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EPR and *ab initio* calculation study on the EI4 center in 4H- and 6H-SiCP. Carlsson,^{1,*} N. T. Son,¹ A. Gali,^{2,3} J. Isoya,⁴ N. Morishita,⁵ T. Ohshima,⁵ B. Magnusson,⁶ and E. Janzén¹¹*Department of Physics, Chemistry and Biology, Linköping University, SE-581 83 Linköping, Sweden*²*Department of Atomic Physics, Budapest University of Technology and Economics, Budafoki út 8., H-1111 Budapest, Hungary*³*Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences, P.O. Box 49, H-1525 Budapest, Hungary*⁴*Graduate School of Library, Information and Media Studies, University of Tsukuba, 1-2 Kasuga, Tsukuba, Ibaraki 305-8550, Japan*⁵*Japan Atomic Energy Agency, 1233 Watanuki, Takasaki, Gunma 370-1292, Japan*⁶*Norstel AB, Ramshällsvägen 15, SE-602 38 Norrköping, Sweden*

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We present results from electron paramagnetic resonance (EPR) studies of the EI4 EPR center in 4H- and 6H-SiC. The EPR signal of the EI4 center was found to be drastically enhanced in electron-irradiated high-purity semi-insulating materials after annealing at 700–750 °C. Strong EPR signals of the EI4 center with minimal interferences from other radiation-induced defects in irradiated high-purity semi-insulating materials allowed our more detailed study of the hyperfine (hf) structures. An additional large-splitting ²⁹Si hf structure and ¹³C hf lines of the EI4 defect were observed. Comparing the data on the hf interactions and the annealing behavior obtained from EPR experiments and from *ab initio* supercell calculations of different carbon-vacancy-related complexes, we suggest a complex between a carbon vacancy-carbon antisite and a carbon vacancy at the third-neighbor site of the antisite in the neutral charge state, (V_C -C_{Si}V_C)⁰, as a new defect model for the EI4 center.

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I. INTRODUCTION

The EI4 center has an effective electron spin $S=1$ and was previously observed in *p*-type 4H- and 6H-SiC irradiated by 2.5 MeV electrons at 400 °C.¹ In both polytypes, the EPR lines show two satellites with a splitting of ~ 11.4 G. The EI4 spectrum is similar to the P4 spectrum reported by Vainer and Ilin^{2,3} in heat-treated *n*-type 6H-SiC, except a difference in the Si hyperfine (hf) splitting of ~ 6.4 G, and may be related to the same defect. These rather isotropic splitting satellites have an intensity ratio of $\sim 20\%$ compared to the main line and were therefore assigned to the hf structure due to the interaction between the electron spin and the nuclear spins of the nearest ²⁹Si ($I=1/2$ and 4.7% natural abundance) neighbors of the defect. Due to low signal intensities, the hf tensors could not be determined. The defect was tentatively assigned to a far-distant pair of carbon vacancies lying in the (11 $\bar{2}$ 0) or equivalent planes based on its C_{1h} symmetry and the angle of 54° between the principal z axis of the fine-structure tensor **D** and the c axis.^{1–3} However, the small and nearly isotropic Si hf splitting can only account for a very low spin density. It is possible that some hf structures were not detected in previous studies due to low signal intensities.

During the last ten years, a considerable effort has been spent on developing high-purity semi-insulating (HPSI) SiC substrates for SiC and III-nitrides-based high-frequency power electronics. In HPSI SiC substrates grown by high-temperature chemical vapor deposition (HTCVD) (Refs. 4–6) or by physical vapor deposition^{7,8} semi-insulating (SI) properties have been achieved using intrinsic defects. In those materials, deep acceptor levels of vacancy-related defects can compensate the residual N shallow donors to pin the Fermi level to one of the deep levels and highly resistive materials with typical resistivity in the range of

