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**Journal**: Physical Review B  
**Volume**: 71  
**Page**: 193202  
**Year**: 2005  
**DOI**: 10.1103/PhysRevB.71.193202

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<th>著者別名</th>
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<td>EPR and theoretical studies of negatively charged carbon vacancy in 4H-SiC</td>
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<td>期刊名</td>
<td>Physical Review B</td>
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<td>期</td>
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<td>2005</td>
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**doi**: 10.1103/PhysRevB.71.193202
EPR and theoretical studies of negatively charged carbon vacancy in 4H-SiC

T. Umeda, Y. Ishitsuka, and J. Isoya
Research Center for Knowledge Communities, University of Tsukuba, Tsukuba 305-8550, Japan

N. T. Son and E. Janzén
Department of Physics and Measurement Technology, Linköping University, S-581 83 Linköping, Sweden

N. Morishita, T. Ohshima, and H. Itoh
Japan Atomic Energy Research Institute, Takasaki 370-1292, Japan
A. Gali
Department of Atomic Physics, Budapest University of Technology and Economics, Budafoki út 8., H-1111 Budapest, Hungary

(Received 5 October 2004; revised manuscript received 19 November 2004; published 23 May 2005)

Carbon vacancies ($V_C$) are typical intrinsic defects in silicon carbides (SiC) and so far have been observed only in the form of positively charged states in $p$-type or semi-insulating SiC. Here, we present electron-paramagnetic-resonance (EPR) and photoinduced EPR (photo-EPR) observations of their negatively charged state ($V_C^-$) in $n$-type 4H-SiC. This EPR center (called HEI1) is characterized by an electron spin of 1/2 in a Si-Si antibonding state of $V_C$. First-principles calculations confirm that the HEI1 center arises from $V_C^-$ at hexagonal sites. The HEI1 spectrum shows a transition between $C_{1h}$ and $C_{3v}$ symmetries due to a fast reorientation effect reflected in the nature of this defect. The photo-EPR data suggest that $V_C^{2-}$ is the dominant form of $V_C$ when the Fermi level lies 1.1 eV below the conduction band.

DOI: 10.1103/PhysRevB.71.193202 PACS number(s): 61.72.Ji, 76.30.Mi, 71.15.—m

Carbon vacancies ($V_C$) are typical intrinsic defects in radiation (ion, electron, etc.)-damaged or semi-insulating silicon carbides (SiC). They remain in as-grown wafers or device structures because of their high thermal stability, and therefore largely influence the electronic properties of SiC, such as the doping efficiency, semi-insulating mechanism, and carrier transport and lifetime. They are often observed in $p$-type or semi-insulating samples by means of electron paramagnetic resonance (EPR): electron-spin-1/2 centers of EI5 and EI6 in 4H-SiC (Refs. 1 and 6) or ID1 and ID2 in semi-insulating 4H-SiC and those of Ky1 to Ky3 in 6H-SiC. The EI5 (ID1/Ky1/Ky2) and EI6 (ID2/Ky3) centers have been identified as positively charged carbon vacancies ($V_C^+$) at quasiequilateral ($k$) and hexagonal ($h$) sites, respectively, and their electronic levels have been studied by photoinduced EPR (photo-EPR). However, their negatively charged state ($V_C^-$), which should also be EPR active with electron spin $S=1/2$, has not been observed yet. This state is important for evaluating the electronic role of $V_C$ in $n$-type or semi-insulating regions. For example, the gap state of $V_C^-$ will act as a dominant deep trap in $n$-type or semi-insulating regions.

In this paper, we present EPR and photo-EPR data on the $V_C^-$ state in 4H-SiC. The $n$-type 4H-SiC samples were prepared by high-temperature electron irradiation. In these samples, we found a new EPR center, named HEI1, whose hyperfine (HF) interactions clearly indicate it originates from a type of $V_C^-$. By comparing the HF parameters with those of first-principles calculations, we conclude that this new center corresponds to $V_C^-$ at the $h$ site. The atomic and electronic structures are strikingly different from those of $V_C^+$, and such a contrast is quite similar to what has earlier been observed for vacancies ($V^\pm$) in silicon. The HEI1 center exhibited a fast reorientation phenomenon due to the nature of $V_C^-$. In the last part, we show photo-EPR data and evaluate the electronic levels of $V_C^-$ in the energy gap of 4H-SiC (3.26 eV).

