Continuous-wave and pulsed EPR study of the negatively charged silicon vacancy with $S = \frac{3}{2}$ and $C_{3v}$ symmetry in $n$-type 4H-SiC

N. Mizuochi, 1, * S. Yamasaki, 2 H. Takizawa, 3 N. Morishita, 3 T. Ohshima, 3 H. Itoh, 3 and J. Isoya 1,†

1University of Library and Information Science, 1-2 Kasuga, Tsukuba-City, Ibaraki 305-8550, Japan
2National Institute of Advanced Industrial Science and Technology (AIST), Advanced Semiconductor Research Center, AIST Tsukuba Central 4, Tsukuba-city, Ibaraki 305-8562, Japan
3Japan Atomic Energy Research Institute, 1233 Watanuki, Takasaki-City, Gunma 370-1292, Japan

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The $T_{2v}$ center, which was suggested to be the excited triplet state ($S = 1$) of the neutral silicon vacancy related defect [Sörman et al., Phys. Rev. B 61, 2613 (2000)] in the electron-irradiated $n$-type 4H-SiC has been studied by continuous wave and pulsed electron paramagnetic resonance (EPR). The spin multiplicity of $T_{2v}$ has been determined to be quartet ($S = 3/2$) by the nutation method of pulsed EPR technique. From the temperature dependence of the signal intensity, it has been revealed that the $T_{2v}$ spectrum is arising from an electronic ground state. From the measurement of the $^{13}$C hyperfine interactions of the nearest neighbors which has been enabled by the selective enhancement of the $T_{2v}$ signals through the spin polarization by a laser light (808 nm) illumination, the center is unambiguously identified to be a single silicon vacancy. It is proposed that the center is a negatively charged silicon vacancy of $C_{1v}$ symmetry with the crystal field distorted slightly from regular tetrahedron. The triply degenerate $t_2$ state of an electronic configuration $a_1^2 t_2$ under $T_d$ symmetry splits into $a_1$ and $e$ by the distortion to $C_{3v}$. The high spin configuration [$a_1 e^2$ or $e^2 a_1$] which reduces the electron repulsion energy is preferred rather than the low spin configuration expected from the symmetry-lowering crystal field alone. The important role of the many-electron effect in determining the ground-state configuration is demonstrated clearly by $T_{2v}$ in which the electron-electron interactions (the electronic repulsion and the electron exchange) compete against the crystal-field splitting.

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I. INTRODUCTION

In crystalline semiconductors, lattice vacancies are one of the most important intrinsic defects that might be introduced during crystal growth and material processing such as ion implantation. Electron paramagnetic resonance (EPR) is one of the most powerful methods to elucidate the geometric and electronic structures of vacancies. Irradiating with energetic particles produces a concentration of vacancies sufficient for a detailed structure determination. Selecting the kind and the concentration of major impurities varies the charge of vacancy.

The structure relaxation of vacancy is determined by a modification of the neighboring bonds. In a simple one-electron model of a single vacancy of tetrahedral semiconductors, defect molecular orbitals, which are linear combinations of the dangling bond orbitals of four atoms around the vacancy, split into an $a_1$ singlet and a $t_2$ triplet under $T_d$ symmetry. 1 The electronic configuration of the ground state of negatively charged vacancy ($V^-$) is $a_1^2 t_2$. From the determination of the effective spin of $S = 3/2$ and the $T_d$ symmetry by using EPR and electron nuclear double resonance (ENDOR) techniques, the ground state of $V^-$ in diamond ($E_g = 5.5eV$) was identified to be $^4A_2$. 2 In $V^-$ of diamond, the repulsion among the highly localized three $t_2$ electrons is lowered by occupying each of three different orbitals. The orbital nondegenerate $^4A_2$ state is not subject to a Jahn-Teller distortion. In silicon ($E_g = 1.1eV$), $V^-$ has a $C_{2v}$ symmetry with $S = 1/2$. 3 The energy stabilization is achieved by the Jahn-Teller distortion, while the electronic repulsion is lowered by an extensive delocalization. The extent of the wave function along the [110] chain was confirmed by ENDOR measurements. 4

Silicon carbide (SiC) is a promising material for high-frequency, high-temperature, and high-power devices. The quality of SiC crystals have been significantly improved by recent developments of the crystal growth techniques. SiC has many polytypes differing in the stacking sequence of Si-C bilayers. Technologically important polytypes are 3C-($T_d^3$, $E_g = 2.39$ eV), 5 4H-($C_{4v}$, $E_g = 3.26$ eV), 5 and 6H-SiC ($C_{6v}$, $E_g = 3.02$ eV). 5 In 3C-SiC, each of silicon and carbon has one site. In the hexagonal crystals (nH-), there are $n/2$ inequivalent sites for each of silicon and carbon. In 4H-SiC, each of silicon and carbon has two inequivalent sites with either hexagonal or quasicubic character.

The single negatively charged vacancy $V_{Si}^-$ was identified in 3C-SiC, 6 4H-SiC, 7 and 6H-SiC. 5 The vacancies are observable after electron irradiation at room temperature, and anneal out around 800 °C. 9 From the isotropic $g$ factor and the absence of the zero-field splitting (ZFS), the ground state is assigned to be spin quartet ($S = 3/2$) state $^4A_2$. In the $T_d$ symmetry, all three $\Delta M_S = \pm 1$ transitions of $S = 3/2$ are superimposed since the ZFS vanishes. In $V_{Si}^-$ of 3C-SiC, the tetrahedral arrangement of the nearest neighbors (i.e., four carbon atoms around the vacancy) was confirmed from the angular dependence of the $^{13}$C hyperfine lines. 6 In $V_{Si}^-$ of 4H-SiC, the spin multiplicity was determined to be quartet ($S = 3/2$) by ENDOR measurements since the ENDOR frequencies $h \nu = |M_S A_{eff} g_S n_B |$ do depend on $M_S$. 7 Even in the hexagonal lattice such as 4H- and 6H-SiC, it has been suggested that
the spin quartet state should be originated from the predominantly tetrahedral character of the local symmetry. The high spin state with no symmetry lowering was also suggested by theoretical studies.\(^1\)

An \(S=1\) ground state is expected for neutral vacancy \((V_{Si}^0, \frac{1}{2}I_2^2)\) and double negative vacancy \((V_{Si}^{2-}, \frac{1}{2}I_2^2)\) from a theoretical study.\(^1\) The vacancy-related defects to which the effective spin of \(S=1\) was assigned from the small ZFS exhibiting \(C_{3v}\) symmetry were observed in 4\(H\)- and 6\(H\)-SiC by EPR,\(^3-5\) and by optically detected magnetic resonance (ODMR).\(^6\) It was suggested that these spectra were arising from the excited triplet state of the carbon-silicon vacancy pair,\(^3,4\) and from the excited triplet state of single vacancy-related defects.\(^5,6\) Those observed in 4\(H\)-SiC were labeled \(T_{V2a}\), and \(T_{V2b}\).\(^6\)

In this work, \(T_{V2a}\) in the electron-irradiated n-type 4\(H\)-SiC has been studied by continuous wave (cw) and pulsed EPR. We will show that \(T_{V2a}\) is a negatively charged silicon vacancy with a quartet (\(S=3/2\)) ground state similar to \(V_{Si}\) of the \(T_d\) symmetry but having the \(C_{3v}\) symmetry.