10^6 – 10^{10} Ω cm can be achieved.^{4–8} There are different types of HPSI SiC materials characterized by different activation energies ranging from ~ 0.6 to ~ 1.6 eV.^{4–8} It has been shown that carrier compensation processes in HPSI 4H-SiC materials are complicated, involving different defects of which the silicon vacancy (V_{Si}), the carbon vacancy (V_C), the carbon antisite-vacancy pairs ($C_{Si}V_C$), and the divacancy (V_CV_{Si}) are the most prominent ones.⁹ The SI properties in different types of HPSI substrates are changed differently with high-temperature annealing. This is due to the interaction of vacancies and other defects which leads to the formation of new complex defects and/or annealing of vacancies. Understanding such processes is important for defect control in order to obtain HPSI SiC materials with stable SI properties. Recently, we have noticed that the EPR spectrum of the EI4 center was also commonly detected in some types of HPSI 6H-SiC substrates.¹⁰ Annealing studies in as-grown HPSI 6H-SiC show that the EI4 center is thermally stable up to at least 1200 °C.¹⁰ Preliminary photoexcitation-EPR (photo-EPR) studies indicate that EI4 is a deep defect and can play a role in carrier compensation processes. Identification of this defect is therefore of fundamental interest for understanding the defect interaction at elevated temperatures and also technologically important for defect control in HPSI SiC substrates.

In this study, the EI4 signal in electron-irradiated HPSI materials has been considerably enhanced after annealing the sample at 700–750 °C, allowing a more detailed study of the hf structures. The detection of additional large-splitting ²⁹Si hf lines and other ¹³C ($I=1/2$ and 1.1% natural abundance) hf structures calls for a new defect model for the EI4 center. Supercell calculations on different V_C -related complexes have been carried out to find possible models that can explain the ²⁹Si and ¹³C hf structures observed in EPR experiments. Combining the data obtained from EPR and su-

percell calculations, we here present a model of a complex between the negative carbon antisite-vacancy pair¹¹ ($C_{Si}V_C^-$) and a third-neighbor positive carbon vacancy^{12,13} (V_C^+) in the neutral charge state, $(V_C-C_{Si}V_C)^0$, for the EI4 center in 4H- and 6H-SiC.

II. EXPERIMENTAL DETAILS

Starting materials used in our study are commercially available *n*- and *p*-type 4H- and 6H-SiC wafers and HPSI substrates grown by HTCVD. Typical residual concentrations of common impurities in HPSI samples are in the range of mid 10^{15} cm⁻³ or less ($\sim 2 \times 10^{15}$ – 6×10^{15} cm⁻³ for the N donors and $\sim 1 \times 10^{15}$ – 3×10^{15} cm⁻³ for the shallow B acceptors). The samples were irradiated at room temperature by 2 MeV electrons with different doses of 2×10^{18} cm⁻², 4×10^{18} cm⁻², and 8×10^{18} cm⁻². The EPR measurements were performed on an X-band (~ 9.5 GHz) Bruker ELEXSYS E580 EPR spectrometer. The sample temperature can be regulated in the range of 6–300 K using a continuous He-flow cryostat or fixed at 77 K using a liquid N₂ dewar. For photo-EPR measurements, a 250 W halogen lamp or a 150 W xenon lamp was used as excitation sources. For monochromatic optical excitation, a Jobin-Yvon 0.25 m single grating monochromator was used together with appropriate optical filters. Annealing was performed on a single sample in Ar-flow ambience for 10 min at each temperature.

III. RESULTS AND DISCUSSION

A. EPR spectra and analysis

In *n*-type commercial 4H-SiC substrates, the EI4 spectrum was not detected after electron irradiation (with electron doses of 1×10^{18} – 4×10^{18} cm⁻² at room temperature and at 850 °C) and annealing (in the range of 200–1200 °C). Similar to the previous study,¹ the EI4 spectrum was observed in all irradiated *p*-type 4H- and 6H-SiC samples. However, after irradiation the signal is still rather weak compared to that of other defects such as V_C^+ . Typical EPR spectra in as-irradiated HPSI 4H-SiC measured in darkness at 77 K are shown in Fig. 1(a). In those samples, weak EI4 signals were observed. The spectrum recorded at room temperature [Fig. 1(b)] shows strong signals of the silicon vacancies.^{14–16} [The T_{V2a} signal¹⁵ in Fig. 1(b) becomes as strong as the middle line under illumination.] With increasing annealing temperature, the intensity of the EI4 spectrum increased whereas the signals of the carbon and silicon vacancies were reduced. After annealing at ~ 750 °C for 4H-SiC and at ~ 700 °C for 6H-SiC the EI4 signal reached its maximum and became comparable with that of V_C^+ , as can be seen in Figs. 2 and 3. The spectra for both 4H- and 6H-SiC measured after annealing are shown in Fig. 2 for the magnetic field, **B**, parallel to the *c* axis of the crystal and in Fig. 3 for **B** $\perp$ **c** in the (11 $\bar{2}$ 0) plane (**B** $\parallel$ [1 $\bar{1}$ 00]).

