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EPR identification of two types of carbon vacancies in 4*H*-SiC

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The EI5 and EI6 centers are typical intrinsic defects in radiation-damaged and semi-insulating 4*H*-SiC. So far, their origins have been assigned to positively charged carbon vacancies (V_C^+) and silicon antisites (Si_C^+), respectively. However, our complete set of ^{29}Si hyperfine (HF) data clearly reveals that both the centers should originate from V_C^+ but their locations are different, i.e., quasicubic sites for EI5 and hexagonal sites for EI6, as recently predicted by the first-principle calculation [M. Bockstedte *et al.*, Phys. Rev. B **67**, 193102 (2003)]. The two types of V_C^+ centers showed remarkable differences in their atomic structures as well as in the temperature dependence of HF interactions, which are closely related to the nature of the two sites.

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Silicon carbide (SiC) has a variety of hexagonal polytypes, represented by 4*H*- and 6*H*-SiC. There are quasicubic (*k*) and hexagonal (*h*) sites in these polytypes with different arrangements of next nearest neighbors, leading to great structural and electronic variations in this material. For example, donors and acceptors have variations in ionization energy, that depend on their substitution sites.[1–3] Thus, the influence of inequivalent sites is not negligible and needs to be understood to control impurities or defects. Recently, theoretical calculations for carbon vacancies have predicted that its positively charged state (V_C^+) should be strikingly different between *k* and *h* sites in 4*H*-SiC, due to different Jahn-Teller distortion behaviors.[4,5] Thus far, however, only one type of V_C^+ (the EI5 center, electron spin $S=1/2$) has been identified by electron paramagnetic resonance (EPR),[6] and another type is missing. Thus, these theoretical calculations have suggested that the EI6 center, originally assigned to the positively charged silicon antisite (Si_C^+),[7] will fit the *h*-site V_C^+ rather than Si_C^+,[4] and alternately the EI5 center will be reassigned to be V_C^+ at the *k* sites.[4,5] Also recent high-frequency (240 GHz) EPR measurement has suggested V_C-related origins for the EI6 center.[8] The Ky3 center in 6*H*-SiC with similar features to EI6 has been considered a *h*-site V_C^+ in this polytype.[9] Despite these theoretical and experimental results, definitive identification has not yet been obtained, because of a lack of decisive experimental data on these centers. In particular, the complete angular dependence of ^{29}Si hyperfine (HF) interactions for EI6 is not yet known, which is necessary to establish the atomic model for this defect. Since both EI5 and EI6 centers show high thermal stability and are hence the dominant defects in 4*H*-SiC,[6–8] their assignment is quite significant.

Consequently, we report on complete ^{29}Si HF data for EI5 and EI6 here, and discuss how their atomic structures were determined. We concluded that both EI5 and EI6 should be V_C^+ centers but their respective locations were *k* and *h* sites, consistent with theoretical predictions. Despite being the same type of defect, their atomic structures were found to be quite different. We demonstrate that this difference is connected to the striking contrast in the temperature dependence for the two V_C^+ centers.

The starting substrates were commercial *p*-type 4*H*-SiC(0001) wafers (room-temperature carrier concentration $=1\times10^{15}/cm^3$) supplied by Nippon Steel Corporation. The 1.5-mm-thick substrates were irradiated at 850 °C with a 3-MeV electron beam for 6 h, up to a total dose of 4×10^{18} e/cm^2. This high-temperature irradiation enabled only EI5 and EI6 to remain dominant in the samples. We then measured the substrates with *X*-band EPR (Bruker E500 system) and pulsed EPR spectrometers (Bruker E580 system). Pulsed EPR was used to directly measure spin relaxation times[10] and to distinguish HF interactions of ^{29}Si and ^{13}C (their respective natural abundances are 4.7% and 1.1%, and nuclear spins for both are $\frac{1}{2}$) by means of the pulsed electron-nuclear-double-resonance (ENDOR) technique. The pulsed ENDOR spectrum was measured through a combination of microwave and rf (radio frequency) pulses in accordance with the Mims sequence ($\pi/2$ pulse–$\pi/2$ pulse–rf pulse–$\pi/2$ pulse–echo).[11]

