(_{1–3}\)) of a V\(_C\)\(_h\) center is distinguishable due to its different HF signature, however, the corresponding EPR signal has not been identified.

On the other hand, V\(_C\)\(_h\) (the IEF center) keeps C\(_{3v}\) symmetry at 5 K [14], although the first principles calculations predicted a possible configuration having C\(_{1h}\) symmetry [16]. As is seen in Fig. 10(d), \(^2\)Si HF splittings are much larger for Si\(_1\) than the other three Si neighbors (Si\(_{1–3}\)) of a V\(_C\)\(_h\), indicating a strong localization on the Si\(_1\) atom (\(\eta_c = 34.4\% - 47.3\%\), see Table 3). The displacement of Si\(_1\) along the [0001] direction away from Si\(_{1–3}\) is the major part of the structure relaxation. Due to the strong spin localization on Si\(_1\), \(^2\)Si HF interaction from Si\(_{1–3}\) atoms behind Si\(_1\) (see Fig. 11) can be also observed. Using a pulsed ENDOR technique, the anisotropy of the Si HF tensors of the nearest-neighbors (Si\(_{1–3}\)) of a V\(_C\)\(_h\) center was resolved as shown in Fig. 13. The IEF EPR spectrum is strongly sensitive to temperature dependence. As temperature increases, the spin distribution on Si\(_1\) is shifted to Si\(_{1–3}\) (Table 3). Accordingly, with B\(|[0001]\), the \(^2\)Si HF splitting decreases for Si\(_1\) and Si\(_{1–3}\), and decreases for Si\(_{1–3}\). At a low temperature limit, the sum of \(\eta_c\) of four nearest-neighbors is the same for V\(_C\)\(_h\) and V\(_C\)\(_k\) (68.0% and 67.6%, respectively), exhibiting a stronger localization than the case of V\(_C\) in silicon (58.5%).

In 4H-SiC, a negatively charged carbon vacancy can be observed (Fig. 2a), which was named the HEI1 center (S = 1/2) [32]. Two angular maps of this center are shown in Figs. 10c further. Depending on temperature, the HEI1 EPR spectrum exhibits C\(_{3v}\) and C\(_{1h}\) symmetries, as similarly to V\(_C\)\(_k\). The transition temperature is about 70 K. In the C\(_{1h}\) configuration (<70 K), the unpaired electron is mainly localized on two Si neighbors (Si and one of Si\(_{1–3}\)) of V\(_C\). This is just the same trend as observed for V\(_C\) in silicon [5, 6]. As a result, two sets of \(^2\)Si HF lines are clearly appeared (Fig. 10c). The structure relaxation takes place as to form a Si–Si bond (or Si–Si or Si–Si) pair. Likewise, the case of V\(_C\)\(_k\), thermally activated reorientation results in C\(_{3v}\) symmetry at high temperatures. Furthermore, the \(^2\)Si satellite line disappears due to the lifetime broadening (Fig. 10f). From the lifetime analysis, the re-orientation activation energy was estimated to be 0.020 eV, which is slightly larger than that for V\(_C\)\(_k\). The sum of \(\eta_c\) of two nearest-neighbors is 67.7%, which is larger again than the case of silicon (55.8%). Comparing with the theoretical A tensors, this V\(_C\)\(_k\) center is assigned to V\(_C\)\(_k\) (Table 2) [32]. The first principles calculation predicted that the V\(_C\)\(_k\) center is distinguishable due to its different HF signature, however, the corresponding EPR signal has not been identified.

Table 3 Orbital parameters of V\(_C\)\(_k\) and V\(_C\)\(_h\) in 4H-SiC obtained from the \(^2\)Si HF tensors of the nearest-neighbors (Si\(_{1–3}\)) of V\(_C\): The spin density distribution on Si is temperature dependent. As temperature increases, the spin relaxation takes place as to form a Si–Si bond (or Si–Si or Si–Si) pair. Likewise, the case of V\(_C\)\(_k\), thermally activated reorientation results in C\(_{3v}\) symmetry at high temperatures. Furthermore, the \(^2\)Si satellite line disappears due to the lifetime broadening (Fig. 10f). From the lifetime analysis, the re-orientation activation energy was estimated to be 0.020 eV, which is slightly larger than that for V\(_C\)\(_k\). The sum of \(\eta_c\) of two nearest-neighbors is 67.7%, which is larger again than the case of silicon (55.8%). Comparing with the theoretical A tensors, this V\(_C\)\(_k\) center is assigned to V\(_C\)\(_k\) (Table 2) [32]. The first principles calculation predicted that the V\(_C\)\(_k\) center is distinguishable due to its different HF signature, however, the corresponding EPR signal has not been identified.
we assume that the ±1/2 levels should be selectively populated and D > 0. Then, the low-field line exhibiting strongly enhanced absorption is assigned to the +3/2 ↔ +1/2 transition (higher level is much less populated, \( p(+3/2) \ll p(+1/2) \)) and the high-field line exhibiting strong emission (the higher level has much larger population, \( p(-1/2) \gg p(-3/2) \)) is assigned to the −1/2 ↔ −3/2 transition. Here, \( p(M_s) \) denote the population of the \( M_s \) level.

Since the microwave-induced transition probability is the same for both of the \( \Delta M_t = \pm 1 \) transitions (upward and downward transitions), the EPR signal intensity is proportional not only to the concentration of the defect but also to the population difference of the two \( M_t \) levels involved in the transition. The strong signal enhancement indicates that the absolute values of the population difference \( |p(+3/2) - p(+1/2)| \) and \( |p(-1/2) - p(-3/2)| \) is much larger than those in thermal equilibrium. No appearance of the +1/2 ↔ −1/2 transition of \( V_{2a} \) indicates that no extra population difference is created under illumination. For simplicity, we assume that the ±1/2 levels are equally populated under illumination (\( p(+1/2) \sim p(-1/2) \)).

