Ligand hyperfine interactions at silicon vacancies in 4H-SiC

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Abstract
The negative silicon vacancy (\(V_{\text{Si}}^{-}\)) in SiC has recently emerged as a promising defect for quantum communication and room-temperature quantum sensing. However, its electronic structure is still not well characterized. While the isolated Si vacancy is expected to give rise to only two paramagnetic centers corresponding to two inequivalent lattice sites in 4H–SiC, there have been five electron paramagnetic resonance (EPR) centers assigned to \(V_{\text{Si}}^{-}\) in the past: the so-called isolated no-zero-field splitting (ZFS) \(V_{\text{Si}}^{-}\) center and another four axial configurations with small ZFS: \(T_{V1a}\), \(T_{V2a}\), \(T_{V1b}\), and \(T_{V2b}\). Due to overlapping with \(^{29}\text{Si}\) hyperfine (hf) structures in EPR spectra of natural 4H–SiC, hf parameters of \(T_{V1a}\) have not been determined. Using isotopically enriched 4H–\(^{28}\text{Si}\)C, we overcome the problems of signal overlapping and observe hf parameters of nearest \(C\) neighbors for all three components of the \(S = 3/2\) \(T_{V1a}\) and \(T_{V2a}\) centers. The obtained EPR data support the conclusion that only \(T_{V1a}\) and \(T_{V2a}\) are related to \(V_{\text{Si}}^{-}\) and the two configurations of the so-called isolated no-ZFS \(V_{\text{Si}}^{-}\) center, \(V_{\text{Si}}^{-\text{(I)}}\) and \(V_{\text{Si}}^{-\text{(II)}}\), are actually the central lines corresponding to the transition \(|1−1/2\rangle \leftrightarrow |1+1/2\rangle\) of the \(T_{V2a}\) and \(T_{V1a}\) centers, respectively.

Keywords: silicon vacancy, hyperfine interaction, electron paramagnetic resonance

(Some figures may appear in colour only in the online journal)

1. Introduction

The silicon vacancy (\(V_{\text{Si}}^{-}\)) in silicon carbide (SiC) was first identified by electron paramagnetic resonance (EPR) in 3C-SiC \cite{[1, 2]}. In the negative charge state, the \(V_{\text{Si}}^{-}\) center has a high-spin configuration (\(S = 3/2\)) but shows no zero-field splitting (ZFS) as expected for the \(T_{4}\) symmetry in cubic crystals, where the dipole–dipole interaction between three spin pairs cancels each other due to high symmetry. Later, Wimbauer and co-workers observed this center in 4H- and 6H–SiC and confirmed its spin \(S = 3/2\) by electron nuclear double resonance measurements \cite{[3]}.. However, in their EPR study, they missed the low- and high-field lines, which later become known to be very weak compared to the central line (CL) of this \(S = 3/2\) center. Therefore, the \(V_{\text{Si}}^{-}\) center in hexagonal polytypes was believed to give rise to only one EPR line like the center in the cubic crystal 3C-SiC with no ZFS \cite{[3]}. We refer to this defect as the no-ZFS \(V_{\text{Si}}^{-}\) center.

Later optically detected magnetic resonance (ODMR) studies reported several ODMR centers with axial symmetry and small ZFS, labelled \(T_{V1a}\), \(T_{V2a}\), \(T_{V1b}\), and \(T_{V2b}\), which were suggested to be related to the V1 and V2 photoluminescence (PL) lines at 1.438 and 1.352 eV, respectively, in 4H-SiC \cite{[4]}. The absence of the CL in the ODMR spectra measured under resonant excitation led to the assignment of these centers to the isolated neutral Si vacancy (\(V_{\text{Si}}^{0}\)) with spin \(S = 1\) \cite{[4]}. Two PL centers are expected for two possible configurations.
of an isolated $V_{\text{Si}}$ defect occupying the hexagonal ($h$) and quasi-cubic ($k$) sites in 4H-\text{SiC} (figure 1(a)) but no concrete assignment of $V_1$ and $V_2$ to the lattice sites was suggested [4]. The $T_{\text{V}_{\text{2}a}}$ and $T_{\text{V}_{\text{2}b}}$ centers were also observed by EPR and assigned to $V_{\text{Si}}$ at the $h$ and $k$ site, respectively [5]. In later EPR studies [6, 7], $T_{\text{V}_{\text{2}a}}$ and $T_{\text{V}_{\text{2}b}}$ were shown to have spin $S = 3/2$ and assigned to $V_{\text{Si}}$ being disturbed by a defect located at a C site along the $c$-axis in the third and seventh neighbor, respectively, as depicted in figure 1(b).