Figure 1(a) shows an EPR spectrum of our sample measured for **B** (magnetic field) $\|[0001]$ (*c* axis). As indicated in the figure, this spectrum consists of an overlapping central line for EI5 and EI6, and their HF satellites (labeled *a* to *g*). Figure 1(b) shows their angular dependence when **B** was rotated from the *c* axis to the *c*-normal direction ($[11\bar{2}0]$). The HF satellites *a*, *b*, and *c* have already been reported by Son *et al.*[6,7] Satellite *a* is a ^{29}Si HF structure for EI6,[7] and satellites *b* and *c* are those for EI5.[6] The present angular dependencies for *a*, *b*, and *c* were generally consistent with those previously reported.[6,7]

As the angular dependencies of other HF satellites (*d* to *g*) have not yet been reported yet, it is unclear whether they belong to EI5 or EI6. To clarify this, we measured the HF structures of satellite *a* (EI6), because this satellite was separate from all of EI5's lines. In Fig. 1(b), the thin light lines along satellite *a* indicate its HF structures, which coincide exactly with satellites *d* and *e*. We therefore concluded that these satellites are part of the EI6's HF structures. We applied similar analysis to satellite *b* or *c* of EI5. We then found that satellites *f* should originate from EI5, which is demonstrated by the thin light lines near satellite *b* [Fig. 1(b)]. Satellite *g* was found to be isotropic and should arise from both EI5 and EI6, because we observed the same isotropic HF splittings in satellites *a* (EI6), *b*, and *c* (EI5). We noted that these results were consistent with the 240-GHz EPR study by Konovalov *et al.*[8] Although they reported only

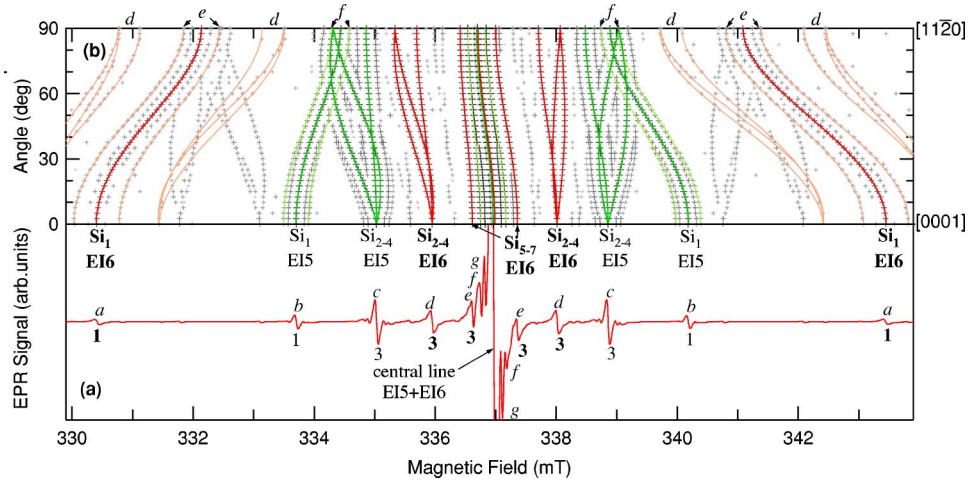

FIG. 1. (Color online) EPR measurements of electron-irradiated *p*-type 4*H*-SiC at 150 K. (a) EPR spectrum for **B**‖[0001]. (b) Angular dependence of signal positions for **B** rotation in the ($\bar{1}$100) plane. Solid lines were calculated using the spin-Hamiltonian parameters given in Table I.

HF splittings for **B**‖[0001], their four values for ID1/EI5 (labeled ID1-1–4) were close to the HF splittings for EI5 (*b*, *c*, *f*, and *g*). Also, the four values labeled ID2-1–4 for ID2/EI6 corresponded to those for EI6 (*a*, *d*, *e*, and *g*), respectively.