If the large population difference between the −1/2 and −3/2 levels (or between the +3/2 and +1/2 levels) attained by illumination should be created also for between the +1/2 and −1/2 levels, as inferred from Fig. 14, the intensity of the +1/2 ↔ −1/2 transition of \( V_{2a} \) can exceed that of the strong \( V_{Si} \) signal. We have tried to transfer the polarization of the +3/2 ↔ +1/2 transition (−1/2 ↔ −3/2 transition) to the +1/2 ↔ −1/2 transition by using 180° pulse of the +3/2 ↔ +1/2 (−1/2 ↔ −3/2) transition. Here, the 180° pulse is used to swap the populations of the levels between which the transition is induced. Then, we need a microwave pulse with frequencies different from the one used for observing the signal of the +1/2 ↔ −1/2 transition (Fig. 15). We have carried out pulsed ELDOR (electron–electron double resonance) experiments at 130 K under illumination of laser light (808 nm).

In the first place, the frequency-swept ELDOR experiments were carried out with the magnetic field fixed at the central signal (Fig. 16). For observing the signal of the +1/2 ↔ −1/2 transition of \( V_{2a} \), which is expected to appear overlapped with that of \( V_{Si} \), a pulse sequence of 3-pulse inversion recovery, \( (180° - \tau_0 - 90° - \tau - 180° - \tau - \text{echo}) \), where \( \tau_0 = 4 \mu s \) and \( \tau = 1 \mu s \) if fixed, was employed, here, \( \tau_0 \) is sufficiently shorter than the spin–lattice relaxation time. Hahn-echo (\( 90° - \tau - 180° - \tau - \text{echo} \)) generated by the second and the third pulses, which has usually a role to make the z component of the magnetization \( M_t \) at time \( \tau_0 \) observable, is used to measure the polarization of the +1/2 ↔ −1/2 transition of \( V_{2a} \) induced by the ELDOR pulse. When no ELDOR pulse is applied, the signal corresponding to the inversion of the \( V_{Si} \) signal was observed. The 180° pulse (duration 80 ns) at \( \tau = 0 \) inverts the population difference of \( V_{Si} \); however does not alter the zero-intensity of the +1/2 ↔ −1/2 transition of \( V_{2a} \) since \( p(+1/2) \sim p(-1/2) \). Thus, the baseline in Fig. 16 corresponds to the echo height of the inverted \( V_{Si} \) signal.

The ELDOR pulse, of which duration (116 ns) was chosen to attain the flipping angle of \( \sim 180° \), was applied at

**Figure 14** Echo-detected EPR spectra of electron irradiated n-type 4H-SiC (130 K, \( B[0001] \)). The intensity of 2-pulse Hahn echo is plotted against the magnetic field strength. Here, the positive peaks correspond to the absorption.

**Figure 15** (online colour at: www.pss-b.com) (a) Pulsed-ELDOR experiment, (b) population under illumination without ELDOR pulse (\( D > 0 \) and selective population onto ±1/2 levels are assumed), (c) population after ELDOR pulse.
lated emission at 9.635 GHz and stimulated absorption brought by the ELDOR pulse of these frequencies, stimulated emission at 9.775 GHz, is ascribed to the appearance of the strong signal from the $+1/2 \leftrightarrow -1/2$ transition of $V_{2a}$.

In the second place, the field-swept ELDOR experiments were carried out to obtain the spectral features of the $+1/2 \leftrightarrow -1/2$ transition of $V_{2a}$. We have three signals, the signal of $+3/2 \leftrightarrow +1/2$ of $V_{2a}$, the central signal ($+1/2 \leftrightarrow -1/2$ of $V_{2a}$, overlapped with $V_{3i}$), and the signal of $-1/2 \leftrightarrow -3/2$ of $V_{2a}$. The first 180° pulse (width 80 ns) is strong enough to invert one of the three signals when the magnetic field is set to the signal, however is not sufficient to flip the other two signals, simultaneously. The intensity of the echo of 3-pulse inversion recovery was measured as a function of the magnetic field strength without ELDOR pulse (Fig. 17(c)) and with applying the ELDOR pulse (Fig. 17(a) and (b)). Although the microwave pulses have the excitation bandwidth exceeding the linewidth of the signals, the resolution of the conventional EPR is achieved by using a large window width for integrating the echo. The frequency (9.635 GHz and 9.775 GHz) and the width of the ELDOR pulse are selected to achieve the flipping angle of $-180^\circ$ for the $+3/2 \leftrightarrow +1/2$ transitions at the magnetic field of the central signal. Without applying ELDOR pulse, we obtained the spectrum shown in Fig. 17(c) which is inverted one of the spectrum shown in Fig. 14(a). We note that the ELDOR pulses at 9.635 GHz and 9.775 GHz did cause a significant change of the central signal. By using the 180° ELDOR pulse of 9.635 GHz, the emission ($p(+1/2) \gg p(-1/2)$) of $+1/2 \leftrightarrow -1/2$ transition of $V_{2a}$ is added to the inverted signal of $V_{3i}$ and the amplitude of the negative signal at the central line is strongly increased. By using the 180° ELDOR pulse of 9.635 GHz, the enhanced absorption ($p(+1/2) \gg p(-1/2)$) of $+1/2 \leftrightarrow -1/2$ transition of $V_{2a}$ dominates over the inverted signal of $V_{3i}$. Thus, in Fig. 17(a), the central line is the pure signal of the $+1/2 \leftrightarrow -1/2$ transition of $V_{2a}$.

In the field-swept spectra, the effect of the ELDOR pulse on the outer signals is somewhat more complicated. In the case of the ELDOR pulse of 9.635 GHz, the low

![Figure 16](https://www.pss-b.com) Frequency-swept pulsed-ELDOR spectrum (130 K, $B_0 || [0001]$). The intensity of 3-pulse inversion recovery of the central signal (9.705 GHz) was monitored as a function of the microwave frequency of the ELDOR pulse.

t = 1 \mu s. The frequency (9.705 GHz) of the 3-pulse inversion recovery sequence as well as the coherent detection is tuned to that of the resonator loaded with the sample. The resonator has a large bandwidth due to low-$Q$ which is inherent to pulse experiments for achieving a short deadtime. When the frequency of the ELDOR pulse was varied (Fig. 16), the echo height is significantly affected at 9.635 GHz and at 9.775 GHz as well as at 9.705 GHz. The change brought at 9.705 GHz is caused by the flipping of the central signal mainly due to $V_{3i}$. The signal of the +1/2 $\leftrightarrow$ -1/2 transition of $V_{2a}$, which is also resonant to 9.705 GHz, was not affected by the flipping by the ELDOR pulse of 9.705 GHz since $p(+1/2) \sim p(-1/2)$. Two frequencies, 9.635 GHz and 9.775 GHz correspond to the $-1/2 \leftrightarrow -3/2$ and $+3/2 \leftrightarrow +1/2$ transitions of $V_{2a}$, respectively, at the magnetic field of the central signal (Fig. 15(c)). We note that these frequencies are $\sim 9.705 \pm 2/0$. The change of the echo intensity brought by the ELDOR pulse of these frequencies, stimulated emission at 9.635 GHz and stimulated absorption at 9.775 GHz, is ascribed to the appearance of the strong signal from the $+1/2 \leftrightarrow -1/2$ transition of $V_{2a}$.