Vacancies occur in various charge states. For identifying the charge state, it is crucial to determine the spin multiplicity. The effective spin of \(T_{V2a}\) and \(T_{V2b}\) was considered to be \(S=1\) from the observation of the two lines split by the ZFS in EPR and ODMR. However, in EPR experiments, it might not be trivial to rule out the assignment of \(S=3/2\) when the central part of the spectrum is superimposed with dominantly strong signals from other defects. In our preliminary report,\(^7\) we used the assignment of \(S=1\) for \(T_{V2a}\) and \(T_{V2b}\). In ODMR experiments, the signals of \(T_{V2a}\) and \(T_{V2b}\) could be selectively extracted by tuning to their optical transitions. However, the intensity of the \(|S, M_S| = |3/2, 1/2| \Rightarrow |3/2, -1/2|\) transition might happen to be suppressed when the signal is detected through some polarization mechanism and when \(S\) and \(M_S\) are good quantum numbers.\(^8,9\) We will show that the nutation method of the pulsed EPR technique\(^10\) has made it possible to measure the effective spin of both \(T_{V2a}\) and \(T_{V2b}\) to be \(S=3/2\).

Both \(T_{V2a}\) and \(T_{V2b}\) were suggested to be silicon vacancy related defects since the shoulders in the lineshape are similar to those arising from \(^{29}\text{Si} (I=1/2, 4.7\%)\) hyperfine interaction of the next-nearest-neighbor (NNN) silicon in \(V_{Si}^0\).\(^6\) For identification of the single vacancy, it is crucial to observe hyperfine interactions of the nearest-neighbor (NN) atoms which are located immediately around the vacancy. To disentangle the angular dependence of the weak \(^{13}\text{C} (I =1/2, \text{natural abundance } 1.1\%)\) hyperfine lines in the presence of superimposing many other signals, selective enhancement of the signals concerned is desirable. We have achieved a selective enhancement of the \(T_{V2a}\) spectrum through a spin polarization of the multiplet sublevels by illuminating with a laser light and could measure the \(^{13}\text{C}\) hyperfine interactions of the NN carbon sites.\(^17\)

In \(V_{Si}\) of the \(T_d\) symmetry, the high spin state \(S=3/2\) is arising from three electrons in the threefold degenerate \(t_2\) state. In a \(C_{3v}\) symmetry, the \(t_2\) triplet splits into an \(a_1\) singlet and an \(e\) doublet. We will demonstrate that the \(T_{V2a}\) center is the case in which the high spin \(S=3/2\) configuration is arising from non-degenerate orbitals split by the symmetry-lowering crystal field.

II. EXPERIMENT

The samples used in our experiments were single-crystal n-type 4\(H\)-SiC (Nippon Steel: nitrogen dopant) with the carrier concentration of circa \(1 \times 10^{17} /\text{cm}^3\). The sample whose thickness is 1.5 mm was cut into a size \((3 \times 15 \text{ mm}^2)\) appropriate for our EPR measurements in \(X\) band. The crystal was irradiated by 3-MeV electrons with the total fluence \(4\times 10^{18} /\text{cm}^2\). The sample was placed on a water-cooled holder so as to avoid beam heating and was kept below 330 K during the electron irradiation.

Pulsed EPR experiments were carried out at room temperature on a Bruker ELEXSYS \(X\)-band spectrometer. The continuous wave (cw) EPR spectra were measured on a Bruker ESP 300 \(X\)-band spectrometer. The temperature was controlled by using an ESR-900 (Oxford Instruments). The calibration of the magnetic field was carried out by measuring simultaneously at room temperature the sample and the perylene cation in conc. \(\text{H}_2\text{SO}_4 (g = 2.005269 \pm 0.000006)\) (Refs. 22 and 23) sealed in the capillary which was co-mounted with the sample. The EPR signal of \(\text{Cr}^{3+}\) in a single crystal of ruby\(^24\) co-mounted with the sample was used as the reference of the spin concentration and was used to monitor the variation of the \(Q\) factor of the cavity during measuring the temperature dependence of the signal intensity. The signal intensity was estimated by double integration of the first derivative signal.

In the laser irradiation experiments, the crystal was illuminated with a continuous wave laser light (808 nm, 1.53 eV) of a Coherent fiber array packaged (FAP) system with a 10-W output during the EPR measurements. The laser light was introduced into the cavity through an optical fiber.

III. RESULTS AND DISCUSSION

A. Determination of the spin multiplicity

The EPR spectrum of the electron irradiated n-4\(H\)-SiC when the magnetic field is parallel to the \(c\) axis (\(B_{||}([0001])\)) is shown in Fig. 1(a). In the central part of the spectrum, the negatively charged silicon vacancy (\(V_{Si}^-, g = 2.0028\)) (Ref. 25) is observed. In both sides of the \(V_{Si}^0\), there are the EPR signals labeled \(T_{V2a}\) and \(T_{V2b}\) which were observed previously by ODMR.\(^6\) The two-line feature of \(T_{V2a}\) and \(T_{V2b}\) was ascribed to the ZFS of \(S=1\). As described below, the \(C_{3v}\) symmetry and the EPR parameters \(g\) and \(D\), under an assumption that \(S=1\), and the \(^{29}\text{Si}\) hyperfine splitting arising from 12 NNN’s which have been determined from the angular dependence of the line positions, agree with those reported in the literature.\(^6\)

