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Spin multiplicity and charge state of a silicon vacancy ($T_{V_{2a}}$) in 4H-SiC determined by pulsed ENDOR

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In this paper, we unambiguously re-determine the spin multiplicity of $T_{V_{2a}}$ by pulsed electron nucleus double resonance technique. The $T_{V_{2a}}$ center is one of the most commonly observed defects in 4H-SiC, and its origin was identified as one belonging to a class of negatively charged silicon vacancy by means of continuous-wave electron paramagnetic resonance (EPR) and the two-dimensional nutation method of pulsed EPR technique. However, a model with the spin multiplicity of triplet ($S=1$) and the neutral charge state has recently been suggested. Our result clearly shows that $T_{V_{2a}}$ is a quartet spin ($S=3/2$) state and thus should be single-negatively charged ($-1$).

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I. INTRODUCTION

In SiC, there are two types of fundamental lattice vacancies: the silicon vacancy and the carbon vacancy. Both of these strongly affect the electrical properties of this material. They are observed by electron paramagnetic resonance (EPR) or optically detected magnetic resonance (ODMR).1 Using EPR or ODMR, these two types can be simply distinguished according to the hyperfine (HF) interactions due to the four nearest-neighbor (NN) atoms of a vacancy. For the carbon vacancy, the NN atoms are Si, so we can observe the NN $^{29}\text{Si}$ (nuclear spin $I=1/2$, natural abundance=4.7%) HF interactions. On the other hand, the NN $^{13}\text{C}$ (I=1/2, natural abundance=1.1%) HF interactions can be observed for the silicon vacancy. Among a number of EPR centers reported so far, those labeled $V_{S}^{2-}$ (I and II) and $T_{V_{2a}}$ in 4H-SiC or 6H-SiC were found to generate the NN $^{13}\text{C}$ HF interactions.2–9 These three centers have been identified as a silicon vacancy distorted along the c axis ($[0001]$) with a $C_{3v}$ symmetry.6,9–12 The g values of $V_{S}^{2-}$ (I) and $V_{S}^{2-}$ (II) cannot be distinguished in the $X$ band. Therefore they were originally assigned as a single center and labeled as $V_{S}^{2-}$.13 From detailed angular analyses of the NN $^{13}\text{C}$ HF interactions with respect to crystal’s rotation, it could be distinguished, and $V_{S}^{2-}$ (I) and $V_{S}^{2-}$ (II) were assigned as the silicon vacancies at the hexagonal and the quasicubic sites, respectively.9 $V_{S}^{2-}$ (I and II) are very close to $T_{d}$ symmetric geometry, while $T_{V_{2a}}$ is relatively distorted, resulting in the different EPR spectra.6,10–12 $V_{S}^{2-}$ (II) do not exhibit zero-field splittings (ZFS) in the conventional $X$-band EPR, indicating that the deviation from $T_{d}$ symmetric geometry is very small. On the other hand, $T_{V_{2a}}$ exhibits ZFS ($|D|=35.1$ MHz). The distortion of $T_{V_{2a}}$, which is manifested in the ZFS, is likely to be caused by a perturbation of the crystal field, presumably by the presence of an accompanying impurity or defect located at some distance along the c axis ($[0001]$).9 As for the HF parameters of NN carbon atoms, the difference between $T_{V_{2a}}$ and $V_{S}^{2-}$ (I and II) is very small. These also indicate that the distortion of $T_{V_{2a}}$ is slightly larger than that of $V_{S}^{2-}$ (I and II). Their HF parameters almost correspond to the theoretical values of the negatively charged vacancy in 4H-SiC.14 In addition, $V_{S}^{2-}$ (I and II) and $T_{V_{2a}}$ are different in terms of thermal stability: $V_{S}^{2-}$ (I and II) were annealed below 900 °C,6,14–16 but $T_{V_{2a}}$ remained up to higher temperatures.17,18 In particular, $T_{V_{2a}}$ was observed not only in irradiated SiC, but also in as-grown high-purity semisolating (HPSI) 4H-SiC,8 which is an important base material for wide-band-gap electronics.18 Therefore a Si vacancy labeled $T_{V_{2a}}$ is recognized as a possible candidate for the carrier-compensation center in this material and is thus a very important defect.