In the second place, the field-swept ELDOR experiments were carried out to obtain the spectral features of the $+1/2 \leftrightarrow -1/2$ transition of $V_{2a}$. We have three signals, the signal of $+3/2 \leftrightarrow +1/2$ of $V_{2a}$, the central signal ($+1/2 \leftrightarrow -1/2$ of $V_{2a}$, overlapped with $V_{3i}$), and the signal of $-1/2 \leftrightarrow -3/2$ of $T_{2a}$. The first 180° pulse (width 80 ns) is strong enough to invert one of the three signals when the magnetic field is set to the signal, however is not sufficient to flip the other two signals, simultaneously. The intensity of the echo of 3-pulse inversion recovery was measured as a function of the magnetic field strength without ELDOR pulse (Fig. 17(c)) and with applying the ELDOR pulse (Fig. 17(a) and (b)). Although the microwave pulses have the excitation bandwidth exceeding the linewidth of the signals, the resolution of the conventional EPR is achieved by using a large window width for integrating the echo. The frequency (9.635 GHz and 9.775 GHz) and the width of the ELDOR pulse are selected to achieve the flipping angle of $-180^\circ$ for the $+3/2 \leftrightarrow +1/2$ transitions at the magnetic field of the central signal. Without applying ELDOR pulse, we obtained the spectrum shown in Fig. 17(c) which is inverted one of the spectrum shown in Fig. 14(a). We note that the ELDOR pulses at 9.635 GHz and 9.775 GHz did cause a significant change of the central signal. By using the 180° ELDOR pulse of 9.635 GHz, the emission ($p(+1/2) \gg p(-1/2)$) of $+1/2 \leftrightarrow -1/2$ transition of $V_{2a}$ is added to the inverted signal of $V_{3i}$ and the amplitude of the negative signal at the central line is strongly increased. By using the 180° ELDOR pulse of 9.635 GHz, the enhanced absorption ($p(+1/2) \gg p(-1/2)$) of $+1/2 \leftrightarrow -1/2$ transition of $V_{2a}$ dominates over the inverted signal of $V_{3i}$. Thus, in Fig. 17(a), the central line is the pure signal of the $+1/2 \leftrightarrow -1/2$ transition of $V_{2a}$.

In the field-swept spectra, the effect of the ELDOR pulse on the outer signals is somewhat more complicated. In the case of the ELDOR pulse of 9.635 GHz, the low

![Figure 17](https://www.pss-b.com) (online colour at: www.pss-b.com) Echo-detected EPR spectrum. The intensity of the 3-pulse inversion recovery was monitored as a function of the magnetic field.
field line corresponding to the $+3/2 \leftrightarrow +1/2$ transition was affected. At the magnetic field, at which the $+3/2 \leftrightarrow +1/2$ transition is resonant to 9.705 GHz, the $+1/2 \leftrightarrow -1/2$ transition is within the bandwidth of the ELDOR pulse of 9.635 GHz. The 180° pulse of 9.705 GHz at $t = 0$ inverts the polarization of the $+3/2 \leftrightarrow +1/2$ signal from the strong stimulated absorption $p(+3/2) \ll p(+1/2)$ to the strong stimulated emission $p(+3/2) \gg p(+1/2)$. This large population difference is decreased by the ELDOR pulse at $t = 1 \mu s$ which transfers the population of $-1/2$ level to $+1/2$ level. In the case of the ELDOR pulse of 9.775 GHz, the high field line corresponding to the $-1/2 \leftrightarrow -3/2$ transition was affected. At the magnetic field at which the $-1/2 \leftrightarrow -3/2$ transition is resonant to 9.705 GHz, the $+1/2 \leftrightarrow -1/2$ transition is flipped by the ELDOR pulse of 9.775 GHz. Thus, the population difference $p(-1/2) \ll p(-3/2)$ after the 180° pulse of 9.705 GHz was nearly cancelled by the ELDOR pulse at 9.775 GHz which transfers the population of $+1/2$ level to $-1/2$ level.

We note that both the line position (or the $g$-value) and the $^{28}$Si HF structure of the $+1/2 \leftrightarrow -1/2$ transition of T$_{V_{2a}}$ is similar to those of V$_{Si}$ as already known from the spin-Hamiltonian parameters determined from the fit of the outer lines. It should be noted that the line width of the $+1/2 \leftrightarrow -1/2$ transition of T$_{V_{2a}}$ is smaller than that of the outer lines and the $^{28}$Si HF structure of second-nearest neighbours is more clearly observed for the signal of the $+1/2 \leftrightarrow -1/2$ transition than for the outer lines. Thus, the distribution of the zero-field splitting ($D$) contributes significantly to the line broadening of the outer lines.

In the third place, the Rabi oscillations (nutations) of $-3/2 \leftrightarrow -1/2$ and $+3/2 \leftrightarrow +1/2$ transitions, respectively, of T$_{V_{2a}}$ driven by the ELDOR pulses at 9.635 GHz and 9.775 GHz, respectively were measured by monitoring the polarization of the $+1/2 \leftrightarrow -1/2$ transition. The magnetic field was fixed at the central signal of Fig. 14.