The starting samples were prepared from a 1.5-mm-thick nitrogen-doped $n$-type 4H-SiC(0001) wafer (room-temperature carrier concentration $\approx 10^{17}$ cm$^{-3}$) made by Nippon Steel Corporation. The samples were uniformly irradiated by 3.5-MeV electrons with a dose of $(2\sim 4) \times 10^{18}$ e/cm$^2$ at 850 °C. This high-temperature irradiation created $V_C^-$ dominantly in the samples, which is evidenced by our $p$-type samples with the same irradiation condition. In addition, the 850 °C annealing held the Fermi level above the midgap, which is necessary for detecting $V_C^-$. EPR measurements were carried out using a Bruker E500 X-band (9.452 GHz) spectrometer. In the photo-EPR measurements, we used a single-grating 0.25-m Jobin-Yvon monochromator and a 150-W xenon lamp. The EPR spectrum was measured in decreasing steps of 10 nm in wavelength. In this system, the uncertainty of the excitation energy was reduced to less than ±0.06 eV.

First-principles LSDA-PZ (local spin density functional approximation within the parametrization of Perdew and Zunger) calculations were carried out to study the negatively charged carbon vacancies in 4H-SiC. We focused our investigation mainly on the resulting geometry and corresponding HF tensors of the defects. We used a 96-atom supercell to model the 4H-SiC with a 23K Monkhorst-Pack K-point set. We have already shown earlier that this supercell and K-point set provides the convergent geometry and total energy for the positively charged carbon vacancies. The convergent geometry and HF tensors were calculated...
HF tensors of the positively charged carbon vacancies in relax until the forces were below 0.5 mhartree/bohr. This the geometry optimization, all the atoms were allowed to
relatively small basis set in the plane-wave expansion
HF tensors for Si 2 , respectively. This suggests that both HF interactions
augmented-wave method. 14,15 This makes it possible to use a
using the CP-PAW code, which utilizes the projector
An EPR spectrum of the n-type sample at 60 K under
room-light illumination is shown in Fig. 1(a). The illumination enhanced the intensities of the EPR signals we want to
Signal positions as a function of the rotation angle of
The signal positions as a function of the rotation angle of
The signal positions as a function of the rotation angle of