The hyperfine (hf) parameters of the interaction between the electron spin and the nuclear spins of nearest neighbor (NNN) C atoms were determined for $T_{\text{V}_{\text{2}a}}$ from its low- and high-field lines [6, 8]. Unexpectedly, the C hf tensor of $T_{\text{V}_{\text{2}a}}$ [6] was different from the two C hf tensors determined from the CL [9]. This supports the existing idea that the strong CL is comprised of the strong signal of the two isolated no-ZFS $V_{\text{Si}}^-$ centers at the $h$- and $k$-site labelled as no-ZFS $V_{\text{Si}}^-$ (I) and $V_{\text{Si}}^-$ (II), respectively [9], and weak CLs of $T_{\text{V}_{\text{2}a}}$ centers. Due to the overlap with the hf structures of next nearest neighbors (NNN) Si atoms, the $T_{\text{V}_{\text{1}a}}$ center is not reported by EPR and its C hf parameters have not been determined so far.

In EPR experiments using very low microwave (MW) powers and low field modulations, Jánzén and co-workers [10] could partly resolve the $T_{\text{V}_{\text{1}a}}$ signal in 4H-\text{SiC} and the $T_{\text{V}_{\text{1}a}}$ and $T_{\text{V}_{\text{3}a}}$ signals in 6H-\text{SiC}. Combining the EPR observation with previously reported ODMR data, they suggested that the $T_{\text{V}_{\text{1}a}}$ and $T_{\text{V}_{\text{2a}}}$ centers in 4H-\text{SiC} and $T_{\text{V}_{\text{1}a}}$, $T_{\text{V}_{\text{2a}}}$ and $T_{\text{V}_{\text{3}a}}$ in 6H-\text{SiC} are related to the ground state of the isolated $V_{\text{Si}}^-$ center at inequivalent lattice sites in these polytypes and, thus, there cannot exist another set of isolated no-ZFS $V_{\text{Si}}^-$ centers. However, it remained unclear why the low- and high-field lines of $T_{\text{V}_{\text{3}a}}$ center are unusually weak compared to the CLs, and why the C hf parameters determined from the CL [9] are different from those determined from the $T_{\text{V}_{\text{2a}}}$ line in [6], if the no-ZFS $V_{\text{Si}}^-$ center does not exist.

Later studies in 6H-\text{SiC} [11] and 15R-\text{SiC} [12] suggested an alternative complex model for the $T_{\text{V}}$ centers comprising of an isolated $V_{\text{Si}}^-$ defect and a neutral C vacancy ($V_{\text{C}}^0$) located at the third and seventh neighbor along the $c$-axis (see figure 1(b)). However, a recent calculation [13] showed that the ($V_{\text{Si}}^- - V_{\text{C}}^0$) complex has spin $S = 1/2$ with spin distribution different from that of the isolated $V_{\text{Si}}^-$ model. From the calculation of ZFS and hf parameters, the $T_{\text{V}_{\text{1}a}}$ and $T_{\text{V}_{\text{2}a}}$ centers were reassigned to the isolated $V_{\text{Si}}^-$ defect at the $h$- and $k$-site, respectively [13]. However, due to the lack of experimental data, especially the NN C hf parameters, no conclusion on the origin of the $T_{\text{V}_{\text{1}b}}$, $T_{\text{V}_{\text{2}b}}$ and no-ZFS $V_{\text{Si}}^-$ centers could be made.

Recently, the $V_{\text{Si}}^-$ centers with axial symmetry and small ZFS, $T_{\text{V}_{\text{1}a}}$ and $T_{\text{V}_{\text{2}a}}$, have emerged as defects suitable for spin quantum bits (qubits) [11, 14–24] and quantum sensing, such as vector magnetometry [25–30], owing to their excellent optical and spin properties. For instance, single spins with long coherence times can be optically addressed and controlled at room temperature [20]. These applications require detailed knowledge on the microscopic model and electronic structure of the defect, especially the hf interactions with neighboring nuclear spins. Therefore, clarification of the microscopic model of the $T_{\text{V}_{\text{1}a}}$ and $T_{\text{V}_{\text{2}a}}$ centers and determination of their C hf parameters are of high interest.