In pulsed experiments, the behaviour of the magnetization is described using a coordinate system rotating with the microwave frequency around the external magnetic field ($\omega_B$, $\alpha_B$). At the resonance condition, the microwave pulse rotates the magnetization around the $x$-axis through the angle

$$\theta(t_p) = (2\pi g\beta_B \hbar / h) t_p = \omega_B t_p,$$

here, $t_p$ is the pulse width, $B$ the microwave rotating field, $\omega_B$ the nutation frequency. The flipping of the microwave pulse changes the $z$-component of the magnetization which is related to the population difference of the two levels between which transition is induced. For the usual case starting from thermal equilibrium ($M_z = M_0$), the oscillation of the $z$-component of the magnetization is

$$M_z \propto M_0 \cos(\omega_B t_p).$$

In our case, we start from large $|M_x|$ ($|M_z| \gg M_0$), with the sign either positive (absorption) or negative (emission) due to polarization, $p(+1/2) \sim p(-1/2) \gg p(+3/2), p(-3/2)$. The oscillation of $M_z$ corresponding to the $-1/2 \leftrightarrow -3/2$ transition by using the ELDOR pulse of 9.635 GHz or that corresponding to the $+3/2 \leftrightarrow +1/2$ transition using the ELDOR pulse of 9.775 GHz causes the oscillation of the population difference between the $+1/2$ and $-1/2$ levels. The population difference between the $+1/2$ and $-1/2$ levels is directly related to the signal height of the $+1/2 \leftrightarrow -1/2$ transition of T$_{V_{2a}}$. Thus, the Rabi oscillations of $-1/2 \leftrightarrow -3/2$ (9.635 GHz) and $+3/2 \leftrightarrow +1/2$ (9.775 GHz) transitions are monitored by measuring the echo signal of the $+1/2 \leftrightarrow -1/2$ transition (9.705 GHz).

The height of the 3-pulse echo at the magnetic field of the central signal was measured as a function of the pulse width of the ELDOR pulse (Fig. 18). The Rabi oscillations were observed for $\sim 1 \mu s$. In Fig. 18, the signal height at zero pulse width (i.e., ELDOR pulse off) corresponds to the height of the inverted signal of V$_{Si}$. The fact that the induced signal exhibits the Rabi oscillations of the $-3/2 \leftrightarrow -1/2$ and $+3/2 \leftrightarrow +1/2$ transitions confirms that the signal of the $+1/2 \leftrightarrow -1/2$ transition is indeed induced.

The difference of the nutation frequency for the two ELDOR frequencies 9.635 GHz and 9.775 GHz is likely to be caused by the difference of $B_1$ for the two frequencies in the pulsed ELDOR setup.

### 4 Divacancy

In silicon, positively and negatively charged divacancies, $[\text{VV}^+]$ and $[\text{VV}^-]$, have been identified by EPR to have $C_{3v}$ symmetry with $S = 1/2$. Removing two adjacent Si atoms produces six dangling bonds ($a$, $b$, $d$, $a', b'$, and $d'$). Unrelaxed divacancy of $D_{3h}$ symmetry has two singlets $\alpha_B$ and $\alpha_{a1}$ in the valence band, and two doublets $e_a$ and $e_b$ in the energy gap, with $e_{a1}$ higher than $e_{a1}$. Since the $e_a$ level is partially occupied ($V_2$: $e_z$, $V_2$: $e_z$), a Jahn–Teller distortion, which reconstructs pair bonds between $a$ and $d$, $a'$ and $d'$, lowers the symmetry to $C_{3v}$. In both $[\text{VV}^+]$ and $[\text{VV}^-]$, the unpaired electron is localized mainly on atoms $a$ and $b'$ in the mirror plane of $C_{3v}$ symmetry. The spin density $\eta^2$ and the sp-hybrid ratio $\beta_{\eta}/\alpha^2$ on figure 18 (online colour at: www.pss-b.com) Rabi oscillations of the $-1/2 \leftrightarrow -3/2$ and $+3/2 \leftrightarrow +1/2$ transitions, respectively, at the ELDOR frequency of 9.635 GHz and 9.775 GHz, respectively. The signal height of the echo signal of 3-pulse inversion recovery (9.705 GHz) of the $-1/2 \leftrightarrow -1/2$ transition was measured as a function of the pulse width of the ELDOR pulse.
these atoms (b and b') are 27.5%, 7.5 for [VV]⁺ and 24.6%, 4.8 for [VV]⁻ [34–36].

The neutral vacancy in silicon is diamagnetic (S = 0). It should be noted that, if [VV]⁺ of D₃₃ symmetry had taken non-orbitally-degenerate 1A₂g (S = 1) state arising from electronic configuration e², then no Jahn–Teller distortion is expected. The neutral divacancy in diamond has S = 1, however, the symmetry is lowered to C₃v [4]. The unpaired electron is mainly localized on four atoms (a, d, a', and d') which are not in the mirror plane, with η₂ = 20% and β/c²a₂ = 9.

The P6/P7 centers (S = 1) in 4H-SiC have been established to be originating from the ground state of the neutral divacancy [V₃₋₈V₃₋₈]⁺, the closest pair of the silicon vacancy (V₃₋₈) and the carbon vacancy (V₃₋₈), through the cooperation between the first principles calculations which supplied the predicted HF parameters and the careful EPR measurements of the ¹³C HF lines, both the angular dependence and the intensity relative to the primary lines. Four configurations (hh, kk with C₃h symmetry, hh, kh with C₁h symmetry) are distinguishable by EPR.

The divacancy was suggested as a model for the P6/P7 EPR centers in heat treatment 6H-SiC in the early 1980s by Vainer and I1′ in [37]. However, the identification was based only on the observed symmetry of the centers (C₁h for P6 and C₃h for P7). Since light illumination was needed for detecting the spectra, the centers were believed to be related to the excited triplet states of the divacancy [37]. These centers are also commonly detected in n-type 6H-SiC by ODMR [38] or in high-purity semi-insulating (HPSI) 4H- and 6H-SiC substrates by EPR [39, 40].

In a later study using MCD (magnetic circular dichroism of the absorption)-detected EPR and first principles calculations by Lingner and co-workers [41], P6/P7 EPR spectra in 6H-SiC were claimed to be the carbon-antisite carbon-vacancy pair in the double positive charge state ([C₃₋₈V₃₋₈]⁺).