In the low-resolution spectra recorded for a large magnetic field region (>250 G in Figs. 2 and 3), each main line of EI4 is accompanied by a pair of satellites with a splitting in the range of ~ 9 –16 G. The intensity ratio of the satellites and the main line is about 20% which is approximately four

FIG. 1. (Color online) Spectra of HPSI 4H-SiC after irradiation with 2 MeV electrons measured with **B** $\parallel$ **c** in darkness at (a) 77 K and (b) 293 K.

times the natural abundance of the ^{29}Si isotope. These satellites were previously observed and assigned to the hf structure of the interaction between the electron spin and nuclear spins of ^{29}Si at four-nearest-neighboring sites.^{1–3} We will show later that each of these broad hf lines consists of several lines which can be resolved in higher resolution spectra. In addition to this inner hf structure, two pairs of large-splitting hf lines were detected as can be seen in Figs. 2 and 3. At the *c* direction (Fig. 2), each pair of lines shows an intensity ratio with the main line of ~ 3 –3.5 %, which is slightly less than the expected intensity ratio for the hf structure of the interaction with one ^{29}Si nucleus ($\sim 4.7\%$). Rotating the magnetic field away from the *c* axis, these hf lines do not split but the relative intensity changes with one pair of lines getting stronger while the other reduces in intensity. For the lowest-field and highest-field lines, one of the pair disappeared at angles of the magnetic field close to $\theta \sim 54^\circ$ off the *c* axis in the (11 $\bar{2}$ 0) plane while the other increases its intensity ratio with the main line to $\sim 4.5\%$, which is approximately the natural abundance of the ^{29}Si isotope (Fig. 4). For two EPR lines, which are split off from the lowest-field and highest-field lines, one pair of hf lines also disappears but at angles of the magnetic field close to $\theta \sim 36^\circ$. For other EPR lines at intermediate fields, the hf lines also vary in intensity but none of the pairs vanishes (Fig. 4). The intensity ratio of the total hf lines (only one pair at $\theta \sim 55^\circ$) with the main line of $\sim 4.5\%$ and the angular variation in the intensity of hf lines suggest that the observed hf lines may be related to the allowed ($\Delta M_S = \pm 1$ and $\Delta m_I = 0$) and “forbidden” ($\Delta M_S = \pm 1$ and $\Delta m_I = \pm 1$) transitions of the hf interaction between the electron spin and the nuclear spin of one ^{29}Si nucleus. Here M_S and m_I are the magnetic quantum numbers of the electron spin and the nuclear spin, respectively.

It is known that for defects having spin $S \geq 1$ with a large zero-field splitting and hf constants, forbidden transitions can

FIG. 2. (Color online) EPR spectra observed in darkness at 77 K for $\mathbf{B} \parallel \mathbf{c}$ in: (a) HPSI 4H-SiC after irradiation with 2 MeV electrons and subsequent annealing at $\sim 750^\circ\text{C}$, (b) HPSI 6H-SiC after irradiation with 2 MeV electrons and subsequent annealing at $\sim 700^\circ\text{C}$. The two large-splitting hf lines of EI4, due to the interaction with ^{29}Si nuclei, are indicated and magnified.

have significant intensities.¹⁷ The effect on the energy of second-order admixtures arising from the cross products of terms in fine-structure parameter D and hf constant A has been evaluated by Bleaney and Rubins.¹⁷ They have shown that a nuclear state $|m\rangle$ becomes admixed with states $|m \pm 1\rangle$ by amounts of order $3D \sin 2\theta / 4g\mu_B B$ and transitions $\Delta M_S = \pm 1$ and $\Delta m_I = \pm 1$ become allowed with intensities in the order of the square of this admixture coefficient, relative to the intensities of the ordinary transitions with $\Delta m_I = 0$. The intensities of the forbidden lines are angular dependent and vanish at directions parallel or perpendicular to the symmetry axis. Below, we show our analysis of the angular dependence of the EI4 spectra in 4H- and 6H-SiC, considering the large-splitting hf structure to be due to the hf interaction of the electron spin with the nuclear spin of one ^{29}Si nucleus.