In this EPR study, using isotopically enriched 4H-\text{SiC} ($^{28}$Si: nuclear spin $I = 0$) with reduced intensity of the hf structures arising from the interaction with NNN $^{28}$Si ($I = 1/2$, 4.68\% natural abundance), we avoid the problems of signal overlapping and determine complete hf parameters of nearest C neighbors for $T_{\text{V}_{\text{1}a}}$ and $T_{\text{V}_{\text{2a}}}$ centers, including their central components. From hf data we suggest a correction of the C hf parameters previously reported for $T_{\text{V}_{\text{2a}}}$ center [6] and assign the so-called no-ZFS $V_{\text{Si}}^-$ (I) and $V_{\text{Si}}^-$ (II) centers [9] to the transition $|–1/2 \leftrightarrow |+1/2\rangle$ of $T_{\text{V}_{\text{2a}}}$ and $T_{\text{V}_{\text{1}a}}$, respectively. This conclusion is further supported by our annealing study, which shows that the unusually strong CL of the $V_{\text{Si}}^-$ center as compared to the low- and high-field lines of $T_{\text{V}_{\text{2a}}}$ arises because it contains contribution from the CLs of $T_{\text{V}_{\text{1}a}}$ and $T_{\text{V}_{\text{2a}}}$ and also from other four $S = 3/2$ centers, including $T_{\text{V}_{\text{1}b}}$, $T_{\text{V}_{\text{2}b}}$ and two new centers. These centers have different annealing behavior compared to the $T_{\text{V}_{\text{1}a}}$ and $T_{\text{V}_{\text{2a}}}$ centers and may be related to complex defects involving $V_{\text{Si}}^-$. 

2. Experiment

The starting material used in this study is isotopically purified 4H-\text{SiC} epilayer grown by chemical vapor deposition (CVD) [31]. The isotope purity of $^{28}$Si in this layer is expected to be 99.85\%, which is the value determined by secondary ion mass spectrometry (SIMS) for other isotopically enriched 4H-\text{SiC} wafers grown in the series [32]. The layers are very low-doped with the residual N-doping concentration of $\sim 5 \times 10^{12} \text{ cm}^{-3}$ as estimated from PL [33]. Free-standing 4H-\text{SiC} CVD layers with a thickness of $\sim 250 \mu\text{m}$ were obtained after removing the substrate by mechanical polishing. After polishing, the layers were annealed at 1130 °C to reduce the concentration of paramagnetic defects at the surfaces created by polishing. The samples
were irradiated by 2 MeV electrons at room temperature to a dose of $4 \times 10^{18}$ cm$^{-2}$ to create high concentration of $V_{Si}$. EPR measurements were performed on an X-band (9.4 GHz) Bruker E500 EPR spectrometer equipped with a He-flow cryostat, allowing sample temperature regulation in the range of 4–300 °C. The concentration or the number of spins of the Si vacancy centers was determined from the EPR signal using the spin counting function calibrated by Bruker.

### 3. Results and discussion

After irradiation, the sample is annealed to 300 °C to remove interstitial-related defects. Figure 2(a) shows the EPR spectrum in irradiated 4H-$^{28}$SiC measured at 292 K in darkness for $B||c$ with a field modulation of 0.2 G and a MW power of 6.325 μW. The inset shows a partly resolved signals of $T_{V1a}$ and $R1$ and an unidentified axial center with $S=1/2$ and $g_S=2.00243$. (b) EPR spectrum in (a) measured with a higher MW of 0.6325 mW showing the signals $R1$, $R2$, $T_{V1b}$ and $T_{V2b}$ (the $T_{V2b}$ signal coincides with the $C_1$ hf of the CL). For clarity, the CL and the top parts of the $T_{V2b}$ lines are not shown in the extended intensity-scale spectrum in (b). For removing signals from interstitial-related centers, the sample has been annealed to 300 °C.

### Figure 2

(a) EPR spectrum in irradiated 4H-$^{28}$SiC measured at 292 K in darkness for $B||c$ with a field modulation of 0.2 G and a MW power of 6.325 μW. The inset shows a partly resolved signals in a 4H interstitial-related defects. Figure 2(a) shows the EPR spectrum calibrated by Bruker.

After irradiation, the sample is annealed to 300 °C to remove interstitial-related defects. Figure 2(a) shows the EPR spectrum in 4H-$^{28}$SiC measured at 292 K in darkness for the $c$-axis with a field modulation of 0.2 G and a MW power of 6.325 μW. The inset shows the extended magnetic field scale in the range of 4–300 °C. The concentration or the number of spins of the Si vacancy centers was determined from the EPR signal using the spin counting function calibrated by Bruker.