Figure 19(a) shows the P6/P7 spectra in as-grown HPSI 4H-SiC substrates detected at 77 K for the magnetic field B||[0001] under illumination of light of photon energies in the range 2.0–2.8 eV. In the 4H polytype, there are two configurations with C₁h symmetry (P6b and P6'b) and two configurations with C₃h symmetry (P7b and P7'b). The P6/P7 centers have the same g-value g = 2.003 and slightly different fine-structure parameters D and E (in unit of 10⁻⁴ cm⁻¹): D(P6b) = D(P7b) = 447, D(P6'b) = 436, D(P7'b) = 408, E(P7b) = 90 and E(P7'b) = 10. The angle between the principal axis of the fine structure tensor and the c-axis for P7b and P7'b is 109.5° and 109°, respectively. Recently, detailed HF structures of the P6 and P7 centers in 4H- and 6H-SiC have been observed [15, 43]. Typical HF structures for parts of the P6b and P6'b spectra in 6H-SiC are shown in Fig. 19(b). As shown in the figure, the large splitting HF lines are from the interaction with three nearest C neighbours of V₃₋₈. The inner HF lines are due to the interaction with nine next-nearest Si neighbors, of which three Si atoms on the bonds along the c-axis has a slightly larger splitting. The HF interaction with three nearest Si neighbours of V₃₋₈ is small and not resolvable. The principal values of the HF tensors determined for the P6b, P6'b and P7'b centers in 4H-SiC are shown in Table 4. The observed HF constants are in good agreement with the values obtained from the supercell calculations of the neutral divacancy model [15, 44]. The P6/P7 centers were therefore identified as different configurations of the neutral divacancy ([V₃₋₈V₃₋₈]⁻). Comparing the observed HF constants with the calculated values for different configurations, it was possible to assign the P6b and P6'b centers to...
the axial C\textsubscript{3v} configurations at the hexagonal and cubic sites [P6\textsubscript{b}: \(V_{5b}(h) - V_{5c}(h)\), P6\textsubscript{b}′: \(V_{5b}(k) - V_{5c}(k)\)] and the P7\textsubscript{b} centers to the monoclinic C\textsubscript{1h} configurations, \(V_{5b}(h) - V_{5c}(k)\) and \(V_{5b}(k) - V_{5c}(h)\), respectively [15]. Figure 20 shows schematic atomic models for the \([V_{5b}V_{5c}]^0\) centers. Using the linear combination of atomic orbital analysis, the spin density on a nearest C neighbor is determined as: \(\sim 1.8-1.9\%\) on the s-orbital and \(\sim 18-19\%\) on the p-orbital for P6\textsubscript{b}, P6\textsubscript{b}′ and P7\textsubscript{b}. The sp-hybrid ratio is \(\beta^2/\alpha^2 \sim 10\) for all the configurations. The total spin density on the three nearest C neighbors of the neutral divacancy is \(60\%\) for the C\textsubscript{3v} configuration (P6\textsubscript{b}/P6\textsubscript{b}′) and \(62\%\) for the C\textsubscript{1h} configuration (P7\textsubscript{b}). In the C\textsubscript{3v} configurations, the spin density is equally distributed among the three nearest C neighbors and the direction of p-orbitals (\(\theta = 107^\circ\)) with respect to the vacancy-neighbor direction (see Fig. 20) is slightly smaller than the tetrahedral angle (109.5°). In the case of P7\textsubscript{b} center, the localization of spins at the C atom along the c-axis is slightly smaller than that at the other two C atoms on the inclined bonds. In both C\textsubscript{3v} and C\textsubscript{1h} configurations, the spin localization on three nearest Si neighbors of \(V_{5c}\) is negligible (\(\sim 1\%\)). With electrons on the e level arising from C dangling bonds of \(V_{5c}\), the spin localization for the neutral divacancy is similar to that of \(V_{5c}: \sim 60-62\%\) on three nearest C neighbors of \(V_{5c}\) in the divacancy and \(62-65\%\) on four nearest C neighbors for \(V_{5c}\).

In as-grown samples, the observation of the P6/P7 centers requires illumination with light of photon energies larger than \(\sim 1.1\) eV. However, in some irradiated 4H- and 6H-SiC samples, the spectra could be detected in the dark even at low temperatures (1.5–8 K) [15, 45]. This confirms that the spectra are related to the ground state, in agreement with the supercell calculations of the neutral divacancy [15, 39]. In the divacancy, three C dangling bonds and three Si dangling bonds create six defect levels. In the axial configuration with C\textsubscript{3v} symmetry, two \(\alpha_l\) levels fall in the valence band and two double generate e levels lie in the band gap. The lower e level arises from the C dangling bonds of the Si vacancy and the upper e level arises from the Si dangling bonds of the C vacancy. In the neutral charge state, there are six electrons, four of them fill the two resonance \(\alpha_t\) levels in the valence band and the other two occupy the lower degenerate e level, giving rise to the spin \(S = 1\) for the ground state. In 4H-SiC, the calculations found the \((+/0)\) and \((0/-)\) levels to be at \(\sim 0.5\) eV and \(\sim 1.4\) eV above the valence band, respectively [15, 44]. Recent EPR studies in irradiated HPSI 4H-SiC substrates [46] show that in the dark at 77 K only the \(V_{5c}\) signal was observed. However, increasing the temperature to 293 K while keeping the sample in darkness, the \([V_{5b}V_{5c}]\) signal could be weakly detected. This suggests that the \((0/-)\) level of \(V_{5b}/V_{5c}\) may lie slightly below the \((+/0)\) level of \(V_{5c}\) at \(\sim E_{V} + 1.47\) eV [47] so that at room temperature it could be partly thermally ionized. Consequently, a part of the total concentration of the divacancy is changed to the neutral charge state and could be detected. This EPR estimation is close to the theoretical prediction of the \((0/-)\) level at \(\sim E_{V} + 1.4\) eV. Recently, the divacancy has been identified as a prominent defect responsible for the semi-insulating properties in HPSI 4H-SiC substrates with thermal activa-

![Figure 20](online colour at: www.pss-b.com) Atomic structures of divacancy centers in 4H-SiC.