## Table I. Spin-Hamiltonian parameters of HEI1 and calculated HF tensors for h-site V−.

<table>
<thead>
<tr>
<th>HEI1 (C1h), 60 K</th>
<th>X(⊥)</th>
<th>Y(⊥)</th>
<th>Z(∥)</th>
<th>θ</th>
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<tr>
<td>g</td>
<td>2.00287</td>
<td>2.00407</td>
<td>2.00459</td>
<td>38°</td>
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<tr>
<td>A(Si1)</td>
<td>7.76</td>
<td>7.76</td>
<td>10.07</td>
<td>7°</td>
</tr>
<tr>
<td>A(Si2)</td>
<td>11.78</td>
<td>11.67</td>
<td>15.19</td>
<td>101°</td>
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<table>
<thead>
<tr>
<th>HEI1 (C3h), 150 K</th>
<th>X(⊥)</th>
<th>Y(⊥)</th>
<th>Z(∥)</th>
<th>θ</th>
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<tbody>
<tr>
<td>g</td>
<td>2.00381</td>
<td>2.00381</td>
<td>2.00401</td>
<td>0°</td>
</tr>
<tr>
<td>A(Si1)</td>
<td>7.79</td>
<td>7.79</td>
<td>10.04</td>
<td>0°</td>
</tr>
<tr>
<td>A(Si2)</td>
<td>Not observed due to broadening</td>
<td></td>
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### Notes:
- **Hamiltonian parameters (g and A)** of HEI1 derived from the fit are shown in Table I. The HF tensors for Si 1 and Si 2 are nearly axial symmetric and can therefore be well examined by a simple LCAO (linear combination of atomic orbitals) analysis of Si’s 3s and 3p orbitals. The directions of the sp-hybridized orbitals for Si 1 and Si 2 were determined as shown in Table I or in Fig. 2(a). The two Si atoms are well fitted to one c-axial Si atom (Si 1 ) and one of three Si atoms in plane (Si 2 ) of a V−. Thus, an unpaired electron of HEI1 is believed to be in the antibonding state of the Si 1 -Si 2 bond. We should mention that this antibonding orbital is repelled by the Si 1 -Si 2 bonding orbital [the bonding orbital can be seen in the EIS center, Fig. 2(b), where Si 1 -Si 2 atomic pair is formed]. This would be a consequence of minimizing the electron repulsion and is thus quite reasonable in our model. The atomic structure shown in Fig. 2(a) has a C1h symmetry with respect to the (1120) plane. This is also consistent with the C1h symmetry of the g tensor for HEI1. Consequently, we conclude that the origin of HEI2 is V−.
- From the LCAO analysis, 14,15,16,17,18 we estimated the distributions of an unpaired electron (g) on Si 1 and Si 2 to be 21.1% and 36.6%, respectively [Fig. 2(a)]. The g values were cal-

### Diagrams:
- [Diagram 1](#): EPR measurements of electron-irradiated n-type 4H-SiC at 60 K. (a) EPR spectrum for B∥[0001]. (b) Angular dependence of signal positions for B rotation in the (1120) plane. Solid lines are simulated angular patterns. For HEI1, the lines were calculated using spin-Hamiltonian Eq. (1) and the parameters in Table I.
- [Diagram 2](#): Atomic models for V− (HEI1) and for V− (EIS). 7 For unpaired-electron orbitals on each Si atom, the direction (θ) and distribution (g) are given in the figure.
culated by the sum of 3s- and 3p-orbital densities, \( \eta^2 \alpha^2 + \eta \beta^2 \), where \( \eta^2 \alpha^2 = A_{iso} \text{(mT)} / 163.93 \), \( \eta \beta^2 = A_{aniso} \text{(mT)} / 4.08 \), \( A_{iso} = (A_1 + 2A_2) / 3 \), \( A_{aniso} = (A_1 - A_2) / 3 \), and \( \alpha^2 + \beta^2 = 1 \).\(^{16}\) One may assume that the Si1 or Si2 HF structure originates from three to six \(^{13}\)C atoms (\( I = 1/2 \)), natural abundance = 1.1%, which would make the intensity ratio of the Si1 or Si2 HF structure about 4.7% (=ideal intensity ratio for a \(^{29}\)Si HF interaction). In this case, however, the \( \eta^2 \) values were calculated to be 26.4% or 40.0% for each \( C \) atom using the atomic coefficients of carbon [\( \eta^2 \alpha^2 = A_{iso} \text{(mT)} / 134.77 \), for 2s-orbital, \( \eta \beta^2 = A_{aniso} \text{(mT)} / 3.83 \), for 2p-orbital].\(^{16}\) Thus, the total distribution was much larger than 100%. Therefore, we can conclude again that the Si1 and Si2 HF structures are due to \(^{29}\)Si.