In the case of \(V_{Si}^0 (S=3/2)\) in \(3\text{C}^*, 4\text{H}^*,\) and \(6\text{H}\)-SiC, the EPR spectrum consists of a single line as in the case of an EPR spectrum of \(S=1/2\), since the ZFS for \(S\geq1\) vanishes under the \(T_d\) symmetry. In a lower symmetry, the effective spin \(S\) is usually determined from the observation of ZFS in which the EPR spectrum splits into \(2S+1\) lines of \(\Delta M_S = \pm 1\) transitions when the ZFS is much smaller in magnitude.
than the microwave energy. However, when the central line arising from the $|S, M_S\rangle = |3/2, 1/2\rangle \Leftrightarrow |3/2, -1/2\rangle$ transition of $S=3/2$ is hidden by an overlap of strong signals from other centers, the effective spin might be assumed to be $S=1$. The angular dependence of the line positions of the outer two lines, $|3/2, \pm 3/2\rangle \Leftrightarrow |3/2, \pm 1/2\rangle$, might be well described as those of the $|1, \pm 1\rangle \Leftrightarrow |1, 0\rangle$ transitions of an $S=1$ case. As shown below, we have determined that, in both $T_{V2a}$ and $T_{V2b}$, the two lines are $|3/2, \pm 3/2\rangle \Leftrightarrow |3/2, \pm 1/2\rangle$ transitions by applying the nutation method of pulsed technique.

Pulsed EPR measures an EPR signal in the time domain following a pulse or a series of pulses. The behavior of the magnetization $\mathbf{M}$ is described by using a coordinate system rotating with the microwave frequency around the external magnetic field $\mathbf{B}_0$. At the resonance condition, the microwave pulse (duration $t_p$, amplitude $B_1$) rotates the magnetization in the $yz$ plane through the angle $(g \beta_s B_1 / \hbar) t_p = \omega_n t_p$ from the $z$ axis, where $\omega_n$ is the nutation frequency. In an $S=1/2$ system, $\omega_n = \omega_1 = g \beta_s B_1 / \hbar$. If all transitions of $S \geq 1$ are excited by the microwave pulse, $\omega_n = \omega_1$. If only an $|S, M_S\rangle \Leftrightarrow |S, M_S\rangle$ transition in the spectrum is excited, the nutation frequency $\omega_n$ of this transition is described as $19-21,26$

$$\omega_n = \sqrt{S(S+1) - M_s^2} \omega_1. \quad (1)$$

If only one of the $|1, \pm 1\rangle \Leftrightarrow |1, 0\rangle$ transitions of $S=1$ is excited, $\omega_n = \sqrt{2} \omega_1$. If only one of the outer two lines of $S=3/2$, $|3/2, \pm 3/2\rangle \Leftrightarrow |3/2, \pm 1/2\rangle$ is excited, $\omega_n = \sqrt{3} \omega_1$, and if only the $|3/2, 1/2\rangle \Leftrightarrow |3/2, -1/2\rangle$ transition is excited, $\omega_n = 2 \omega_1$.

We used a three-pulse sequence $(t_{p0} - \tau_1 - t_{p11} - \tau_2 - t_{p111} - \text{echo})$, as shown in Fig. 2. As a result of the nutation driven by the microwave pulse with the duration $t_{p0}$, the $z$ component of the magnetization $M_z$ is $M_z \approx M_0 \cos(\omega_0 t_{p0})$, where $M_0$ is an initial magnetization. The $M_z$ is stored during the interval $\tau_1$ (4 $\mu$s, fixed) which is sufficiently shorter than the spin-lattice relaxation time. The second and third pulses $(t_{p11} = t_{p111} = 20$ $\text{ns}$, $\tau_2 = 1$ $\mu$s, fixed) were used to monitor $M_z$ in the form of an echo. In the two-dimensional (2D) nutation experiment, the time-sweep mode spectra, echo intensity vs $t_{p0}$ was measured as a function of the ex-
was incremented in 512 steps. In accumulation, two-step
varied in 80 steps with 4-ns increments. The magnetic field
noted
the crystal where
in the range of 1000 ns with 8-ns step. At the orientation of
ternal magnetic field strength
. The pulse duration
was varied in 80 steps with 4-ns increments. The magnetic field
was incremented in 512 steps. In accumulation, two-step
phase cycling
[0, 0, 0]-[0, π, 0] was employed. The echo intensity was obtained by integrating the echo shape sampled in the range of 1000 ns with 8-ns step. At the orientation of the crystal where
was nearly along [0001], the signals from
, 
, and
, and an unidentified center (denoted
here) were observed. The examples of the integrated echo intensity with respect to
are illustrated in Fig. 3. For each magnetic field, the integrated echo intensity of the
scan was apodized using a sine-bell function, was expanded to 512 points by zero filling, and was Fourier-transformed to give nutation frequencies and corresponding intensities. The contour plot of the 2D nutation data, in which the nutation intensities were obtained as a function of the 2D array
, is shown in Fig. 4. The small splitting in the magnetic field positions of
was caused by a misalignment. We note the nutation frequency peaks centered at 9.2, 13.0, 15.9, and 18.3 MHz, respectively. Since these frequencies correspond to the ratio $1: \sqrt{2}: \sqrt{3}: 2$, the transitions are assigned as shown in Table I. Thus, for both
and
, the spin multiplicity has been determined to be $S = 3/2$. The effective spin of
was determined to be $S = 1$.

For
, the nutation frequencies of
and $2\omega_1$ were observed. The frequency $\omega_1$ corresponds to a non-distorted configuration (labeled $V_{\text{Simd}}$) in which all three $\Delta M_S = \pm 1$ transitions are excited by the microwave pulse. The frequency $2\omega_1$ corresponds to a slightly distorted configuration (labeled $V_{\text{Sid}}$) in which only the $3/2, 1/2 \leftrightarrow 3/2, -1/2$ transition is excited because the ZFS is larger than $B_1$. For the slightly distorted configuration, the EPR signals corresponding to the $3/2, \pm 3/2 \leftrightarrow 3/2, \pm 1/2$ transitions were not observed in both cw and pulsed measurements. It is likely that both amplitude and direction of the ZFS are distributed, observed in both cw and pulsed measurements. It is likely that both amplitude and direction of the ZFS are distributed, and the EPR signals are too broad to be detected as separate signals.

B. Temperature dependence of signal intensity

There have been controversies whether
and
are the ground
or excited state. As shown below, we have confirmed that both spectra
and
are arising from the ground state from the temperature dependence of the EPR signal intensity. The temperature dependence of the EPR signal intensity at thermal equilibrium is caused by the population among the spin levels and by the temperature dependence of the concentration of the defects at the particular electronic state from which the EPR signal is observed.