### Table 4 Principal values of the HF tensors (in unit of mT) of the neutral divacancy in 4H-SiC.

<table>
<thead>
<tr>
<th>center symmetry</th>
<th>atom</th>
<th>HF tensors</th>
<th>(\eta_s^2) (%)</th>
<th>(\beta^2/\alpha^2)</th>
<th>(\theta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([V_{5b}(h) - V_{5c}(h)]^0)</td>
<td>C\textsubscript{1,3}</td>
<td>1.89</td>
<td>1.78</td>
<td>3.93</td>
<td>20.1</td>
</tr>
<tr>
<td>P6\textsubscript{b} (C\textsubscript{3v})</td>
<td>Si\textsubscript{1,3}</td>
<td>~0.1</td>
<td>~0.1</td>
<td>~0.1</td>
<td>0.6</td>
</tr>
<tr>
<td>total</td>
<td>62.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([V_{5b}(k) - V_{5c}(k)]^0)</td>
<td>C\textsubscript{1,3}</td>
<td>1.68</td>
<td>1.61</td>
<td>3.71</td>
<td>19.7</td>
</tr>
<tr>
<td>P6\textsubscript{b}′ (C\textsubscript{3v})</td>
<td>Si\textsubscript{1,3}</td>
<td>~0.1</td>
<td>~0.1</td>
<td>~0.1</td>
<td>0.6</td>
</tr>
<tr>
<td>total</td>
<td>60.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([V_{5b}(k) - V_{5c}(h)]^0)</td>
<td>C\textsubscript{1}</td>
<td>1.86</td>
<td>1.86</td>
<td>3.93</td>
<td>19.9</td>
</tr>
<tr>
<td>P7\textsubscript{b} (C\textsubscript{1h})</td>
<td>C\textsubscript{2,3}</td>
<td>1.71</td>
<td>1.61</td>
<td>3.89</td>
<td>21.2</td>
</tr>
<tr>
<td>total</td>
<td>62.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
tion energies of ~1.5–1.6 eV, which may be associated to the single acceptor level (0/−) of [V_{\text{Si}}V_{\text{C}}] [46].

The no-phonon lines related to the P6 centers in irradiated n-type 6H-SiC substrates were found to reach their maximum intensity after annealing at ~900 °C and to be disappeared after an 1200 °C anneal [48]. In electron-irradiated HPSI 4H- and 6H-SiC substrates, the EPR signals of the divacancy were annealed out at higher temperatures (~1400 °C), whereas in as-grown HPSI materials with low concentrations of defects and residual impurities (N and B) their intensities only started decreasing after annealing at 1600 °C [46].

In 6H-SiC, the relation between the P6/P7 triplet states and the no-phonon lines of the near-infrared photoluminescence (PL) band has been confirmed (P6a–c: 1.075, 1.048 and 1.011 eV; P7a–c: 1.049, 1.030 and 0.999 eV) [41]. In 4H-SiC samples with strong EPR signals of the neutral divacancy, five strong absorption lines were also detected at 0.9975, 1.0136, 1.0507 and 1.0539 eV [49]. These lines were also weakly detected in PL. Weak PL emissions may be the reason why the P6/P7 centers in 4H-SiC have not been detected by optical detection of magnetic resonance. In 4H-SiC, the correlation between these no-phonon lines and the P6/P7 EPR centers has not been confirmed.

5 Antisites and antisite–vacancy pairs Antisites and antisite-vacancy (AV) pairs are fundamental native defects in compound semiconductors. In SiC, both carbon antisite (C_{\text{Si}}) and silicon antisite (Si_{\text{C}}) can be easily formed [50, 51]. For AV pairs, carbon AV pairs (C_{\text{Si}}V_{\text{C}}) can be stable [52, 53].

Carbon antisite is expected to be one of the most common and abundant defects in SiC, because of its lowest formation energy among various native defects [50, 51]. However, the presence of C_{\text{Si}} has not been clear yet, because the first principles theory [50, 51] predicted that C_{\text{Si}} has no gap states and it will be invisible for any electrical and optical measurements. Recently, however, in neutron irradiated 6H-SiC after 700 °C anneal, a C_{\text{Si}} center (S = 1/2) was reported by Baranov et al. [54]. A single strong ^1\text{C} HF interaction (A_{1} = 8.1 mT, A_{2} = 3.0 mT, see Fig. 21(a)) was detected in the EPR spectrum of this center, suggesting the contribution of a C_{\text{Si}} atom to this HF interaction. However, this is not a final proof of the C_{\text{Si}} center, because carbon AV pairs [55] (see the text in later) and divacancies [56] can show similar strong ^1\text{C} HF interactions when they are positively charged. Nevertheless, C_{\text{Si}} is a particularly interesting defect, because it is the “anion” antisite in SiC. An anion antisite in GaAs (AS_{\text{Ga}} in the EL2 center) exhibits a famous bistability [57], in which the AS_{\text{Ga}} atom can stay either a four-fold-coordinated position or a three-fold-coordinated position. This bistability is accompanied with a change in the electrical and optical activity of the antisite center. By analogy with this phenomenon, an inactive C_{\text{Si}} center (sp^3-coordinated position) may transform into an active one (sp^2-coordinated position) in SiC. The Baranov’s center may be explained by the latter one.

![Figure 21](online colour at: www.pss-b.com) Angular maps for carbon antisite-related EPR centers. (a) Baranov’s center in 6H-SiC [54], (b) HEI9 centers or c-axial pairs of C_{\text{Si}}V_{\text{C}} in 4H-SiC [55], (c) HEI10 centers or basal pairs of C_{\text{Si}}V_{\text{C}} in 4H-SiC [55], (d) SI5 center or c-axial pairs of C_{\text{Si}}V_{\text{C}} in 4H-SiC in LT configuration and (e) in HT configuration [53]. These maps were simulated on “EPR in Semiconductors” (http://www.kc.tsukuba.ac.jp/div-media/epr/) using a microwave frequency of 9.400 GHz and B rotation from [0001] to [1120] (from 0° to 90°). Primary and ^1\text{C}/^2\text{Si} HF lines are denoted by, for example, “\text{C}” and “\text{Si}”, respectively. “\text{Si}_{3}\text{V}” and “\text{Si}_{3}\text{V}” atoms are three Si neighbors of V_{\text{C}}. *EPR parameters are gradually changed as a function of the temperature.