It is worth noting that there is a close similarity between \( V^+ \) and \( V^0 \) in \( Si \) and \( V^0_C \) in SiC. For \( V^+ \) (G2), an unpaired electron distributes on two Si atoms by 26.5% \( \times \) 2 (totally 53%) and for \( V^0 \) (the G1 center) the distribution is divided among four Si atoms by 14.5% \( \times \) 4 (totally 58%).\(^{10}\) From Figs. 2(a) and 2(b), we can see the same trend in \( V^0_C \) (HEI1) and \( V^0_{C2} \) (EI5), although the lower crystal symmetry of \( 4h \)-SiC breaks the equality of Si1,4 and causes some deviations from the case of silicon. Since both the \( V^+ \) state and the \( V^0_C \) state consist of a combination of Si dangling-bond orbitals, such a similarity can naturally be expected.\(^{17}\) However, it is interesting that the wave functions of the \( V^+ \) and \( V^0_C \) states were found to be quantitatively close, despite their energetic positions in the gap being completely different.\(^{9,10}\)

In Table I, we compare the measured HF tensors with the calculated ones for \( V^0_C \) at the \( h \) site. The first-principles calculations revealed that \( h \) and \( k \) sites cause completely different behaviors in \( V^0_C \). At \( h \) sites, Jahn-Teller distortion makes a \( Si_1-Si_4 \) bond and an unpaired electron distributes on the \( Si_1-Si_3 \) side, which is consistent with what we observed in the HEI1 center. At \( k \) sites, however, an unpaired electron is located in the \( Si_3-Si_4 \) side, and hence there should appear another EPR center with quite different angular dependence of the HF satellites. The obtained geometry of \( V^0_C \) at both sites agrees very well with the results of an earlier calculation by Zywietz et al.,\(^9\) e.g., at \( h \) sites, the bond lengths are 2.5 Å for \( Si_1-Si_4 \) and 2.9 Å for \( Si_1-Si_2 \), which are very close to Zywietz’s values of 2.6 Å and 2.9 Å, respectively. Here, we compare \( h \)-site \( V^0_C \) with HEI1. (Further details of the results of the calculations will be reported elsewhere.) As is seen in the table, perfect agreement between the HEI1 center and \( h \)-site \( V^0_C \) is obtained in both the principal values and the directions of the HF tensors. Therefore, we conclude that the HEI1 center originates from \( V^0_C \) at the \( h \) site. The reason we could not observe \( k \)-site \( V^0_C \) is still unclear. However, we speculate that this may be related to dynamic reorientation effects, because such a dynamics was clearly observed in the HEI1 center.

The HEI1 spectrum exhibits a thermal-reorientation phenomenon, as shown in Figs. 3(a) and 3(b). As the temperature was raised, the \( Si_1 \) HF structure broadened and it eventually disappeared 70 K [Fig. 3(a)]. Simultaneously, the \( Si_1 \) HF structure is averaged into a single line [Fig. 3(b)], when the magnetic field is aligned off-angles (\( \neq 0^\circ \)). Above 70 K, the HEI1 spectrum showed a simple \( C_{3v} \) symmetry (see Table I).\(^{18}\) This transition can be explained by the thermal reorientation of the defect. For HEI1, an unpaired electron is located in one of three equivalent bonds, \( Si_1-Si_2 \), \( Si_1-Si_3 \), and \( Si_1-Si_4 \) [see the inset of Fig. 3(c)]. Thus, the unpaired electron can hop among these three states by thermal activation. Since \( Si_2,3,4 \) atoms are \( C_{3v} \)-symmetry related, the thermal-averaging limit also exhibits a \( C_{3v} \) symmetry. During the thermal reorientation, the unpaired electron always stays on \( Si_1 \) but fully jumps among \( Si_3,3,4 \). Therefore, only the \( Si_2 \) HF structure is strongly affected by the lifetime broadening, which is determined by the reorientation speed. Figure 3(c) shows the temperature dependence of reorientation lifetime (\( \tau \)), which was deduced from the inverse of the lifetime broadening width (1/\( \Delta \omega \))\(^7\). Since \( Si_{2,3,4} \) atoms are \( C_{3v} \)-symmetry related, the thermal-averaging limit also exhibits a \( C_{3v} \) symmetry. During the thermal reorientation, the unpaired electron always stays on \( Si_1 \) but fully jumps among \( Si_{3,3,4} \). Therefore, only the \( Si_3 \) HF structure is strongly affected by the lifetime broadening, which is determined by the reorientation speed. Figure 3(c) shows the temperature dependence of reorientation lifetime (\( \tau \)), which was deduced from the inverse of the lifetime broadening width (1/\( \Delta \omega \))\(^7\). Since \( Si_{2,3,4} \) atoms are \( C_{3v} \)-symmetry related, the thermal-averaging limit also exhibits a \( C_{3v} \) symmetry.