We measured the temperature dependence of the signal intensity of $V_{\text{Si}}$, $V_{\text{V2a}}$, and $V_{\text{V2b}}$ in the temperature range between 125 and 300 K. As seen from Fig. 5, the signal intensity decreases as the temperature increases in all three defects. Under 125 K, the intensity of the
and the
signals were not free from the saturation effect even at the lowest power available in our equipment. Both the
and

\begin{table}[h]
\centering
\caption{The nutation frequencies and their assignments.} \label{tab:1}
\begin{tabular}{|c|c|c|c|}
\hline
Defect center & Observed $\omega_n$ (MHz) & Assignment of the transitions & Predicted $\omega_n$ \\
\hline
$V_{\text{V2a}}$ and $V_{\text{V2b}}$ & 15.9 & $|3/2, \pm 3/2\rangle \leftrightarrow |3/2, \pm 1/2\rangle$ & $\sqrt{3}\omega_1$ \\
$V_{\text{Sid}}$ & 18.3 & $|3/2, 1/2\rangle \leftrightarrow |3/2, -1/2\rangle$ & $2\omega_1$ \\
$V_{\text{Simd}}$ & 9.2 & $|3/2, \pm 3/2\rangle \leftrightarrow |3/2, \pm 1/2\rangle$ and $|3/2, 1/2\rangle \leftrightarrow |3/2, -1/2\rangle$ & $\omega_1$ \\
$T_x$ & 13.0 & $|1, \pm 1\rangle \leftrightarrow |1, 0\rangle$ & $\sqrt{2}\omega_1$ \\
\hline
\end{tabular}
\end{table}
where $N$, $k_B$, $h$, $\nu$, and $P_j$ are the concentration of the paramagnetic center, Boltzmann’s constant, Plank’s constant, the microwave frequency employed, and the transition probability of the transition at $B_j$, respectively. For $T_{V_{2a}}$ and $T_{V_{2b}}$, the temperature dependence of the sum of the intensities of the $|3/2,\pm 3/2\rangle\leftrightarrow|3/2,\pm 1/2\rangle$ transitions observed ($B_{00}$[[0001]]) was fitted to one calculated from Eq. (2) by least squares method with $\nu=9.438$ GHz used in the experiment. A good fitting shown in Fig. 5 suggests that the $T_{V_{2a}}$ and $T_{V_{2b}}$ spectra arise from the electronic ground state. It is established that the $V_{Si}^{-}$ spectrum arises from the electronic ground state.\cite{7} In $V_{Si}^{-}$, the four $M_5$ levels are equally spaced since the three $\Delta M_5=\pm 1$ transitions are superimposed. The temperature dependence of the signal intensity of $V_{Si}^{-}$ was well fitted to one calculated as the sum of the three $\Delta M_5=\pm 1$ transitions by using Eq. (2). In the temperature range studied (125 K \(\lesssim T \)), Eq. (2) is further simplified to

$$I_j \propto \frac{NP_j e^{-(i-1)h\nu/k_BT}-e^{-h\nu/k_BT}}{\sum_{i=1}^{3} e^{-(i-1)h\nu/k_BT}},$$

(2)

where $N$, $k_B$, $h$, $\nu$, and $P_j$ are the concentration of the paramagnetic center, Boltzmann’s constant, Plank’s constant, the microwave frequency employed, and the transition probability of the transition at $B_j$, respectively. For $T_{V_{2a}}$ and $T_{V_{2b}}$, the temperature dependence of the sum of the intensities of the $|3/2,\pm 3/2\rangle\leftrightarrow|3/2,\pm 1/2\rangle$ transitions observed ($B_{00}$[[0001]]) was fitted to one calculated from Eq. (2) by least squares method with $\nu=9.438$ GHz used in the experiment. A good fitting shown in Fig. 5 suggests that the $T_{V_{2a}}$ and $T_{V_{2b}}$ spectra arise from the electronic ground state. It is established that the $V_{Si}^{-}$ spectrum arises from the electronic ground state.\cite{7} In $V_{Si}^{-}$, the four $M_5$ levels are equally spaced since the three $\Delta M_5=\pm 1$ transitions are superimposed. The temperature dependence of the signal intensity of $V_{Si}^{-}$ was well fitted to one calculated as the sum of the three $\Delta M_5=\pm 1$ transitions by using Eq. (2). In the temperature range studied (125 K \(\lesssim T \)), Eq. (2) is further simplified to

$$I_j \propto \frac{NP_j h\nu}{k_BT} \frac{1}{4-(6h\nu/k_BT)},$$

(3)

As shown in Fig. 5, the signal intensity varies linearly with $1/T$ in the temperature studied (125 K \(\lesssim T \)). The difference of the gradient among the centers arises from the difference in the spin concentration and from the difference in the number of transitions summed to estimate the intensity. In $V_{Si}^{-}$, the signals of the $|3/2,\pm 3/2\rangle\leftrightarrow|3/2,\pm 1/2\rangle$ transitions of $V_{Si,d}$, which are too broadened to be observed as separate signals and constitute a part of the foot of the $V_{Si}^{-}$ signal, were likely to be included in the estimation of the intensity obtained by double integration.

We fitted the temperature dependence of the signal intensity in the limited temperature range of 125 K \(\lesssim T \approx 300 \text{ K} \), since it was difficult to measure quantitatively the signal intensity in low temperatures due to the saturation effect and the passage effect. The increase of the signal intensity with the decrease of the temperature in the range of 125 K \(\lesssim T \approx 300 \text{ K} \) alone cannot exclude a possibility that $T_{V_{2a}}$ might arise from a low-lying electronic excited state. By using the equation for the temperature dependence of the signal intensity of a thermally accessible electronic excited state,\cite{27} we note that the linear increase of the signal intensity with $1/T$ in this limited temperature range is applicable not only for an EPR signal from an electronic ground state but also for that from a low-lying electronic excited state with an energy higher than the electronic ground state by $\Delta E \approx -0.005 \text{ eV}$, where $\Delta E$ is the energy separation from the electronic ground state. Since the $T_{V_{2a}}$ signal was observed at 10 K, it is determined that the $T_{V_{2a}}$ signal arises from an electronic ground state.