Still we may not understand a complete nature of C_{\text{Si}} in SiC, so that further studies will be necessary from experimental and theoretical view points.

On the other hand, silicon antisite attracts less attention than C_{\text{Si}} because their influences will be limited to a heavily p-doped region. All its gap levels are close to the valence band edge [50]. There is only one probable assignment for the Si_{\text{C}} center; a series of the H centers (E_{\text{V}} = 0.18 - 0.51 eV) in the deep level transient spectroscopy (DLTS) spectrum of neutron irradiated 3C-SiC may originate from Si_{\text{C}} in different charge states [50]. For the Si_{\text{C}} center (S = 1/2), a detectable ^2\text{Si} HF interaction (A_{1} = 3.2–3.4 mT, A_{2} = 0.7–0.9 mT) due to a Si_{\text{C}} atom was predicted by first principles theory [16]. How-ever, such a signature was not reported for any p-type samples.

An AV pair is a fundamental native defect, because it is a counterpart of a monovacancy in compound semiconductors [53]. For example, in an AB compound semiconductor, an A vacancy and a B antisite–B vacancy pair can
be transformed from one to another by simply moving a B atom. Carbon AV pair (anion AV pair in SiC) is expected to be important in p-type and SI SiC. In p-type SiC, a C_\text{c}SiV_\text{c} pair is energetically rather favorable than a V \text{c}_\text{Si} [52, 58]. This relationship is also true for some SI SiC substrates, depending on their Fermi levels [46, 52, 53]. Such a trend is commonly seen in anion AV pairs in GaAs [59] and in ZnO [60], according to theoretical calculations. However, the presence of AV pairs has been confirmed only in SiC. By means of a combination of EPR and first principles calculation, the HEI9/10 centers (S = 1/2) in irradiated p-type 4H-SiC were identified as the C_\text{c}SiV_\text{c} pairs [55]. Figure 22 shows schematic atomic structures of the C_\text{c}SiV_\text{c} centers. Their typical spectrum is shown in Fig. 2(b). Since there are four inequivalent configurations (kh, hh, kh, and hk) for any pairing center in 4H-SiC, four types of HEI9/10 (9a, 9b, 10a, and 10b) can be resolved. The HEI9a and 9b centers correspond to \text{C}_\text{c}Si\text{V}_\text{c} (the \text{c}-axis pairs, C_{\text{V}_{\text{c}}} symmetry), while HEI10a and 10b are \text{h}-axis pairs (basal pairs, \text{h}-axis symmetry). All of them exhibit a single strong 13C HF interaction due to a C_\text{c} atom (Fig. 21(b) and (c)). Their 13C HF interactions (A_e = 8.2–9.9 mT, A_c = 2.2–3.7 mT) indicate a very strong localization (55–58%) and a very strong p-character (f^2/a^2 = 12–16) on the C_{\text{c}} atom as shown in Table 5. The 2nd and 3rd largest HF interactions arise from 29Si atoms in the V\text{c} side and outer shells. Accordingly, the HEI9/10 EPR spectrum involves many 29Si HF satellites (A = 1.7–2.9 mT). The C_{\text{c}}SiV_\text{c} centers were often more abundant than V\text{c} (see Fig. 2(b)). However, their EPR signals were greatly underestimated at low temperatures owing to a strong saturation effect. In 6H-SiC, there are no reports for the relevant centers, however, the Baranov’s center mentioned above [54] may be consistent with a c-axial C_{\text{c}}SiV_\text{c} pair in 6H-SiC, because we can find a close similarity between Figs. 21(a) and (b). In 4H-SiC, the electronic levels (the a and a’ levels for c-axial and basal pairs, respectively) of C_{\text{c}}SiV_\text{c} were deduced to be E_c + 1.4–1.5 eV (E_c = 1.2–1.3 eV in theory) [55]. The C_{\text{c}}SiV_\text{c} centers are annealed out at 1100–1200°C in irradiated SiC, which is almost the same behavior as V\text{c} [55].

Table 5 Orbital parameters of carbon antisite-related centers in 4H-SiC calculated from experimental 13C and 29Si HF tensors [53, 55]: The spin density n^e_i, the sp hybrid ratio \beta/\alpha^2, and the direction of the p-orbital \theta with respect to the Cartesian coordinate (see Fig. 22 for the definition).

<table>
<thead>
<tr>
<th>center, symmetry</th>
<th>atom</th>
<th>n^e_i (%)</th>
<th>\beta/\alpha^2</th>
<th>\theta</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEI9a: [C_{\text{c}}(h)-V_\text{c}(h)]^+</td>
<td>C_{\text{Si}}</td>
<td>55.1</td>
<td>16.4</td>
<td>0°</td>
</tr>
<tr>
<td>[C_{\text{Si}}(k)-V_\text{c}(k)]^+</td>
<td>C_{\text{Si}}</td>
<td>58.6</td>
<td>12.6</td>
<td>0°</td>
</tr>
<tr>
<td>HEI10a: [C_{\text{Si}}(h)-V_\text{c}(h)]^+</td>
<td>C_{\text{Si}}</td>
<td>56.8</td>
<td>15.4</td>
<td>109°</td>
</tr>
<tr>
<td>HEI10b: [C_{\text{Si}}(k)-V_\text{c}(k)]^+</td>
<td>C_{\text{Si}}</td>
<td>56.0</td>
<td>16.1</td>
<td>109°</td>
</tr>
<tr>
<td>SI5 (C_{\text{Si}}), 30 K</td>
<td>Si_{\text{c}}</td>
<td>30.3</td>
<td>3.5</td>
<td>total 60.6</td>
</tr>
<tr>
<td>SI5 (C_{\text{Si}}), 100 K</td>
<td>Si_{\text{c}}</td>
<td>17.6</td>
<td>3.2</td>
<td>108°</td>
</tr>
<tr>
<td>SI5</td>
<td>Si_{\text{a}}</td>
<td>5.3</td>
<td>2.7</td>
<td>0°</td>
</tr>
</tbody>
</table>