The EPR spectrum of $T_{V_{2a}}$ exhibits ZFS,2,3,5 indicating that $T_{V_{2a}}$ is a high spin state ($S>1/2$). Initially, the spin multiplicity of $T_{V_{2a}}$ was assigned to triplet ($S=1$), and $T_{V_{2a}}$ was thus regarded as a neutral Si vacancy.5 Later, from the two-dimensional (2D) nutation method of pulsed EPR technique, the spin multiplicity was clearly determined to be quartet ($S=3/2$). Accordingly, the charge state was reassigned to be a single-negatively charged state ($-1$). After this reassignment, however, the spin-1 ($S=1$) models were reported again based on a pulsed EPR study7 and a continuous-wave (cw) EPR study.8 Thus the spin multiplicity or the charge state of $T_{V_{2a}}$ is currently controversial. In contrast with $T_{V_{2a}}$, quartet ($S=3/2$) and negative charge ($-1$) have been concluded for $V_{S}^{2-}$ (II).13

It is important to determine the spin multiplicity of $T_{V_{2a}}$ for several reasons. One reason is that the charge state strongly influences the thermal stability of Si vacancies. First-principles calculations predicted that negatively charged Si vacancies could be stable in HPSI and n-type SiC, while other charge states of the silicon vacancy should not be stable because of their high formation energies. This naturally explains why Si vacancies are absent in $p$-type...
materials. The spin-1 model for $T_{V_{2\alpha}}$, however, calls the above idea into question. Furthermore, there is the other question of why $V_{Si}^{(I,II)}$ and $T_{V_{2\alpha}}$ are simultaneously observed in thermal equilibrium (in dark). For the coexistence of the $-1$ and $0$ charge states, the Fermi level should be very close to the ionization level of ($-0$) which was calculated to be located at 1.2–1.3 eV (Ref. 20) or 0.7–0.8 eV (Ref. 19) above the valence-band maximum. On the contrary, the equilibrium coexistence was observed in a variety of sample conditions such as different dopant concentrations and different radiation conditions. Furthermore, so far, except for the suggestion of the triplet state ($S=1$) on $T_{V_{2\alpha}}$, the electronic states of single vacancies which have a high spin ground state ($S>1/2$) in semiconductors are limited to the orbitally nondegenerate $^4A_2$ state ($S=3/2$), which is not subject to Jahn-Teller distortion. They are a single-negatively charged Si vacancy in $3C$-, $4H$-, $6H$-SiC, a single-negatively charged vacancy in diamond, and a neutral Ga vacancy in GaP. The interactions between electrons such as the exchange interaction and the electron repulsion affect the determination of the ground state. For its elucidation, the experimental determination of the spin multiplicity of the ground state is important. Thus the spin multiplicity and charge state are related to significant issues that we have to answer.

In spin multiplicity determination, electron nucleus double resonance (ENDOR) spectroscopy can give crucial information. Treating the first order, the energy levels and the ENDOR frequencies for a spin system incorporating $S$ and $I$ are given by

$$E_{M_S M_I} = M_S g_S \mu_B B + (M_I A_{eff} - g_I \mu_B B) M_I$$

and

$$\nu = (1/\hbar) |M_S A_{eff} - g_S \mu_B B|,$$

respectively, where $M_S$ and $M_I$ are the magnetic quantum numbers ($|M_S| \leq 2S+1$, $|M_I| \leq 2I+1$) of electron spin and nuclear spin, respectively, $g_S \mu_B$ is the electron Zeeman splitting, $B$ is the applied magnetic field, $A_{eff}$ is the HF splittings, and $g_I \mu_B B/\hbar$ is the frequency of nuclear Zeeman splitting. Obviously, the ENDOR frequencies should be completely different depending on whether $M_S$ values are $-1$, $0$, $+1$ ($S=1$) or $-3/2$, $-1/2$, $+1/2$, $+3/2$ ($S=3/2$). In fact, the spin multiplicity of quartet ($S=3/2$) for $V_{Si}$ has been unambiguously determined in this way. In this paper, we also demonstrate such a determination for $T_{V_{2\alpha}}$ using a high-resolution pulsed-ENDOR spectrometer.

**II. EXPERIMENT**

The sample used in our experiments was single-crystalline $n$-type $4H$-SiC (Nippon Steel: nitrogen dopant) with the carrier concentration of approximately $1 \times 10^{17}$/cm$^3$. A sample 1.5 mm thick was cut to a size ($3 \times 15$ mm) appropriate for our EPR measurements in the X band. The crystal was irradiated by 3-MeV electrons with the total fluence of $4 \times 10^{18}$/cm$^2$. The sample was placed on a water-cooled holder to avoid beam heating and was kept below 300 K during the electron irradiation.