The $T_{V1b}$ and $T_{V2b}$ centers are known to have $C_3v$ symmetry and the electron spin $S=3/2$ is confirmed for $T_{V2b}$. The $R1$ and $R2$ lines do not split when rotating the magnetic field away from the $c$-axis. Thus, their symmetry is also $C_3v$. This means that the principal direction of their ZFS tensor is along the $c$-axis and these centers have ZFS close to that of $T_{V2a}$. Such small ZFS suggests that these centers are likely to have spin $S=3/2$ and not $S=1$. The reason is that in an $S=3/2$ system with three unpaired electrons, there are three spin pairs ($S_1S_2$, $S_2S_3$, $S_3S_1$), whose dipole–dipole interaction in high symmetry crystals may partly cancel each other resulting in a small contribution to the ZFS tensor. (For an $S=1$ system with only one spin pair there is no such cancelation and the ZFS is expected to be large.) Thus, with $S=3/2$, the $R1$, $R2$, $T_{V1b}$ and $T_{V2b}$ centers will have their CL overlapping with the CL of $T_{V1a}$ and $T_{V2a}$. We list here their fine-structure parameter $D$ for $S=3/2$ determined from our experiments: $R1$: 0.8 G (2.24 MHz), $R2$: 14.1 G (39.4 MHz), $T_{V1b}$: 11.6 G (32.6 MHz), and $T_{V2b}$: 7.15 G (20.0 MHz).

Figure 3 shows the doubly integrated intensities of the low- and high-field lines of $T_{V2a}$ and $T_{V1a}+R1$ centers and the CL in as-irradiated and annealed samples. To avoid problem with base line correction, we fit each line with a mixed Gaussian
and Lorentzian shape and do double integration on the fitting line. Here the intensity of the CL in the sample annealed at 700 °C is set to 1 for easy comparison. Within the experimental error, no noticeable changes in the intensity of the \( T_{V2a} \), \( T_{V1a} + R1 \) and CLs are observed in the annealing temperature 20–600 °C. As can be estimated from figure 3, the intensity ratio between the CL and the \( T_{V2a} \) line or the two low-field lines (\( T_{V2a} \) and \( T_{V1a} + R1 \)) is ~5 and ~1.7, respectively.

After annealing at 700 °C, the \( R1 \), \( R2 \), and \( T_{V1b} \) signals are not observed as can be seen in figures 4(a) and (b). The resonance line at the position of \( T_{V2b} \) and the \( C1 \) hf line of the CL is reduced by 47%, suggesting that the \( T_{V2b} \) center is also annealed out. With the disappearance of these signals, the intensity of the CL is drastically decreased (see also figures 3 and 4). The ratio between the intensity of the CL and the sum of intensities of two low-field (or high-field) lines (\( T_{V2a} \) and \( T_{V1a} + R1 \)) is found to decrease from ~1.7 to ~1.0 when the \( R1 \), \( R2 \), \( T_{V1b} \) and \( T_{V2b} \) signals disappear (figure 3). This suggests that (i) the unusually strong CL, as compared to the low- and high-field \( T_{V2a} \) lines, is due to the contribution from other \( S = 3/2 \) centers (\( R1 \), \( R2 \), \( T_{V1b} \) and \( T_{V2b} \)), and (ii) after annealing at 700 °C, the CL of the spectrum is purely from the transitions \( |\pm 1/2\rangle \leftrightarrow |\pm 1/2\rangle \) of the \( T_{V1a} \) and \( T_{V2a} \) centers.

The above intensity ratio between the CL and the low-field \( T_{V2a} \) line of ~5 is much smaller than the corresponding ratio when comparing the peak height. When measuring with a low MW power (0.2 \( \mu \)W) and a field modulation (0.3 G), the ratio between the intensity of the CL and the \( T_{2a} \) line is about 43 \( [6] \), which is similar to the intensity ratio of ~41 obtained by comparing the peak height for the spectrum in figure 2(a) measured with a MW power of 6.325 \( \mu \)W and a field modulation of 0.2 G. However, if comparing the integrated intensity, this ratio reduces to ~8. When measuring with a higher MW power of 0.6325 mW, this intensity ratio decreases to ~5 (figure 4) (or ~18 if comparing the peak height).