Table 5 shows that the SI5 center at 50 K. The 29Si HF interaction of the LT configuration (A_e = 13 mT, A_c = 10 mT) indicates that the degree of localization (60.6%) and the sp-hybridization ratio (3.5, see Table 5) are quite similar to those of V\text{c} (Table 3). It should be mentioned that the SI5 center is extremely sensitive to photo illumination. In SI and n-type 4H-SiC (E_c = E_c – 1.1 eV), the C_{\text{c}}SiV_\text{c} centers (S = 0) are dominantly formed, and they can be easily converted into C_{\text{c}}SiV_\text{c} by photo excitation of electrons to the conduction band [53]. This causes a drastic increase in the SI5 signal as is seen in Fig. 2(a). Such a photo sensitivity cannot be seen in the HEI9/10 signals (Fig. 2(b)). Judging from the photo response of the SI5 center, the (–/–2) and (0/–) ionization levels were deduced to be E_c–1.05–
1.35 eV and $E_C = 1.24–1.4$ eV, respectively [46] ($E_C = 0.9$ eV and $E_C = 1.0$ eV in theory, respectively [53]). Due to these two levels, the $C_{6h}V_C$ pairs can contribute to the SI mechanism that exhibits a carrier activation energy of 1.1–1.3 eV [46].

In the last place of this section, we mention that the $C_{6h}V_C$ centers will be detectable in other spectroscopic techniques. In electron irradiated n-type 6H-SiC after 1000 °C anneal, the presence of a c-axial $C_{6h}V_C$ pair was strongly suggested by two-dimensional angular correlation of positron annihilation technique [63]. The basal $C_{6h}V_C$ pairs were not observed in this study, and in n-type 4H-SiC, too [53]. The reason why the basal pairs are hidden in n-type samples remains an unresolved problem.

6 Conclusion Vacancy-related defects such as monovacancy, divacancy, and antisite-vacancy pairs in 4H-SiC have been studied by EPR. The comparison of the obtained HF parameters with those predicted from the first principles calculations played a critical role in identification of $V_C^-(h)V_C^-(k)$, $V_C^- (h)$, $[V_C^-V_C^-]$, and $[C_{6h}V_C^-]$. The measurements of the angular dependence of the $^{13}$C/$^{29}$Si satellite lines from the nearest-neighbors, which are crucial for identification, have revealed the detailed geometric and electronic structures.

From the orbital parameters estimated from the $^{13}$C/$^{29}$Si hyperfine tensors by using a simple LCAO model, the following points, which were predicted to a considerable extent by theoretical studies, have been evidently confirmed.

1. The localization of spin densities on the nearest-neighbors ($\eta_{\text{ortho}}$) of monovacancies in 4H-SiC is larger than that in silicon and significantly smaller than that in diamond.

2. The positively charged vacancy ($V_C^+$) has slightly larger localization and higher p-character than the negatively charged vacancy ($V_C^-), similarly to $V^-$ and $V^+$ in silicon. $\eta_{\text{ortho}}$ and the sp-hybrid ratio $\beta^2/\alpha^2$ are 68%, 5.3–5.9 for $V_C^-(h)V_C^-(k)$, 61%, 3.6 for $V_C^-(h)$, and 58%, 5.6 and 54.6%, 3.4 for $V^-$ and $V^+$ in silicon [5, 6, 19].

3. Similar to $V^-$ and $V^+$ in silicon, Jahn–Teller distortion is significant for both $V_C^-(h)V_C^-(k)$ and $V_C^-(h)$ in 4H-SiC, and hence $V_C^-(h)$ takes low spin configuration ($S = 1/2$). On the other hand the electron–electron repulsion favors the high spin configuration for $V_C^+$ ($S = 3/2$), similar to $V^+$ in diamond. The distance 3.08 Å between the nearest-neighbors of unrelaxed vacancy is not strikingly larger than Si–Si bond length (2.35 Å in silicon), however, fatallier larger than C–C bond length (1.54 Å in diamond). Thus, silicon dangling bonds in $V_C^-$ form pairing bonds easily while carbon dangling bonds in $V_C^+$ are likely to be parted from each other [27]. It should be noted that the distance between the nearest-neighbors of unrelaxed vacancy in 4H-SiC is shorter than that of silicon (3.83 Å) and longer than that of diamond (2.52 Å).

4. The Jahn–Teller distortion is remarkably different between $V_C^-(h)$ ($C_{6h}$) and $V_C^-(k)$ ($C_{6v}$) in 4H-SiC. The slight difference in the small distortion from tetrahedral structure between $V_C^-(h)$ and $V_C^-(k)$ has been revealed.

5. The sp-hybrid ratio (~12) for the nearest-neighbor carbon atoms in $V_C^-$ is significantly higher than that (~5) of the nearest-neighbor silicon atoms in $V_C^+$. The large p-character in $V_C^-$ is ascribed to the outward displacement of carbon atoms forming more sp$^2$-like bonds with the next-nearest-neighbors which results in more p-like contribution to the wave function of the unpaired electron.

6. The neutral divacancy [$V_C^-V_C^-]^0$ in 4H-SiC, in which the unpaired electrons are mainly confined on carbon atoms of nearest-neighbors of $V_C^+$, takes high-spin state ($S = 1$), whereas Jahn–Teller distortion gives rise to the ground state of $S = 0$ for [$V_C^-V_C^-]^0$ in silicon. The localization (~60%) on the six nearest-neighbors (with negligibly small spin density on three silicon atoms) is smaller that of [$V_C^-V_C^-]^0$ in diamond (82%) [4] and slightly larger than that in silicon (59.3% and 54.6% for [$V_C^-V_C^-]^0$ and [$V_C^-V_C^-]^0$, respectively) [34].

Acknowledgements Here we review our works from the experimentalist side. Our identification of point defects has been achieved with collaboration with theoretical groups, A. Gali (Budapest University of Technology and Economics) and M. Bockstedte (Universität Erlangen-Nürnberg). We would like to thank Dr. H. Hara (Bruker Biospin, Japan) for his help with the pulsed-ELDOR experiments.

References