Figures 5(a) and 5(b) show the experimental angular dependences of the EI4 spectrum in 4H- and 6H-SiC, respectively, including both the main lines (filled black rings) and the large-splitting ^{29}Si hf lines (hollow black rings) measured with the magnetic field rotating in the $(11\bar{2}0)$ plane. The angular dependences can be described by the following spin-Hamiltonian:

FIG. 3. (Color online) [(a) and (b)] The full spectra for $\mathbf{B} \perp \mathbf{c}$ in the $(11\bar{2}0)$ plane for 4H- and 6H-SiC, respectively. The two large-splitting hf lines due to the interaction with ^{29}Si nuclei are indicated and partly magnified.

$$H = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I}, \quad (1)$$

where μ_B is the Bohr magneton and the $\mathbf{D}$ and $\mathbf{A}$ tensors represent the spin-spin interaction and the hf interaction, re-

FIG. 4. (Color online) (a) The lowest-field line and (b) the next lowest-field line of EI4 in 4H-SiC measured with 55° angle between $\mathbf{B}$ and $\mathbf{c}$ in the $(11\bar{2}0)$ plane. The large-splitting hf structures due to the interaction with ^{29}Si nuclei are indicated. Part of this hf structure is magnified and shown also for 45° angle between $\mathbf{B}$ and $\mathbf{c}$.

FIG. 5. (Color online) The measured angular dependence of the main lines of EI4 (filled rings) and the wide hf structure from the interaction with ^{29}Si (hollow rings) and the simulated ditto (curves) in (a) $4H\text{-SiC}$ and (b) $6H\text{-SiC}$. The magnetic field was rotated in the $(11\bar{2}0)$ plane, from $\mathbf{B}\parallel\mathbf{c}$ ($\theta=0^\circ$) to $\mathbf{B}\parallel[1\bar{1}00]$ ($\theta=90^\circ$). The positions where only the hf lines corresponding to the transitions $\Delta M_S = \pm 1$ and $\Delta m_I = 0$ were detected are marked with red circles.

spectively. The number of four EPR lines corresponding to each transition of a spin $S=1$ center suggests that the defect has C_{1h} symmetry. In this case, the mirror plane reduces the six possible defect orientations to four and both the principal axes g_{xx} and g_{zz} are in the $(11\bar{2}0)$ plane. Similarly, the $\mathbf{A}$ tensor is also constrained in C_{1h} symmetry. The $\mathbf{D}$ tensor is a traceless second-rank tensor commonly described by the fine-structure parameters D and E , which are defined as $D=3D_{zz}/2$ and $E=(D_{xx}-D_{yy})/2$. Here, D and E are the fine-structure parameters representing the zero-field splitting due to the axial and orthorhombic crystal fields, respectively. In the fit, second-order effect is also taken into account. For determination of the $\mathbf{g}$ tensor, different fits using variable principal g values or a fixed isotropic g value were performed. We found that if setting the g values to be variable, we obtained anisotropic g values similar to the previous reports.^{1,2} However, the best fit can also be obtained using an isotropic g value of 2.004. We believe that the anisotropy of the EI4 spectrum is caused by the large zero-field splitting and set the value $g=2.004$ for the EI4 center. The fine-structure parameters were determined as $D=344 \times 10^{-4} \text{ cm}^{-1}$ and $E=65 \times 10^{-4} \text{ cm}^{-1}$ for $4H\text{-SiC}$ and $D=328 \times 10^{-4} \text{ cm}^{-1}$ and $E=64 \times 10^{-4} \text{ cm}^{-1}$ for $6H\text{-SiC}$. The angle α between the principal z axis of the $\mathbf{D}$ tensor and the c axis is 54° for both $4H\text{-}$ and $6H\text{-SiC}$. Taking into account also the $\Delta M_S = \pm 1$ and $\Delta m_I = \pm 1$ transitions, the large-splitting hf structure consisting of two pairs of lines could be described by one $\mathbf{A}$ tensor, representing the interaction of the electron spin with the nuclear spin $I=1/2$ of one ^{29}Si nucleus. The principal values of the $\mathbf{A}$ tensor (also in the unit of 10^{-4} cm^{-1}) were determined as $A_{xx}=63$, $A_{yy}=58$, and