We notice that the linewidth of \( T_{V1a} \) and \( T_{V2a} \) counted from the maximum to the minimum of the absorption peak, is ~0.44 G and ~0.39 G when measured at the MW power of 0.6325 mW and 6.325 \( \mu \)W, respectively, while the corresponding linewidths of \( T_{V2b} \) and \( R1 \) are significantly narrower (~0.24 G and ~0.2 G). These narrow lines show no or very little reduction in peak height with decreasing the MW power by two orders of magnitude from 0.6352 mW to 6.325 \( \mu \)W. Comprising of \( T_{V1a} \), \( T_{V2a} \) and other four centers (\( T_{V1b} \), \( T_{V2b} \), \( R1 \) and \( R2 \)) with \( T_{V2b} \) and \( R1 \) having significantly narrower linewidth, the CL has also narrow linewidths (corresponding values: ~0.29 G and 0.22 G at high and low MW power, respectively) as expected. We observe almost no change in the peak height of the CL, while the peak height of the \( T_{V2a} \) line is reduced by a factor of 2. This may explain the large variation in the intensity ratio between the CL and the \( T_{V2a} \) line as estimated from the peak height. When measuring with high MW powers (>1 mW) saturation starts to occur for \( T_{V2a} \) but not yet for the \( R1 \), \( R2 \), \( T_{V1b} \) and \( T_{V2b} \) centers. This can also lead to the increase of the intensity ratio. We also notice that the Si vacancy centers have long spin-lattice relaxation time so measuring with high modulation frequencies and high MW powers will reduce the in-phase signal and increase the out-phase signal. Therefore, optimized MW power and lock-in phase for obtaining maximum intensity of the CL are often not suitable for measuring the \( T_{V2a} \) signal and can decrease the low- and high-field \( T_{V2a} \) lines approaching the noise level.

After annealing at 700 °C, all the components of \( S = 3/2 \) \( T_{V1a} \) and \( T_{V2a} \) centers corresponding to the transitions \( |3/2\rangle \leftrightarrow |1/2\rangle \), \( |1/2\rangle \leftrightarrow |1/2\rangle \) (the CL), \( |1+1/2\rangle \leftrightarrow |1+3/2\rangle \) and their NN C hf lines can be clearly detected as can
The hf structure of the interaction with NN C1 and C2,4 atoms of TV2a can be detected, as seen in ×10 intensity scale. The unidentified center has \( g = 2.00403 \). Figure 5 shows the EPR spectrum of irradiated 4H-\(^{28}\)SiC after annealing at 820 °C measured at 292 K in darkness for B \( \perp c \). The hf structures are well resolved from the CL 4.0 G and TV2a centers is accompanied by two pairs of the C hf lines. The pair with a larger splitting \( 28.5 \text{ G for } TV_{V2a} \) and 28.6 G for \( TV_{V1a} \) shows an intensity ratio of \( \sim 1\% \) and should be from the interaction with one NN \(^{13}\)C atom along the \( c \)-axis (labelled as C1 in figure 1(a)). The other pair with a smaller hf splitting \( 13.2 \text{ G for } TV_{V2a} \) and 14.0 G for \( TV_{V1a} \) is from the hf interaction with three equivalent NN \(^{13}\)C atoms in the basal plane (labelled as C2,4).

Figure 4(c) shows the high-field line of \( TV_{V2a} \) of the spectrum in figure 4(b) measured with a higher field modulation of 0.6 G. The red curve is the simulated spectrum including the hf interaction with three equivalent C atoms (hf splitting of 13.2 G) and with one C atom (hf splitting of 28.5 G). The excellent agreement between the experiment and the simulation confirms that the hf structures are due to the hf interaction between the electron spin and the nuclear spin of one \(^{13}\)C atom along the \( c \)-axis (labelled as C1 in figure 1(a)). The red curve is the simulated spectrum including the hf interaction with NN C1 and C2 atoms (hf splitting of 0.6 G). The thin dotted curves are their corresponding hf lines.

Within the interference of the hf structure from the NN Si atoms, the \( TV_{V1a} \) and \( TV_{V2a} \) signals and their NN C hf lines can be detected in all directions of the magnetic field. Their angular dependences with the magnetic field rotating in the (1 0 0) plane shown in figure 6 can be described by the spin Hamiltonian

\[
\mathcal{H} = \mu_B g \cdot B \cdot S + S \cdot D \cdot S + \sum_i S \cdot A_i \cdot I_i. \tag{1}
\]

Here \( \mu_B \) is the Bohr magneton, the electron spin is \( S = \frac{3}{2} \), the nuclear spin of \(^{13}\)C nucleus is \( I = \frac{1}{2} \), and \( g, D, \) and \( A_i \) are the g-tensor, the second rank fine-structure tensor, and the hf tensor, respectively. The subscripts \( i \) denote the NN nuclei C1 and C2,4. The parameters obtained from the best fits are given in table 1 and equation (1) are plotted as dotted curves in figure 6.