Comparing the HF structures of EI5 and EI6, it is immediately clear that satellites *a* and *d* for EI6 have the same angular patterns as those of *b* and *c* for EI5. Their intensity ratios are also the same, i.e., $b:c=1:3$ for EI5 and $a:d=1:3$ for EI6, as is estimated in Fig. 1(a). The angular dependence of *c* and *d* clearly revealed that these satellites consist of three HF structures with intensity ratios of 1:1:1. Furthermore, the symmetry of *a* and *b* coincided with that of the Si dangling bond (DB) on the Si_1 atom (axially symmetrical around the *c* axis, see Fig. 2), and the three HF structures in *d* and *c* were also axially symmetrical around the Si DBs on three Si atoms, i.e., Si_2, Si_3, and Si_4. Summarizing this, both EI5 and EI6 centers revealed four ^{29}Si HF structures that corresponded to four Si atoms surrounding a carbon vacancy. Therefore, it is quite reasonable to identify the EI6 center as a carbon vacancy (V_C^+), similar to the EI5 center,[6] rather than a silicon antisite (Si_C^+).[7] In the original Si_C^+ model,[7] only the EPR spectrum for **B**‖[$\bar{1}$100] was measured and then satellite *d* was assigned to a combination of two HF structures from the Si_1 and Si_2 atoms in Si_C^+. However, this assignment does not fit our complete angular data.

The EI6 center has another HF satellite *e*. We carried out pulsed-ENDOR measurements (10 K) on this satellite by fixing a magnetic field at its position and scanning the frequency of the rf pulse. The inset in Fig. 3 shows a typical ENDOR spectrum, where three ^{29}Si HF splittings can clearly be observed. The relative intensity of this satellite in the cw-EPR spectrum [Fig. 1(a)] also indicates the contribution of three Si atoms. Although the angular dependence of this satellite indicates an axial symmetry around the *c* axis [Fig. 1(b)], looking through the higher resolution ENDOR (Fig. 3) reveals that the symmetry axis is slightly tilted from the *c* axis. Judging from this symmetry and the number of Si atoms, satellite *e* should originate from the Si_5, Si_6, and Si_7 atoms in a carbon vacancy (Fig. 2).

We determined spin-Hamiltonian parameters, *g* and *A* (HF) tensors, for the Si_1 to Si_7 atoms by simulating the angular dependence of corresponding HF satellites. All the *g* and *A* tensors were well described by axially symmetrical tensors. The solid lines in Fig. 1(b) show an excellent agreement between the experiment and simulation. The spin-Hamiltonian parameters are summarized in Table I. We also confirmed that these parameters could perfectly reproduce the angular-dependence data with respect to different rotation planes (**B** was rotated from [0001] to [$\bar{1}$100]). For EI5, the parameters remained almost unchanged with decreasing the temperature. For EI6, however, they were obviously temperature dependent above 10 K. The table also shows theoretical *A* tensors recently calculated by Bockstedte *et al.*[4] Similar theoretical results were also independently reported by Gali *et al.*[5] Comparing these theoretical values with our experimental parameters, the EI5 center is in good agreement with V_C^+ at the *k* site, and the EI6 center fits well with that at the *h* site. Therefore, we concluded that the origins of EI5 and EI6 are both V_C^+ and their respective locations should be *k* and *h* sites. It should also be noted that the theoretical calculation[4] predicted much smaller *A* principal values for Si_C^+ and these were inconsistent with our experimental parameters.

The conclusion that both EI5 and EI6 centers are the same

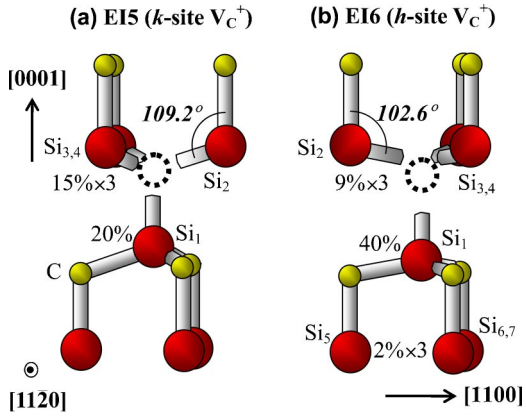

FIG. 2. (Color online) (a) Atomic models for EI5 (*k*-site V_C^+) and (b) for EI6 (*h*-site V_C^+). The percentages represent the unpaired-electron densities on each Si atom. The $\theta_\parallel$ values for the Si_{2-4} DBs are also indicated. All these values were estimated at 150 K.