**III. RESULTS AND DISCUSSION**

The electron spin-echo (ESE) spectrum of the electron-irradiated $n$-type $4H$-SiC at room temperature taken with the magnetic field along the c axis ([0001] axis). The microwave frequency was $\nu = 9.599$ GHz. The arrows indicate the magnetic field positions where the ENDOR spectra were measured.

Electron spin-echo (ESE) detected EPR and pulsed ENDOR experiments were carried out at room temperature in a dark condition on a Bruker ELEXSYS X-band spectrometer. ESE experiment was performed using a two-pulse sequence ($p_1$, $\tau$, $p_2$) with the duration of microwave pulses $p_1$ and $p_2$ of 20 ns each and delay times $\tau$ of 1.2 $\mu$s. Pulsed ENDOR experiments were performed using a three-pulse sequence ($p_1$, $\tau$, $p_2$, $T$, $p_3$) with microwave pulses $p_1$, $p_2$, and $p_3$ 20 ns wide and delay times $\tau$ and $T$ of 800 ns and 16.2 $\mu$s, respectively. During the time $T$ an intense radiofrequency pulse 10 $\mu$s wide was applied to the sample. Spectra were obtained by monitoring the echo while scanning the radiofrequency. In both experiments, the delay of 1 ms was used for repeating the pulse sequence in accumulation.
shows the energy-level splitting for a spin quartet \( S = 3/2 \) state with one nucleus \( I = 1/2 \), which was calculated using the successive three terms in Eq. (1). As indicated in Figs. 2 and 3, \( A_1 \), \( A_2 \), \( B_1 \), and \( B_2 \) were assigned to the transitions of the \( M_S = 3/2 \) manifold, and \( C \) was assigned to the transition of the \( M_S = 1/2 \) manifold. The present data and analysis are consistent with those reported previously for \( V_S^{-}I,II \), except that we could resolve small splittings of about 0.25 MHz between \( A_1 \) and \( A_2 \) and between \( B_1 \) and \( B_2 \). In the previous study, these splittings were not detectable due to a broad linewidth \( 0.3–0.5 \) MHz. Therefore our pulsed ENDOR measurements have higher resolution than those of the previous CW ENDOR studies. We think the origin of these splittings is site splittings for the following reason. We found a signal-intensity ratio of approximately 3:1 for the \( A_1 \) and \( A_2 \) lines and for the \( B_1 \) and \( B_2 \) lines. As shown in Fig. 4, the 12 NNN Si atoms are classified into three types: nine basal and three \( c \)-axial Si atoms according to their locations relative to the NN C atoms. Therefore two split lines with intensity ratio 3:1 are expected for the relevant HF satellite when \( B \parallel c \), which is quite consistent with our observation. We calculated the ENDOR frequencies of the transitions of the \( |M_S| = 3/2 \) for \( B = 342.3 \text{ mT} \) using \( A_{\text{eff}} = 7.99 \) and 8.15 MHz and \( g_n = -1.1106 \). They correspond

### TABLE I. Observed and calculated resonant ENDOR frequencies of \( V_S^{-}I,II \) and \( T_{V_{2a}} \)

<table>
<thead>
<tr>
<th>( V_S^{-}I,II )</th>
<th>Obs. (MHz)</th>
<th>Calc. (MHz) (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu_{A1} )</td>
<td>14.86</td>
<td>14.88</td>
</tr>
<tr>
<td>( \nu_{A2} )</td>
<td>15.11</td>
<td>15.12</td>
</tr>
<tr>
<td>( \nu_{B1} )</td>
<td>9.10</td>
<td>9.09</td>
</tr>
<tr>
<td>( \nu_{B2} )</td>
<td>9.35</td>
<td>9.33</td>
</tr>
<tr>
<td>( \nu_{C} )</td>
<td>6.89</td>
<td>6.89, 6.97</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( T_{V_{2a}} )</th>
<th>Obs. (MHz)</th>
<th>Calc. (MHz) (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu'_{A1} )</td>
<td>14.76</td>
<td>14.77</td>
</tr>
<tr>
<td>( \nu'_{A2} )</td>
<td>15.53</td>
<td>15.55</td>
</tr>
<tr>
<td>( \nu'_{B1} )</td>
<td>9.00</td>
<td>8.98</td>
</tr>
<tr>
<td>( \nu'_{B2} )</td>
<td>9.79</td>
<td>9.76</td>
</tr>
<tr>
<td>( \nu'_{C1} )</td>
<td>6.83</td>
<td>6.84</td>
</tr>
<tr>
<td>( \nu'_{C2} )</td>
<td>7.06</td>
<td>7.10</td>
</tr>
</tbody>
</table>

\(^a\)The calculated frequencies were derived from Eq. (1) by using the parameters described in the text.