$A_{zz}=86$ for $4H\text{-SiC}$ and $A_{xx}=60$, $A_{yy}=60$, and $A_{zz}=83$ for $6H\text{-SiC}$. The angle β between the principal z axis of the $\mathbf{A}$ tensor and the c axis is 5.3° for $4H\text{-SiC}$ and 1.1° for $6H\text{-SiC}$. The mean deviation in the fits is $\sim 0.5 \text{ G}$, which gives the corresponding uncertainty in the determination of D , E , and $\mathbf{A}$ parameters $\sim 0.5 \times 10^{-4} \text{ cm}^{-1}$. The principal values of the $\mathbf{D}$ and $\mathbf{A}$ tensors obtained from the least-square fit to the experimental data are given in Table I. The simulated angular dependences using the obtained parameters and the spin-Hamiltonian [Eq. (1)] are also plotted in Figs. 5(a) and 5(b) for $4H\text{-}$ and $6H\text{-SiC}$, respectively. The simulated angular dependences of the hf peak positions fits very well with the measured positions, as can be seen in Fig. 5. The measured intensity ratio between each hf pair and the main line for different angles is in fair agreement with the intensity ratios calculated in the simulation.

In the case of the EI4 center, the principal z axis of both the $\mathbf{g}$ and $\mathbf{D}$ tensors is $\sim 54^\circ$ and close to this angle the forbidden lines disappear for some defect orientations (Figs. 4 and 5). For other defect orientations, the forbidden lines vanish at angles close to $\theta \sim 36^\circ$ which is the direction of the principal x axis of the $\mathbf{g}$ and $\mathbf{D}$ tensors (Fig. 5). In Fig. 5 the positions where only $\Delta M_S = \pm 1$ and $\Delta m_I = 0$ hf lines were detected are marked with large circles. From the angular dependences of the peak positions and the intensities of these hf lines we conclude that the observed large-splitting hf structure is caused by the interaction of the electron spin and the nuclear spin of one ^{29}Si atom located approximately along the c axis, which will be referred to as Si_1 .

Figures 6(a) and 6(b) show high-resolution EPR spectra measured for $\mathbf{B}\parallel\mathbf{c}$. A weak hf structure with a splitting of $\sim 24.9 \text{ G}$ for $4H\text{-SiC}$ and $\sim 24.0 \text{ G}$ for $6H\text{-SiC}$ can be seen. As indicated in Fig. 6(a), this structure actually consists of two pairs of satellites. The lines do not split when the magnetic field direction is changed and for high-dose-irradiated ($8 \times 10^{18} \text{ cm}^{-2}$) $4H\text{-SiC}$ the angular dependence of the peak positions and intensities could be partly determined for both pairs. The intensity ratio between one of these pairs [the outer one in Fig. 6(a)] and the main line is $\sim 1\%$ for all angles between $\mathbf{B}$ and the c axis, which is typical for the hf structure due to the interaction of the electron spin and the nuclear spin of one ^{13}C nucleus while for the other pair the intensity ratio is lower. Although the signal-to-noise ratio of ^{13}C hf lines is rather good in samples irradiated with high electron doses of $8 \times 10^{18} \text{ cm}^{-2}$, their angular dependence with $\mathbf{B}$ rotating in the $(11\bar{2}0)$ plane could not be followed due to overlapping between eight EPR main lines (four with double intensity and four with single intensity) and their associated ^{29}Si hf lines (Fig. 5). In order to reduce the overlapping between the lines and to increase the line intensity we used samples cut along the $[1\bar{1}00]$ direction. With $\mathbf{B}$ rotating in the $(1\bar{1}00)$ plane, the number of main EPR lines for a spin $S=1$ reduces to six (all with double intensity) and we could observe ^{13}C hf structures not only for the lowest line but also for higher field lines at some directions. Figure 7 shows some EPR spectra in $4H\text{-SiC}$ measured at different directions with $\mathbf{B}$ rotating in the $(1\bar{1}00)$ plane. The ^{13}C hf lines are indicated in pairs. In the figure, all the spectra are shown on the same magnetic field range of 50 G and the hf splittings