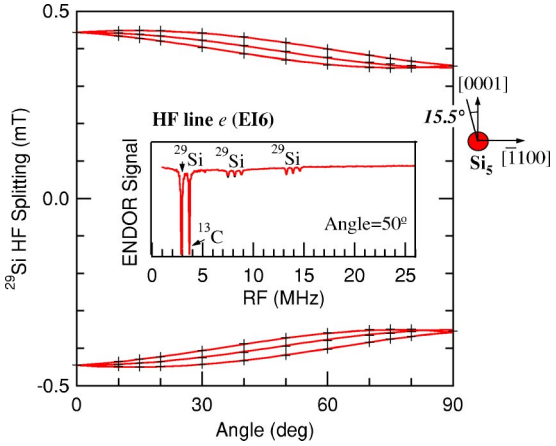

FIG. 3. (Color online) ^{29}Si HF splitting of satellite *e* for EI6 resolved by pulsed ENDOR at 10 K, and a typical ENDOR spectrum (inset).

type of defect can explain the following facts obtained from the experiments. (i) Their g tensors were quite similar, (ii) they appeared simultaneously in the form of an overlapping EPR signal, and (iii) they had similar high thermal stability. Although it has been reported that the annealing-out temperature is lower for EI5 (450–850 °C) (Refs. 6 and 7) than for EI6 ($\geqslant$1000 °C),[7] our isochronal-annealing study (1000, 1200, and 1500 °C for 30 min) revealed that EPR intensities of EI5 and EI6 were unchanged at 1000 °C, and decreased to 3% at 1200 °C and to almost zero at 1500 °C, as compared to their initial intensities. A similar but more detailed result was also reported by the other group.[12] In fact, they were dominant and observed in high-purity semi-insulating 4*H*-SiC obtained through high-temperature growth.[8] Since V_C^+ can capture an electron of the donor, carbon vacancies may play an important role for the Fermi-level pining in such semi-insulating materials.

The A tensors we determined revealed the atomic structures of two types of V_C^+, which we found to be greatly different. For EI5, the direction $\theta_\parallel$ of the Si_{2-4} DBs determined from the $A(Si_{2-4})$ tensor was 109.2° (Fig. 2 and Table I), which is just the tetrahedral angle (109.28°). Thus, the EI5 center appears to have a tetrahedral structure. Using a LCAO (linear combination of atomic orbitals) approximation, we could estimate the wave function for this defect in terms of the 3s- and 3p-orbital densities, $\eta^2\alpha^2$ and $\eta^2\beta^2$, on each Si_i atom, where $\eta^2\alpha^2 = A_{iso}(\mathrm{mT})/163.93$, $\eta^2\beta^2 = A_{aniso}(\mathrm{mT})/4.08$, $A_{iso} = [A_\parallel(Si_i) + 2A_\perp(Si_i)]/3$, $A_{aniso} = [A_\parallel(Si_i) - A_\perp(Si_i)]/3$, and $\alpha^2 + \beta^2 = 1$.[6,7,13] For EI5, the unpaired electron distributes nearly equally on Si_{1-4} atoms (see Fig. 2). For EI6, on the other hand, the direction $\theta_\parallel$ of the Si_{2-4} atoms decreased towards 90°, indicating a planar structure, and thus a nonbonding character was expected between Si_1 and Si_{2-4} atoms. As a result, the unpaired-electron density is localized on the Si_1 atom by 40% (Fig. 2). However, the sums of unpaired-electron distributions on Si_{1-4} atoms were kept to the same value ($\sim$66%) for EI5 and EI6.