The concentration of a defect at the particular charge state might depend on the temperature dependence of the position of the Fermi level. In our sample, the concentration of $V_{Si}^{-}$, which is the dominant defect created by the electron irradiation, was estimated to be similar to the carrier concentration at room temperature before the electron irradiation. The EPR signal of the nitrogen donor, which had been the dominant EPR signal before the electron irradiation, could not be observed after the electron irradiation. It is likely that an electron is transferred from nitrogen to $V_{Si}^{-}$. This indicates that the Fermi level lies around the center of the band gap after the electron irradiation. In this situation, it is likely that the Fermi level position does not depend on the temperature. We note that the signal intensity ratios $T_{V_{2a}}/V_{Si}^{-}$ and $T_{V_{2b}}/V_{Si}^{-}$ are constant above 170 K (1/T=5.88 \times 10^{-3} \text{ K}^{-1})$. The spin concentrations of $V_{Si}^{-}$, $T_{V_{2a}}$, and $T_{V_{2b}}$ with the assignment of $S=3/2$, were estimated to be $5 \times 10^{17}/\text{cm}^3$, $5 \times 10^{16}/\text{cm}^3$, and $2 \times 10^{16}/\text{cm}^3$, respectively.

C. EPR parameters

1. Spin polarization

The $C_{3v}$ symmetry and the EPR parameters $g$ and $D$ (with the assignment of $S=1$), and the $^{29}\text{Si}$ hyperfine coupling...
and between the ODMR.\textsuperscript{16} However, the \(^{13}\)C hyperfine splittings of NN atoms, which are crucial in identifying silicon vacancy, were not observed.\textsuperscript{28,29} In our electron-irradiated sample, the height of the signal intensity of \(T_{V_{2a}}\) is 43 times smaller than that of \(V_{Si}\). As seen from the spectrum in Fig. 1(a), many weak unidentified signals were observed besides the signals of \(V_{Si}\), \(T_{V_{2a}}\), and \(T_{V_{2b}}\). The signal intensities of these weak signals correspond to several percentages of that of the primary lines of \(T_{V_{2a}}\) and interfere with measuring the angular dependencies of the hyperfine lines of NN atoms. The selective enhancement of the EPR signal of \(T_{V_{2a}}\) enabled us to measure the \(^{13}\)C hyperfine splittings. In Figs. 1(b) and 1(c), the EPR spectra \(B_{0}[[0001]]\) taken under the laser illumination (808 nm, 1.53 eV) are shown. The EPR signal of \(T_{V_{2a}}\) was selectively enhanced through the spin polarization of the multiplet sublevels. In Fig. 1(b), the strong signal in the central part is considered to be arising mostly from that of \(V_{Si}\) because the intensity is similar to that in the dark. We note that the lineshape of the EPR spectrum of \(T_{V_{2a}}\) under laser illumination exhibits mixed phase, absorptive in the low field line and emissive in the high field line and that the signal height of the \([3/2, \pm 3/2] \leftrightarrow [3/2, \pm 1/2]\) transitions of \(T_{V_{2a}}\) matches that of \(V_{Si}\). When the power of the laser light was decreased, the peak height of the \([3/2, \pm 3/2] \leftrightarrow [3/2, \pm 1/2]\) transitions of \(T_{V_{2a}}\) decreased, while that of \(V_{Si}\) was similar to that in the dark, as shown in Fig. 1(c). In the spectrum under illumination, the central line (the \([3/2, 1/2] \leftrightarrow [3/2, -1/2]\) transition), which is as weak as that in the dark is hidden underneath the \(V_{Si}\) signal.

The pattern of the polarized spectrum \((B_{0}[[0001]])\) of \(T_{V_{2a}}\) indicates that either the \(M_{S}=\pm 1/2\) levels or the \(M_{S}=\pm 3/2\) levels should be preferentially populated, with little population difference both between the \(M_{S}=\pm 1/2\) levels and between the \(M_{S}=\pm 3/2\) levels, but with a large population difference between the \(M_{S}=\pm 1/2\) levels and the \(M_{S}=\pm 3/2\) levels. In three unpaired electron system, the effective spin of electronic excited states is either \(S=1/2\) or \(3/2\). Since a low-field line of absorption form and a high-field line of emission form are nearly the same peak height, and since the \([3/2, 1/2] \leftrightarrow [3/2, -1/2]\) transition is only slightly polarized, we assume that spin polarization should occur through an intersystem crossing from the excited doublet state to the Zeeman sublevels of the ground quartet state due to the spin-orbit mechanism. It is likely that the ground quartet state \(Q_{0}\) is excited to an excited quartet state \(Q_{1}\) by the laser light, and then transfers to an excited doublet state \(D\), as shown in Fig. 6.

Upon the rotation with \(B_{0} \perp [11\overline{2}0]\), the peak height of the polarized signals varies with the variation of the splitting between the \([3/2, \pm 3/2] \leftrightarrow [3/2, \pm 1/2]\) transitions, with the maximum at \(B_{0}[[0001]]\) \((\theta'=0)\) and with the minimum (little polarization) at \(\theta'=55^\circ\). The pattern of the polarized spectrum in which the low-field line of the absorptive line shape and the high-field line of the emissive line shape had nearly the same peak height did not vary upon the rotation from \(B_{0}[[0001]]\) to \(B_{0}[[1\overline{1}00]]\). The central line of the \([3/2, 1/2] \leftrightarrow [3/2, -1/2]\) transition remained slightly polarized upon the rotation from \(B_{0}[[0001]]\) to \(B_{0}[[1\overline{1}00]]\). Since the \(T_{V_{2a}}\) center has an isotropic \(g\) and a zero-field splitting which is smaller by two orders of magnitude than the Zeeman interaction \(g\beta B\) at the microwave frequency of the \(X\) band, the mixing of different \(M_{S}\) states in the spin eigenfunctions of the ground quartet state is small in any direction of the external magnetic field. It is likely that this specific feature of the \(T_{V_{2a}}\) center might cause the \([3/2, 1/2] \leftrightarrow [3/2, -1/2]\) transition to be little enhanced in any direction of the external magnetic field.