Within the linear combination of atomic orbitals approximation, the wave function of the unpaired electron close to a neighboring C atom can be written as a superposition of the electronic wave function \( \psi_r \) and \( \psi_p \) of s and p orbitals

\[
\psi = \eta \left( \alpha \psi_r + \beta \psi_p \right). \tag{2}
\]

Here \( \alpha^2 + \beta^2 = 1 \) and \( \eta^2 \alpha^2 \) and \( \eta^2 \beta^2 \) are the spin density on the s and p orbitals, respectively, which are proportional to the isotropic and anisotropic components of the hf A tensor. The isotropic part \( a \) and anisotropic part \( b \) can be estimated as \( a = (A_0 + A_1)/3 \) and \( b = (A_0 - A_1)/3 \). For the case of the A tensor of C2,4 atoms with C1h symmetry but nearly axially symmetric along the X-axis, \( a \) and \( b \) can be approximated as: \( a = (A_X + A_Y + A_Z)/3 \) and \( b = [A_X - (A_Y + A_Z)/2]/3 \). For \(^{13}\)C...
Table 1. Spin-Hamiltonian parameters of the negative Si vacancy $T_{V1a}$ and $T_{V2a}$ centers in 4H–SiC at room temperature. The polar angle $\theta$ and azimuthal angle $\varphi$ of the principal axes of the $\alpha$- and $\beta$-tensors are given in degrees with $\theta = 0$ and $\theta = 90$ corresponding to the [0001] and [1100] directions, respectively, while $\varphi = 0$ and $\varphi = 90$ corresponding to the [11?0] and [1?10] directions, respectively. $X$, $Y$, and $Z$ are the principal axes of the tensors. The $D$ and $A$ values are given in MHz using the conversion $A (\text{MHz}) = A (G) \times 2.802495$. The errors in the determination of parameters: $\pm 0.00005$ for the $g$-value, $\pm 0.3$ MHz for $D (T_{V1a})$, $\pm 0.5$ MHz for $D (T_{V2a})$, and $\pm 0.5$ MHz for principal values of principal axes of the $\alpha$-tensor. The values of $\eta^2\alpha^2$ and $\eta^2\beta^2$ are the spin densities in $s$ and $p$ orbitals, respectively. The $A$-values of the $T_{V2a}$ center in [6] and the no-ZFS $V_{Si}^\alpha$ (I) and $V_{Si}^\beta$ (II) centers in [9] are also given for comparison.

| Parameters | Angle | $X$     | $Y$     | $Z$     | $\eta^2\alpha^2$ (%) | $\eta^2\beta^2$ (%) | $\eta^2$ (%) |
|------------|-------|---------|---------|---------|----------------------|----------------------|---------------|
| $T_{V1a}$  | $g$   | $\theta$| 90°     | 90°     | 0°                   | 1.3                  | 14.7          | 16.0         |
| $D = 2.5$  | $\theta$ | 32.9    | 32.9    | 80.2    | 1.3                  | 14.1                 | 15.4          |
| $A(C_1)$   | 0°     | 78.7    | 29.1    | 30.6    | 3.6                  | 45.5                 | 49.1          |
| $A(C_{24})$| $\theta$ | 109.3° | 90°     | 19.3°   |                      |                      |               |
| $\Sigma \eta^2(C_{14})$ | 4.9 | 60.2 | 65.1 | | | |
| $T_{V2a}$  | $g$   | $\theta$| 90°     | 90°     | 0°                   | 1.3                  | 14.1          | 15.4         |
| $D = 35.0$ | $\theta$ | 34.5    | 34.5    | 80.0    | 1.3                  | 14.1                 | 15.4          |
| $A(C_1)$   | 0°     | 75.3    | 28.2    | 29.5    | 3.6                  | 43.3                 | 46.9          |
| $A(C_{24})$| $\theta$ | 110.9° | 90°     | 20.9°   |                      |                      |               |
| $\Sigma \eta^2(C_{14})$ | 4.9 | 57.4 | 62.3 | | | |
| $A(C_1)\alpha$ | 34.8 | 34.8 | 80.3 | 1.3 | 14.1 | 15.4 |
| (160 K)    | $\theta$ | 90°     | 90°     | 0°     |                      |                      |               |
| $A(C_{24})\beta$ | 75.8 | 31.3 | 27.2 | 3.6 | 43.3 | 46.9 |
| (160 K)    | $\theta$ | 107.5° | 17.5°   | 90°    |                      |                      |               |
| $\Sigma \eta^2(C_{14})\beta$ | 4.9 | 57.4 | 62.3 | | | |
| no-ZFS $V_{Si}^\alpha$ (I) | $A(C_1)\beta$ | 33.2 | 33.2 | 80.1 | 1.3 | 14.6 | 15.9 |
| $\theta$ | 90°     | 90°     | 0°     |                      |                      |               |
| $A(C_{24})\beta$ | 76.3 | 28.3 | 28.2 | 3.5 | 44.7 | 48.2 |
| $\theta$ | 110°    | 90°     | 20°    |                      |                      |               |
| $\varphi$ | 0°      | 90°     | 0°     |                      |                      |               |
| $\Sigma \eta^2(C_{14})\beta$ | 4.8 | 59.3 | 64.1 | | | |
| no-ZFS $V_{Si}^\beta$ (II) | $A(C_1)\beta$ | 33.8 | 33.8 | 80.1 | 1.3 | 14.4 | 15.7 |
| $\theta$ | 90°     | 90°     | 0°     |                      |                      |               |
| $A(C_{24})\beta$ | 79.4 | 31.4 | 31.2 | 3.8 | 44.8 | 48.6 |
| $\theta$ | 109.2°  | 90°     | 19.2°  |                      |                      |               |
| $\varphi$ | 0°      | 90°     | 0°     |                      |                      |               |
| $\Sigma \eta^2(C_{14})\beta$ | 5.1 | 59.2 | 64.3 | | | |