The structural distortion for EI6 became maximum when the temperature decreased to 10 K, as can be seen from angle $\theta_\parallel$ (Table I). The 10-K ENDOR data of Fig. 3 reveal distortion at Si_{5-7} atoms in this situation. By simulating the experimental angular pattern (solid lines in figure), the symmetry axis of the $\mathbf{A}(Si_{5-7})$ tensor was found to have tilted outward by 15.5° from the c axis. This again indicates that the EI6 center (h site V_C^+) deforms considerably towards a planar structure. With this deformation, the unpaired electron

TABLE I. Spin-Hamiltonian parameters of EI5 and EI6 centers. The spin Hamiltonian H is given by $H = \mu_B \mathbf{B}\cdot\mathbf{g}\cdot\mathbf{S} + \Sigma\mathbf{S}\cdot\mathbf{A}\cdot\mathbf{I}$, where μ_B is the Bohr magneton, **g** is a g tensor (principal values are $g_\parallel$ and $g_\perp$), **S** is an electron spin operator, **A** is a HF tensor for each atom in the wave function, and **I** is a nuclear spin operator corresponding to each A tensor. Principal values of **A** are expressed in mT using a conversion factor that 1 mT = 28.02 MHz. $\theta_\parallel$ is the angle between the $A_\parallel$ principal axis and the c axis (see also Fig. 2). The table also contains previous EPR parameters reported by Son *et al.* (Refs. 6 and 7). The $A(Si_{2,3,4})$ tensor in Ref. 6 was not axial symmetrical and showed a different $\theta_\parallel$ value (95°); however, this result was obtained using an extra fitting parameter of a misalignment angle. Since we did not use such a parameter and did check the fitting in two different orientation data, our $A(Si_{2,3,4})$ tensor will be more reliable. In the bottom, theoretical A tensors obtained by the *ab initio* calculation (Ref. 4) are shown.

	g		**A**(Si_1)		**A**($Si_{2,3,4}$)			Other **A**		
	$g_\parallel$	$g_\perp$	$A_\parallel$	$A_\perp$	$A_\parallel$	$A_\perp$	$\theta_\parallel$	$A_\parallel$	$A_\perp$	A_{iso}
EI5 ($S=\frac{1}{2}$, C_{3v})			HF *b*			HF *c*		HF *f*		HF *g*
(150 K)	2.00322	2.00484	6.49	4.47	5.18	3.63	109.2°	0.40	0.29	0.2
Ref. 6 (138 K)	2.00322	2.00484	6.46	4.46	5.02	3.75	95°			
EI6 ($S=\frac{1}{2}$, C_{3v})			HF *a*			HF *d*		HF *e* [**A**($Si_{5,6,7}$)]		HF *g*
(293 K)	2.0032	2.0046	12.29	8.45	3.21	2.20	103.6°	0.72	0.57	
(150 K)	2.00305	2.00472	13.06	8.97	2.97	2.01	102.6°	0.75	0.59	0.2
(50 K)	2.00279	2.00489	14.26	9.77	2.58	1.72	101.0°	0.82	0.64	0.2
(10 K)	2.0026	2.0052	15.48	10.61	2.11	1.39	97.7°	0.87	0.69	0.2
Ref. 7 (138 K)	2.00302	2.00473	13.21	9.07						
Theory (Ref. 4)			**A**(Si_1)			**A**(Si_2)			**A**($Si_{3,4}$)	
k-site V_C^+ (C_{1h})		7.04	4.36	4.07	5.54	3.32	3.11	5.75	3.89	3.68
h-site V_C^+ (C_{3v})		14.29	9.82	9.82	1.54	0.79	0.71	1.54	0.79	0.71