In the case of a polarization of the triplet \((S=1)\) through the intersystem crossing due to the spin-orbit mechanism, either the \(M_{S}=\pm 1\) levels or the \(M_{S}=0\) level are preferentially populated with no population difference between the \(M_{S}=\pm 1\) levels when the external magnetic field \((B_{0})\) is along the principal axis \(Z\) of the zero-field splitting \(D\), when \(D\) is axially symmetric. In this case, the two \(M_{S}=\pm 1\) transitions have the same peak height and one exhibits an absorptive line shape and the other an emissive line shape. Both pattern of the polarized spectrum and the strength of the polarization depend on the angle between \(B_{0}\) and \(Z\), since the \(M_{S}\) states are mixed in the eigenfunctions of the spin Hamiltonian at an arbitrary direction of the magnetic field. The degree of the mixing depends on the relative amplitude between the zero-field splitting and the Zeeman interaction. It has been shown that the two \(M_{S}=\pm 1\) transitions have the same peak height, and one exhibits an absorptive line shape and the other an emissive line shape in any direction of the magnetic field when the zero-field splitting \(|D|\) is very small compared to the Zeeman interaction.\textsuperscript{30} In the case of a quartet arising from a doublet-triplet pair with a relatively small zero-field splitting \(|D|=87\text{ MHz}, |E|=0\), it was confirmed by the simulation of the polarization calculated by using the first-order perturbation approximation that the \([3/2, 1/2]\)
\( \langle \psi | 3/2, -1/2 \rangle \) transition is only slightly enhanced in any direction of the magnetic field.\(^{19}\)

In the theoretical studies, the intravacancy transition energy of \( V_{\text{Si}}^{2} \) is calculated to be 1.57 and 1.40 eV at cubic and hexagonal sites, respectively.\(^{31}\) Furthermore, the energy level position of \( V_{\text{Si}}^{2} \) is calculated to be 1.19 and 1.28 eV above the valence band at cubic and hexagonal sites, respectively.\(^{11}\) If we assume that the energy level position of \( T_{\text{V}}^{2a} \) is similar to that of \( V_{\text{Si}}^{2} \), the energy of our laser illumination \(~808\) nm, 1.53 eV\) is not large enough to bring up to the conduction band, but is sufficient to excite the intravacancy transition of \( T_{\text{V}}^{2a} \) because the band gap in 4\(^{\text{H}}\)-SiC is estimated to be 3.26 eV.\(^{5}\)

2. \( ^{29}\text{Si} \) hyperfine interaction of next-nearest-neighbor (NNN) atoms

First we have confirmed the \( ^{29}\text{Si} \) hyperfine interactions arising from 12 NNN atoms which were reported in an ODMR study.\(^{16}\) The \( ^{29}\text{Si} \) hyperfine lines which appear as shoulders of the primary line of the spectrum taken with \( B_{||}[0001] \) are labeled \( b \) and \( c \) (Fig. 7). Using the natural abundance of \( ^{29}\text{Si} \) (4.6832\%),\(^{32}\) it is calculated that the probability for one \( ^{29}\text{Si} \) atom among the 12 NNN atoms it is 0.3316, for two \( ^{29}\text{Si} \) atoms it is 0.0896, for three \( ^{29}\text{Si} \) atoms 0.01469, and for four \( ^{29}\text{Si} \) atoms 0.0016. Thus the intensity ratio of the \( ^{29}\text{Si} \) NNN hyperfine lines with respect to the central line labeled \( a \) is calculated to be 0.273 \((b/a)\) and 0.037 \((c/a)\), respectively. As shown in Fig. 7, the observed spectrum is simulated using the calculated intensity ratio and Lorentzian line shape, with a \( ^{29}\text{Si} \) hyperfine coupling constant of 8.7 MHz. From the angular dependence of the line positions of \( b \) and \( c \), the \( ^{29}\text{Si} \) hyperfine interaction of the NNN Si atoms was estimated to be isotropic within the resolution of the EPR measurements.

FIG. 7. The \( ^{29}\text{Si} \) hyperfine coupled signals of \( T_{\text{V}}^{2a} \) in \( n\)-type 4\(^{\text{H}}\)-SiC. The lowest field primary line with the magnetic field along the [0001] axis is shown. The observed spectrum is indicated by the dotted line. The assignments of the hyperfine lines \( b \) and \( c \) are described in the text. The solid line indicates the simulated spectrum that is derived from the occupation of \( ^{29}\text{Si} \) \((I = 1/2, \text{natural abundance 4.7\%}) \) at the 12 NNN silicon sites.

FIG. 8. The \( ^{13}\text{C} \) hyperfine satellites of \( T_{\text{V}}^{2a} \) in \( n\)-type 4\(^{\text{H}}\)-SiC with the magnetic field along the [0001] axis. The lowest field primary line is shown. The labels \( d \) and \( e \), for the assignment of the NN carbon sites, are described in the text.

3. \( ^{13}\text{C} \) hyperfine interaction of nearest-neighbor (NN) atoms

Now we report the observation of the \( ^{13}\text{C} \) hyperfine lines (Fig. 8 and 9). Weak satellite lines in the spectrum taken with \( B_{||}[0001] \) are labeled \( d \) and \( e \), as shown in Fig. 8. The intensity ratios of \( d \) and \( e \) with respect to the central line were 0.005 \((d/a)\) and 0.016 \((e/a)\), respectively. The signal inten-
The angular dependence of the line positions of 13C hyperfine splitting is shown in Fig. 11. Each point represents the line position observed. The angular dependence of the 13C hyperfine splitting is shown in Fig. 12. The spin-Hamiltonian parameters were obtained by fitting observed field strengths and microwave frequencies to the spin Hamiltonian

$$H = \beta_S \cdot \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{B} + \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S} + \sum_i (\mathbf{S} \cdot \mathbf{A}_i \cdot I_i - g_n \beta_\nu I_i \cdot \mathbf{B}),$$  

where the electron spin $S = 3/2$ and the nuclear spin $I = 1/2$ for 13C ($g_S = 1.40483$) and 29Si ($g_N = -1.1106$).  

g, D, and A denote the $g$ matrix, the ZFS tensor, and the hyperfine matrix, respectively. The subscripts $i$ denote any of these nuclei. The least-squares fitting was carried out by using computer program EPRFOR in which the resonant magnetic fields are calculated by exact diagonalization of the spin Hamiltonian matrix. The spin Hamiltonian parameters were obtained by using a crystal coordinate system in which the $z$ axis is [0001] and the $x$ axis is [1̅1̅0]. One rotation with $B_0$ in the (1̅1̅0) plane is sufficient to determine $g$, $D$, and $A$ of the axial carbon $A^{13}$C(C1), which have a $C_{3v}$ symmetry. In the case of the basal carbon, $A$ of the C2 site $A^{13}$C(C2) was determined by applying the appropriate symmetry transformations to utilize the line positions of other sites as the line positions that should be obtained for the C2 site by the rotation in different planes. The results are summarized in Table II. For the basal carbons, the parameters of one particular site, C2 which is located on (1̅1̅0), are given. By applying the appropriate symmetry transformations, the parameters belonging to other basal carbon sites can be obtained. For the least-squares fitting, the line positions read from the spectra taken at every 2.5° were used. The parameters $g$ and $D$ were obtained from the primary lines. The number of measured line positions used for fitting and the root-mean-square deviations achieved are included in Table II. The solid curves in Figs. 11 and 12 are calculated by using the parameters obtained. As shown in Table II, the EPR parameters $g$ and $D$ and the 29Si hyperfine coupling constant of the NNN atoms ($A_{2p, i}^{29}$SiNNN) agree with those reported in the literature, except that $D$ in the latter was obtained with the assignment of $S = 1$. The EPR parameters $g$ and $D$ of the $T_{v2b}$ site are listed in Table II.