$^a$ From [6].
$^b$ Values measured at room temperature from [9]. Here the $D$ values ($D = 3D_{q3}/2$) are given for the case of $S = 3/2$.

Atoms with $A$-values given in MHz, $\eta^2\alpha^2 = a/3776.92$ and $\eta^2\beta^2 = b/107.39$ [34, 35]. The obtained spin densities on NN C atoms of $T_{V1a}$ and $T_{V2a}$ centers are given in Table 1.

As can be seen in Table 1, the spin density of $T_{V1a}$ (65.1%) is a bit higher than that of $T_{V2a}$ (62.3%). It is also evident that the hf parameters and the spin density of $T_{V1a}$ and $T_{V2a}$ centers are very similar to the corresponding values of the no-ZFS $V_{Si}^\alpha$ (II) and $V_{Si}^\beta$ (I) centers, respectively, from [9]. Thus, we believe that the previously reported no-ZFS $V_{Si}^\alpha$ (I) center is actually the CL corresponding to the transition $|1/2\rangle \leftrightarrow |1+1/2\rangle$ of the $T_{V2a}$ center, while the no-ZFS $V_{Si}^\beta$ (II) center is the CL of the $T_{V1a}$ center. Consequently, the so-called no-ZFS $V_{Si}^\beta$ centers do not exist.

The principal hf values and the angles of principal axes of the $C$ hf tensor determined in our study for the $T_{V2a}$ center are different from the previously reported values [6]. More
precisely, according to our data, the principal values $A_3$ and $A_2$ of the $A(T, \varphi)$-tensor and the corresponding angles $\theta$ and $\varphi$ of these principal axes reported in [6] should be interchanged.

Previous EPR, PL and ODMR studies of irradiated SiC suggested that $V_{\text{Si}}$ becomes mobile at ~700 °C and are annealed out at ~750 °C–800 °C [1, 4]. Comparing the low- and high-field lines of $T_{V_{\text{Si}}}$ in samples annealed at 600 °C and 700 °C (figure 2), we estimate that annealing at 700 °C reduces the concentration of the Si vacancy $T_{V_{\text{Si}}}$ by ~25%. This is consistent with the annealing behavior of the Si vacancy in 3C–SiC in this temperature range [1]. Annealing at 820 °C reduces the Si vacancy by ~85% (figure 3) but the signal including its C hf structures can still be clearly detected (figure 5). We have noticed that in irradiated natural 4H–SiC annealed at 1180 °C, the EPR signals of the $T_{V_{\text{Si}}}^1$ and $T_{V_{\text{Si}}}^2$ centers and their NNN Si hf structure can still be weakly observed.

The gradually annealing behavior of the Si vacancy can be explained by its metastable properties [36]. At ~700 °C, the C vacancy is stable, but the Si vacancy becomes mobile and can find a C vacancy to form the divacancy [37]. The $V_{\text{Si}}$ center can also capture a C atom nearby to form an antisite-vacancy pair $\text{CSi}_2^-$ [38] as has also been predicted by calculations [36]. However, the energy barrier for dissociation of the $\text{CSi}_2^-$ complex, which leads to the recovery of the isolated $V_{\text{Si}}$ center, is only a bit higher than the formation energy of the pair [36]. Due to these competing processes in formation and dissociation of the $\text{CSi}_2^-$ pairs, the Si vacancy is not annealed out completely when it becomes mobile but gradually in a large temperature range.