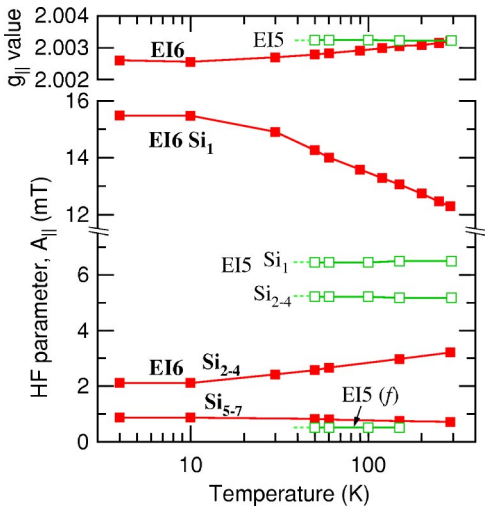

FIG. 4. (Color online) Temperature dependence of spin-Hamiltonian parameters for EI5 and EI6.

for EI6 became more localized on the Si_1 atom (47%); however, the total η^2 on the Si_{1-4} atoms was found to be almost unchanged (68%).

Despite being the same type of defect, the EI5 center had invariant g and A values, while those for EI6 were considerably temperature dependent, as plotted in Fig. 4. We think this difference is closely related to the symmetry of the distortions. The theoretical calculation for the k site predicted that the pseudo Jahn-Teller effect generates a pair of Si_1 and Si_2 atoms (a Si_3-Si_4 pair is also formed).[4] Although this distorted configuration indicated a C_{1h} symmetry,[4] there are three equivalent configurations (Si_1-Si_2, Si_1-Si_3, and Si_1-Si_4 pairs), because the Si_{2-4} atoms are C_{3v} symmetry related. Thus, thermally activated reorientation between the three configurations possibly occurs, which enabled us to observe their average state with a C_{3v} symmetry.[14] We speculated that due to the pairing of Si_1 and Si_{2-4} atoms, the average state of EI5 is always confined and approaches a tetrahedral structure at relevant temperatures ($\geqslant 50$ K), resulting in unchanging g and HF parameters. However, the h-site V_C^+ had only one orientation for distortion (planar distortion along c axis) retaining C_{3v} symmetry, and hence no reorientation effect could take place. Furthermore, this type of distortion enabled the Si_1 atom to move a great deal because of the nonbonding character of Si_1 and Si_{2-4} atoms. This made it possible to observe structural change in EI6 with decreasing temperature. The theoretical calculation for EI6 also predicted the presence of a C_{1h}-distorted structure, in addition to the C_{3v} state. However, we did not observe such a state even at 4 K, and therefore the C_{3v}-distorted state shown here will be energetically preferable.

The presence of reorientation in the symmetry-related configurations in EI5 and the absence of such dynamic effects in EI6 could also be inferred from the much faster spin relaxation in the former rather than the latter center. From three-pulse inversion recovery measurements of pulsed EPR,[10] we found that the spin-lattice relaxation time (T_1) was three times shorter for EI5 (4.8×10^{-6} sec) than for EI6 (13.0×10^{-6} sec) at 80 K. This can be also confirmed by conventional EPR where the EI6 signal was much more easily saturated to microwave power, compared to the EI5 signal. Also, a similar motional effect was detected in the Ky1 and Ky2 centers in 6H-SiC which were assigned to V_C^+ at the k_1 and k_2 sites (two inequivalent quasicubic sites).[9]

In summary, we found a complete set of ^{29}Si HF parameters for EI5 and EI6 centers through EPR and pulsed ENDOR techniques. Although they were originally assigned to V_C^+ (for EI5) and Si_C^+ (for EI6), our complete data demonstrated that both EI5 and EI6 were V_C^+ centers but their locations should have been k and h sites, as recently suggested by the theoretical calculations.[4,5] This conclusion was also supported by facts obtained by experiments, such as similar g values, their coexistence, and the same thermal stability. Despite being the same kind of defect, the two types of V_C^+ were found to be quite different in structural distortion and temperature dependence, which could reasonably be explained by the symmetry of distortions at k and h sites.

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[14] Below 50 K, we found that EI5 exhibited a C_{1h}-symmetric g tensor and complicated HF structures. This C_{1h} symmetry is consistent with the theoretical prediction (Ref. 4) and supports our model for the thermally activated reorientation.