D. Model of the $T_{v2b}$ center

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

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

where the summation is over the surrounding carbon ($ns$, $np$: 2s, 2p) and silicon ($ns$, $np$: 3s, 3p) atoms on which the unpaired electrons are delocalized. The fractional unpaired electron population ($\eta_i^2$) on the atom concerned and the hybrid ratio ($\beta_i^2/\alpha_i^2$, where $\alpha_i^2 + \beta_i^2 = 1$) are estimated from the hyperfine parameters. The results are listed in Table III. In the wave function of the unpaired electron, 62.3% of
FIG. 11. Angular dependence of the line positions of $T_{V_{2a}}$. The crystal was rotated with the magnetic field in the (1120) plane (from $\theta'=0^\circ$ for $\mathbf{B}_0||[0001]$ to $\theta'=90^\circ$ for $\mathbf{B}_0||[1\bar{1}00]$). The open squares, the filled circles, and the filled squares represent the primary lines, the $^{13}$C hyperfine lines of the axial carbon sites, and the $^{13}$C hyperfine lines of the basal carbon site, respectively. The solid curves are calculated from the spin Hamiltonian parameters obtained.

The $^{13}$C hyperfine splitting of four NN carbons, and the $^{29}$Si hyperfine splitting of the NN atoms of $T_{V_{2a}}$ are similar to those of $V_{Si}$ (Tables II and III).

It has been considered that not only the $V_{Si}$ center in 3C-SiC but also those in 4H-SiC and in 6H-SiC have a $T_d$ symmetry which makes the ZFS vanish.\textsuperscript{7,8} The criterion between nondistorted ($V_{Snd}$) and distorted ($V_{Sid}$) forms in the nutation experiments lies on the relative magnitude between $|D|$ and $B_1$. For $V_{Si}$ in 4H-SiC, in addition to nondistorted form in which all three $\Delta M_s = \pm 1$ transitions are simultaneously excited by the microwave pulse, the presence of a distorted configuration in which the ZFS exceeds the excitation band width ($B_1 \sim 0.3$ mT) of the microwave pulse employed was revealed. Since the outer two lines ($3/2$, $\pm 3/2$) of the distorted configuration could not be observed in both cw and pulsed experiments, these lines are likely to be broadened by a distribution of ZFS. The distortion of the random character is likely to originate from lattice strains and/or site-to-site variation of the locations of impurities and defects. The similar behavior in the nutation experiments was observed in the substitutional Ni$^+$ center ($S=3/2$) in diamond.\textsuperscript{20}

The $T_{V_{3a}}$ center which is also a negatively charged silicon vacancy is an analogue of $V_{Si}$. In the cases of $T_{V_{2a}}$, the magnitude of the ZFS can be defined with a relatively narrow distribution (the linewidth $\Delta B_{pp}$ of 0.08 mT at 160 K). In our experiments, the origin of the distortion of the crystal field of $T_{V_{2a}}$ was not determined. Probably, the distortion might be caused by presence of some nonparamagnetic point defect such as a positively charged nitrogen, an interstitial.
TABLE II. EPR parameters of $T_{V2a}$ and $T_{V2b}$.

<table>
<thead>
<tr>
<th>Defect</th>
<th>Principal values</th>
<th>Principal directions</th>
<th>$T/K$</th>
<th>comments</th>
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<tbody>
<tr>
<td>$T_{V2a}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$g$ a</td>
<td>$g_{iso} = 2.0029 \pm 0.0001$</td>
<td></td>
<td>160</td>
<td>This work</td>
</tr>
<tr>
<td>$g$</td>
<td>$g_{iso} = 2.004 \pm 0.002$</td>
<td></td>
<td>2</td>
<td>Ref. 16</td>
</tr>
<tr>
<td>$g$</td>
<td>$g_{iso} = 2.0032$</td>
<td></td>
<td>300</td>
<td>Ref. 15</td>
</tr>
<tr>
<td>$D$ (MHz)</td>
<td>$</td>
<td>D</td>
<td>= 35.1 \pm 0.1$, $</td>
<td>E</td>
</tr>
<tr>
<td>$D$ (MHz)</td>
<td>$</td>
<td>D</td>
<td>= 70 \pm 0.5$ ($S=1$)</td>
<td>($</td>
</tr>
<tr>
<td>$D$ (MHz)</td>
<td>$</td>
<td>D</td>
<td>= 66$ ($S=1$)</td>
<td>($</td>
</tr>
<tr>
<td>$A^{13}C(C1)$ a</td>
<td>$A_{1}(C1) = 80.3 \pm 0.1$</td>
<td>($</td>
<td>D</td>
<td>=60$ ($S=1$)</td>
</tr>
<tr>
<td>$A^{13}C(C1)$ a</td>
<td>$A_{1}(C1) = 34.8 \pm 0.2$</td>
<td>($</td>
<td>D</td>
<td>=60$ ($S=1$)</td>
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<tr>
<td>$A^{13}C(C2)$ a</td>
<td>$A_{1}(C2) = 75.8 \pm 0.4$</td>
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<td>D</td>
<td>=60$ ($S=1$)</td>
</tr>
<tr>
<td>$A^{13}C(C2)$ a</td>
<td>$A_{1}(C2) = 31.3 \pm 0.2$</td>
<td>($</td>
<td>D</td>
<td>=60$ ($S=1$)</td>
</tr>
<tr>
<td>$A^{13}C(NNN)$</td>
<td>$A_{1}(SiNNN) = 8.7 \pm 0.1$</td>
<td>160</td>
<td>This work</td>
<td></td>
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<tr>
<td>$T_{V2b}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$g$</td>
<td>$g_{iso} = 2.0029 \pm 0.0001$</td>
<td></td>
<td>160</td>
<td>This work</td>
</tr>
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<td>$g_{iso} = 2.004 \pm 0.002$</td>
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<td>Ref. 15</td>
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<td>E</td>
</tr>
<tr>
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<td>D</td>
<td>= 36 \pm 0.5$ ($S=1$)</td>
<td>($</td>
</tr>
<tr>
<td>$D$ (MHz)</td>
<td>$</td>
<td>D</td>
<td>= 39$ ($S=1$)</td>
<td>($</td>
</tr>
<tr>
<td>[1.5mm] $V_{Si}$</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

TABLE III. Hyperfine and orbital parameters of $T_{V2a}$.