FIG. 2. (Color online) ENDOR spectrum the electron-irradiated \( n \)-type 4H-SiC at room temperature taken with the magnetic field along the \( c \) axis ([0001] axis). (a) Spectrum of \( V_S^{-}I,II \) at 342.3 mT. (b) Spectrum of \( T_{V_{2a}} \) at low-field side (339.8 mT). (c) The spectrum of \( T_{V_{2a}} \) at high-field side (344.8 mT).

FIG. 3. Energy-level schemes under \( A_{\text{eff}} > 0 \), \( g_n < 0 \), and \( D > 0 \). (a) Energy levels showing the effects of successive terms in Eq. (1) and ENDOR transitions at constant magnetic field. (i) Addition of electron Zeeman interaction. (ii) Addition of the first-order HF interaction. (iii) Addition of nuclear Zeeman interaction. (b) Energy levels with respect to magnetic field and EPR transitions in quartet for \( D > 0 \) at the \( B \parallel c \) axis.
the same samples, the concentration of
from the difference in
tings excludes the possibility that the small splittings come
significant difference in signal intensity of the small split-
has a small shoulder on the high-frequency side, suggesting
due to many superpositions of small frequencies of HF inter-
the spectrum at the low-frequency region is very complicated
is estimated to be around 1.1–1.2 MHz, could not be identi-

Assuming \( S=1 \), the ENDOR frequencies for \( B=339.8 \) and
344.8 mT were calculated to be 5.6±0.2 and 11.4±0.2 MHz,
respectively, using the reported values of \( A_{\text{eff}} \) parameters [8.7
MHz (Ref. 6) and 8.35 MHz (Ref. 12)]. As seen from Figs.
2(b) and 2(c), the signal was not observed around these
frequencies. Therefore we can conclude that the spin multiplicity
of \( T_{V_{2a}} \) is not triplet (\( S=1 \)) but must be quartet (\( S=3/2 \)).

It is also notable that the signals labeled \( \nu_A \) and \( \nu_C \) were
observed only in the low-field transition and the signals labeled
\( \nu_B \) were observed only in the high-field transition, as
shown in Figs. 2(b) and 2(c). This can be reasonably explained
by the spin-3/2 model. The sign of the HF coupling constant of the
NNN \( ^{29}\text{Si} \) atoms, which was reported to be isotropic as reported previously.\(^{13}\) On the other hand, the ZFS parameter \( D \) was reported to be positive from the W-band
EPR measurement at 1.2 K.\(^{7}\) When \( D>0 \), the transition of
\( |S, M_S|=|3/2, 3/2 \rangle \leftrightarrow |3/2, 1/2 \rangle \), \( |S, M_S|=|3/2, 3/2 \rangle \leftrightarrow |3/2, 1/2 \rangle \)
should be observed on the low-field side, while the transition of
\( |3/2, -1/2 \rangle \leftrightarrow |3/2, -3/2 \rangle \) should be observed on the high-field side, as illustrated in Fig. 3(b).
Under \( A_{\text{eff}}>0 \) and \( D>0 \), it can be derived from Eq. (2) that the signals
labeled \( \nu_A \) and \( \nu_C \) should be observed only in the low-field transition and the signals labeled \( \nu_B \) should appear only on the high-field side. These also support our conclusion.