The origin of the $T_{V_{\text{Si}}}^1$ and $T_{V_{\text{Si}}}^2$ centers has not so far been clarified. Unlike the $T_{V_{\text{Si}}}^1$ and $T_{V_{\text{Si}}}^2$, centers, which can be detected by ODMR using resonance excitation on the V1 and V2 PL lines, respectively, or off-resonance below-bandgap excitation, the $T_{V_{\text{Si}}}^1$ and $T_{V_{\text{Si}}}^2$ signals were only detected under above-bandgap excitation [4]. The $T_{V_{\text{Si}}}^1$ signal is overlapped with the hf lines from the hf interaction with 12 NNN Si atoms and has not been reported by EPR. The $T_{V_{\text{Si}}}^2$ signal was previously assigned to the ground state of the isolated neutral Si vacancy, $V_{\text{Si}}^0$, at the quasi-cubic site [5]. Its spin was corrected to be $S = 3/2$ in nutation experiments [6]. From the observation of the signal at 10 K, Mizuochi and co-workers [6] suggested that $T_{V_{\text{Si}}}$ should be related to the ground state of the $V_{\text{Si}}$ center being disturbed by a defect along the $c$-axis.

In our studies, we also observe the $T_{V_{\text{Si}}}^1$ and $T_{V_{\text{Si}}}^2$, R1 and R2 signals at low temperatures (e.g. down to 16 K). Therefore, they are likely related to ground states of defects. Since the $T_{V_{\text{Si}}}^1$ and $T_{V_{\text{Si}}}^2$ signals are related to the ground states of the isolated $V_{\text{Si}}$ center at two possible configurations (at the hexagonal and quasi-cubic lattice sites, respectively), the $T_{V_{\text{Si}}}^1$, $T_{V_{\text{Si}}}^2$, R1 and R2 centers cannot be related to the isolated $V_{\text{Si}}$ center.

Our annealing studies shows that the $T_{V_{\text{Si}}}^1$ and $T_{V_{\text{Si}}}^2$, R1 and R2 centers are annealed out at lower temperatures than the $V_{\text{Si}}^-$. These signals could not be detected in samples annealed at 700 °C, in which the $T_{V_{\text{Si}}}^2$ center including its hf structure due to the interaction with a single C atom could still be clearly observed. Thus, the annealing behavior also supports the conclusion that these signals are not related to the isolated Si vacancy.

It is noticed that there are similarities between these centers and the $V_{\text{Si}}$ center. They have an isotropic $g$-value of ~2.0029, spin $S = 3/2$ with small ZFS, $C_3v$ symmetry and are observed together in irradiated materials. Furthermore, the $T_{V_{\text{Si}}}^1$, $T_{V_{\text{Si}}}^2$, R1 and R2 centers disappear after annealing at ~700 °C when the Si vacancy becomes mobile. All these suggest that these centers may belong to a family of complex defects involving a negative Si vacancy and a defect located along the $c$-axis, which should be an intrinsic defect carrying no electron spin. The identification of these defects requires further investigations.

4. Summary

In summary, using isotopically enriched ultra-pure 4H–$^{28}$SiC CVD layers we could detect clear EPR spectra of the $T_{V_{\text{Si}}}^1$ and $T_{V_{\text{Si}}}^2$, centers in darkness and determine their ZFS and N N C hf parameters. The analysis of the intensity of the low- and high-field lines and the CL in the as-irradiated sample and in samples annealed at different temperatures suggests that the unusually high intensity of the CL as compared to the intensity of the low- and high-field $T_{V_{\text{Si}}}$ lines is due to the contribution of other $S = 3/2$ centers (R1, R2, $T_{V_{\text{Si}}}^1$, and $T_{V_{\text{Si}}}^2$) to the CL. Annealing studies show that the $T_{V_{\text{Si}}}^1$, $T_{V_{\text{Si}}}^2$, R1 and R2 centers are annealed out at ~700 °C, and, hence, cannot be related to the isolated $V_{\text{Si}}^-$. Center. From the similarity in the hf parameters and the spin density, it is suggested that the previously reported no-ZFS $V_{\text{Si}}^-$ (I) and $V_{\text{Si}}^-$ (II) centers are the CL corresponding to the transition $|1\rangle \leftrightarrow |1\rangle$ of the $T_{V_{\text{Si}}}^2$ and $T_{V_{\text{Si}}}^1$, centers, respectively. Thus, the no-ZFS $V_{\text{Si}}^-$ centers proposed earlier do not exist. We also show that the Si vacancy is gradually annealed out in a large temperature range (700 °C–1200 °C). This annealing behavior can be useful for fine tuning the Si vacancy concentration in engineering well separated single $V_{\text{Si}}$ emitters.

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