<table>
<thead>
<tr>
<th></th>
<th>$A_{iso}$ (MHz)</th>
<th>$A_{aniso}$ (MHz)</th>
<th>$\eta^2$</th>
<th>$\beta^2/\alpha^2$</th>
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</thead>
<tbody>
<tr>
<td>$A^{13}C(C1)$</td>
<td>50.0 \pm 0.1</td>
<td>15.1 \pm 0.1</td>
<td>0.154</td>
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<tr>
<td>$A^{13}C(C2-4)$</td>
<td>44.8 \pm 0.5</td>
<td>15.5 \pm 0.2</td>
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<tr>
<td>$A^{13}C(V_{Si})^a$</td>
<td>49.3</td>
<td>15.4</td>
<td>0.157</td>
<td>11.0</td>
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<tr>
<td>$A^{29}Si_{NNN}$ a</td>
<td>8.7 \pm 0.1</td>
<td>0.0 \pm 0.1</td>
<td>0.0019</td>
<td></td>
</tr>
<tr>
<td>$A^{29}Si_{NNN}$ b</td>
<td>8.35</td>
<td>0</td>
<td>0.0018</td>
<td></td>
</tr>
<tr>
<td>$A^{29}Si_{NNN}$ c</td>
<td>8.5</td>
<td>0</td>
<td>0.0019</td>
<td></td>
</tr>
</tbody>
</table>

a $A^{13}C(V_{Si})$ indicates the $^{13}C$ hyperfine matrix of the NN atoms of the $V_{Si}$ reported in Ref. 7.

b $A^{29}Si_{NNN}$ of $V_{Si}$ reported in Ref. 7.

c $A^{29}Si_{NNN}$ of $T_{V2a}$ reported in Ref. 16.

Silicon atom, or a carbon vacancy located at a certain distance away from the vacancy along [0001]. Although the $^{13}C$ hyperfine interaction has not been measured, $T_{V2a}$ is likely to be another analog of $V_{Si}$, in which either the carbon or the location of the accompanying defect is different from $T_{V2a}$. A silicon vacancy-related $S=3/2$ defect having $C_{3v}$ symmetry with the ZFS $|D|=68.7 \times 10^{-4}$ cm$^{-1}$ (206 MHz) was found in $p$-type 6H-SiC irradiated with low-energy electrons (300 keV). In this case, three $M_{S}=\pm 1$ transitions were clearly observed without being interfered by any other dominant signals. A model of a Frenkel pair (a pair of silicon vacancy and an interstitial silicon atom) was suggested.

In 4H-SiC, it is expected that two types of silicon vacancies should be produced, each corresponds to each of two types of silicon sites, one with cubic character and the other with hexagonal character. For both the $V_{Si}$ and $T_{V2a}$ spectra, it has not been determined whether the silicon vacancy corresponds to one of the two types of silicon sites or the resolution of our EPR technique is not sufficient to resolve the two spectra, each arising from each of two kinds of silicon vacancies.

In $V_{Si}$ which is a negatively charged silicon vacancy of the $T_d$ symmetry, the high-spin state $S=3/2$ is arising from three parallel spins in the threefold-degenerate $t_2$ orbitals. This configuration with the three electrons in three different orbitals minimizes the electron repulsion by allowing the electrons stay far apart. The conservation of the $T_d$ symmetry is ascribed to the orbitally nondegenerate $^4A_2$ state ($a_1^2t_2^2$)
electron effect in determining the ground state configuration is demonstrated clearly in $T_{V_{2a}}$, which does have the crystal field splitting competing against the many-electron effect.

IV. SUMMARY

The $T_{V_{2a}}$ center in electron irradiated $n$-4$H$-SiC, for which a structural model was not established, has been studied by cw- and pulsed EPR. We have assigned our spectra to arise from the $T_{V_{2a}}$ center since the EPR parameters agree with those reported.\textsuperscript{15,16} From the temperature dependence of the EPR signal intensity at thermal equilibrium, it has been determined that both spectra $T_{V_{2a}}$ and $T_{V_{2b}}$ arise from the ground state. The spin multiplicity of $T_{V_{2a}}$ and $T_{V_{2b}}$ has been determined to be quartet ($S=3/2$) by the nutation method of pulsed EPR. By enhancing the EPR signals of $T_{V_{2a}}$ with illumination of the laser light (808 nm), $A^{13}$C's of the four NN carbon atoms of $T_{V_{2a}}$ have been determined. The EPR parameters $g$, $D$, and $A_{iso}$SiNN obtained in the present work agree with those reported in the literature, except that $D$ was obtained with the assignment of $S=1$ in the latter. Since the NN atoms are four carbon atoms arranged in a configuration close to a regular tetrahedron, since these carbons have a relatively large spin density (62.3%), since the NNN atoms are 12 silicon atoms, and since the effective spin is $S=3/2$, the $T_{V_{2a}}$ center has been identified as an analog of a negatively charged silicon vacancy $V_{Si}$. Thus the $T_{V_{2a}}$ spectrum arises from the ground state $4A_2$. The EPR parameters and the similarity of the principal values of $A^{13}$C between axial and basal carbon, is likely to be caused by a perturbation of the crystal field, and possibly by the presence of an accompanying impurity or defect. The vacancies reported to have a high-spin $2A_2$ ground state in which the many-electron effect dominates over the energy gain attained by a Jahn-Teller distortion are limited to those having $T_d$ symmetry.\textsuperscript{2,6,36,37} It should be noted that $T_{V_{2a}}$ is the case in which three parallel spins are occupied in three orbitals, among which $a'_1$ and two orbitals of the $e$ doublet are split by the crystal field of the $C_{3v}$ symmetry.

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\begin{thebibliography}{99}
\bibitem{1} Present address: Institute of Library and Information Science, University of Tsukuba, 1-2 Kasuga, Tsukuba-City, Ibaraki, 305-8550, Japan.
\bibitem{2} Present address: Research Center for Knowledge Communities, University of Tsukuba, 1-2 Kasuga, Tsukuba-City, Ibaraki, 305-8550, Japan.
\end{thebibliography}