In the ENDOR spectrum of Fig. 2, several signals other than those of the NNN \( ^{29}\text{Si} \) atoms were observed. We tenta-

tively consider that they are due to HF interactions at distant
sites. As for \( \nu_D, \nu_E, \nu_F, \) and \( \nu_G \) in Figs. 2(a) and 2(c), they are tentatively assigned as the signals from third NN \( ^{13}\text{C} \) HF
interaction. In the case of \( \nu_D \) and \( \nu_E \) in Fig. 2(c), assuming that
\( A_{\text{eff}} \) is 1.69 MHz and the sign of it is positive, it is expected to be observed at 4.5 and 6.2 MHz in high-field
transition. The frequency of \( \nu_E \) is 4.5 MHz and also corre-
sponds to it. By using the value of 1.69 MHz, the other two signals were expected to be observed at 1.2 and 2.8 MHz.
However, we could not identify them because the spectrum at the low-frequency region is very complicated due to many
superpositions of small frequencies of HF interaction at distant
sites. The frequencies of \( \nu_D \) (6.2 MHz) and \( \nu_F \) (4.5
MHz) in Fig. 2(a) also correspond to the calculated frequencies
of 6.2 and 4.5 MHz by using \( A_{\text{eff}}=1.66 \) MHz. As for the
signal at 10.3 MHz in Fig. 2(a), it may be tentatively assigned to fourth NN Si atoms. Assuming that \( A_{\text{eff}} \) is 4.94
MHz, the signals at 5.4 and 10.3 MHz are expected to be observed. These correspond well to the signals observed at
5.3 and 10.3 MHz in Fig. 2(a). Probably, other signals are also ENDOR frequencies at distant sites. In the previous
study,\(^{13}\) these lines were not observed. Maybe this comes

![Diagram of Vacancy](image)
from the different sensitivity of the signals due to the different measurement method with the present study.

Previously, Son et al. suggested that $T_{\nu 2a}$ should be a triplet spin state, because its spectrum did not exhibit the central $|S, M_S|=3/2, 1/2\rangle \leftrightarrow |3/2, -1/2\rangle$ transition in the dark. In their EPR measurement, however, other signals stronger than the $T_{\nu 2a}$ signal were observed at around the field position where the central transition should appear. It is therefore unclear whether the central transition of a quartet state was really absent or not. As for the measurements under light illumination, Son et al. proposed the polarization model with a triplet ground state and a singlet excited state. On the other hand, we have proposed the model to explain little results of ours were obtained from 2D nutation experiments. The estimated $TV$ ratios were not consistent with those of our previous nutation experiments, resulting in the controversy. However, it should be mentioned that those results of ours were obtained from 2D nutation experiments. In principle, the 2D technique gives more accurate and reliable $\omega_n$ ratios, especially when the detected ESE signal consists of two or more signals having different $\omega_n$.27,28

The present conclusion that $T_{\nu 2a}$ should have a quartet spin ($S=3/2$) and should be negatively charged is consistent with the theoretical aspects. The (0/+1) and (−/+1) levels of the silicon vacancy were predicted to be 0.2–0.3 eV and 0.7–0.8 eV above the valence-band top of 4H-SiC, respectively, which are much lower than the mid gap. Therefore, from the theoretical viewpoint, the silicon vacancy is expected to be negatively charged in our n-type SiC. The coexistence of $T_{\nu 2a}$ and $V^\circ_{\nu 1}$ in our samples is quite understandable because they were both negatively charged states of the silicon vacancy. In addition, the spin-3/2 model also explains the high thermal stability of $T_{\nu 2a}$. According to the first-principles calculation, the formation energy of the silicon vacancy is higher for the neutral charge state than for the negatively charged state, resulting in higher thermal stability for the latter state. This will be related to the fact that the $T_{\nu 2a}$ centers could be present in HP SiC even after 1600 °C annealing.18

IV. SUMMARY

The spin quartet ($S=3/2$) state and the negatively charged $(-1)$ state of $T_{\nu 2a}$ in 4H-SiC have been confirmed by pulsed ENDOR measurements. After demonstrating the spin-multiplicity determination for the known center $V^\circ_{\nu 1}$ (II) ($S=3/2$), we applied the same procedure to the $T_{\nu 2a}$ center. We could observe signals that we assigned to the transitions of the $|M_S|=3/2$ manifold. The observation of the $|M_S|=3/2$ manifold and lack of observation of the transition of the $|M_S|=1$ one at the frequencies expected in the case of $S=1$ clearly indicate that the spin multiplicity of $T_{\nu 2a}$ is quartet ($S=3/2$) and not triplet ($S=1$).


26 Strictly, when the magnetic field is parallel to the $c$ axis, two lines with intensity ratio 1:3 are expected in $T_d$ and three lines with intensity ratio 1:2:1 are expected in $C_{3v}$. We consider that the observation of two lines is due to the small distortion of $V_{S/I}$ from $T_d$ as reported previously (Refs. 6 and 9).