We also carried out photo-EPR measurements at 77 K to...
estimate the energy position of $V_C^-$. The changes in EPR intensities of the central line (“main”) and HF lines (“HF”) for HEI1 and EI5 are shown in Fig. 4(a). For both centers, the “main” and “HF” curves showed the same behavior, demonstrating that there was no interference from the other signals. Without illumination, only $V_C^-$(HEI1) and other HEI centers were observed; $V_C^-(Ei5)$ and EI6) was completely absent. This is reasonable for our $n$-type sample. With 1.1-eV light excitation, all EPR signals increased or decreased simultaneously, because it became possible to excite electrons from levels at the Fermi level ($E_F$) to the conduction band, which caused different charge states for the EPR centers. This excitation increased the HEI1 signal drastically, indicating that $V_C^-+e^-$ (conduction band) was generated from $V_C^{2-}$. Namely, most of the $V_C$ were converted to $V_C^{2-}$, when $E_F$ was located at $E_C$ (conduction-band bottom) $-1.1$ eV. This suggests that the $(-1/2)$ level is located below $E_C$ $-1.1$ eV or $E_V+2.2$ eV. Alternatively, another explanation would be that $V_C^{-}$ is slightly more stable than $V_C^-$ (the so-called weak negative-$U$ behavior), and hence $V_C^{-}$ became dominant in the dark. In fact, the present calculations predicted $U$=0.33 eV for $h$-site $V_C^-$. In the previous calculation, $U$ was also negative for both $h$-site and $k$-site $V_C^-$(0.29 eV). However, we have to note that the total energy of the charged defect represents a problem in the supercell approach. Since the appropriate charge correction for a defect in a solid is still being debated in the literature, the negative-$U$ property for $V_C^-$ is not yet proven entirely by theory. When we further increased the photon energy to 1.8–1.9 eV, the EI5 signal ($V_C^-$) became detectable. This indicates that the (+/0) level of $V_C$ is located below $E_C$ $-1.8$ eV or $E_V$ (valence-band top) +1.5 eV, which is in agreement with the previous work ($E_V+1.47$ eV).2 Figure 4(b) summarizes these results.

In summary, we have reported EPR measurements of a negatively charged state of carbon vacancies ($V_C^-$) in 4H-SiC. We found an EPR center, HEI1, and its $^{29}$Si HF interactions were well described by an unpaired electron (S $=1/2$) in the antibonding state of Si$_1$ and Si$_2$ of $V_C$. First-principles calculations showed that the HEI1 center corresponds to $h$-site $V_C^-$. It is worth noting that there is a close similarity between $V_C^-(HEI1)/V_C^-(Ei5)$ and V$^-(G1)/V^-(G2)$ in silicon. Photo-EPR measurements suggested that $V_C^{2-}$ becomes dominant when $E_F=E_C-1.1$ eV. The HEI1 spectrum revealed a thermally activated reorientation effect, in which the reorientation caused the lifetime broadening of a particular HF structure (Si$_2$), resulting in a missing HF structure in the thermally averaging limit.

7 T. Umeda, J. Isoya, N. Morishita, T. Ohshima, T. Kamiya, A. Gali, P. Deák, N. T. Son, and E. Janzén, Phys. Rev. B 70, 235212 (2004); Table I of this paper included a misprint. For “El6 ($C_{5h}$) at 5 K, our EPR,” the correct $g$ parameters are $g_x=g_y=2.0052$ and $g_z=2.0026$.
19 Using the Makov-Payne charge correction, $U$ was calculated to be $+0.07$ eV.