TABLE I. Spin-Hamiltonian parameters for the EI4 center in 4*H*- and 6*H*-SiC. An isotropic *g* value of 2.004 was determined for both the 4*H* and 6*H* polytypes. α is the angle between the principal *z* axis of the **D** tensor and the *c* axis of the crystal and β is the angle between the principal *z* axis of the **A** tensor and the *c* axis, both in the (11 $\bar{2}$ 0) or equivalent plane. The principal values of the **A** tensors, and the fine structure parameters *D* and *E*, are given in the unit of 10^{-4} cm^{-1} . The estimated error for the *D*, *E*, and *A*(Si₁) parameters is about $\sim 0.5 \times 10^{-4} \text{ cm}^{-1}$ while for the *A*(C_{Si}) and other *A*(Si₂₋₄) principal values it can be up to $\sim 2 \times 10^{-4} \text{ cm}^{-1}$. The calculated values (Cal.) of the corresponding **A** tensors of the (V_C-C_{Si}V_C)⁰ defect in 4*H*-SiC are also given. The calculated hyperfine constants are technically converged well within 1%. The spin densities on the *s* and *p* orbitals of the neighboring atoms, as approximated from the hf tensors, are given in percentage, and the isotropic (*a*) and anisotropic (*b*) parts of the **A** tensors are given in the unit of 10^{-4} cm^{-1} . For Si₂₋₄ atoms the third principal values could not be determined in the experiment. The atom labels are from Fig. 12.

	<i>D</i>	<i>E</i>	α (deg)	<i>A</i> _{xx}	<i>A</i> _{yy}	<i>A</i> _{zz}	β (deg)	<i>a</i>	<i>b</i>	<i>s</i> (%)	<i>p</i> (%)	<i>s+p</i> (%)
4 <i>H</i>	344	65	54									
<i>A</i> (Si ₁)												
Exp.				63	58	86	5	69	9	4	23	27
Cal.				57	57	79	0					
<i>A</i> (C _{Si})												
Exp.				14	14	42	71	23	9	0.6	8	9
Cal.				10	10	35	71					
<i>A</i> (Si ₂)												
Exp.				~ 10	~ 11	$\sim 8-15$						
Cal.				12	12	15						
<i>A</i> (Si ₃)												
Exp.				~ 10	~ 13	$\sim 8-15$						
Cal.				14	14	18						
<i>A</i> (Si ₄)												
Exp.				~ 13	~ 15	$\sim 8-15$						
Cal.				15	15	19						
6 <i>H</i>	328	64	54									
<i>A</i> (Si ₁)												
Exp.				60	60	83	1	204	23	4	20	25

can be directly compared. The angular dependence of the ¹³C hf splittings with **B** rotating in the (1 $\bar{1}$ 00) plane is shown in Fig. 8. The ¹³C hf lines with splitting smaller than ~ 16 G are merged in the region of the inner ²⁹Si hf structure and could not be determined. Similar to the large-splitting ²⁹Si hf discussed above, the analysis of the angular dependence of the ¹³C hf splittings in the (1 $\bar{1}$ 00) showed that the hf lines belong to the allowed and forbidden transitions of the interaction with one ¹³C nucleus. The principal values of the **A** tensor were determined as $A_{xx}=A_{yy}=14 \times 10^{-4} \text{ cm}^{-1}$, $A_{zz}=42 \times 10^{-4} \text{ cm}^{-1}$ and the angle between the principal *z* axis of the **A** tensor and the *c* axis is 71° . The uncertainty is $\sim 2 \times 10^{-4} \text{ cm}^{-1}$. The obtained ¹³C hf parameters are listed in Table I. The simulation of the ¹³C hf splittings from the allowed and forbidden transitions using the obtained parameters are plotted as solid and dashed curves, respectively, in Fig. 8.

In addition to the weak ¹³C hf structure, three pairs of hf lines in the region 9–16 G were also detected in both 4*H*- and 6*H*-SiC (Fig. 9). In the low-resolution spectra, these hf structures appear as a pair of single and broad lines (Figs. 2 and 3). From their intensity ratio with the main line, this hf structure can be attributed to the hf interaction involving four to five Si atoms and possibly also C atoms. When rotating the magnetic field away from the *c* axis, the hf splittings

slightly change and for most angles the structure consists of two strong- and equal-intensity pairs of lines and one weaker pair of lines with slightly higher splitting. At $\theta \sim 55^\circ$, where no forbidden transitions should be expected, the weak pair is hardly detectable and only two strong lines are detected, as can be seen in Fig. 4. It is difficult to decide whether the weaker pair is from forbidden transitions or if it is a normal transition that is more or less detectable depending on overlapping and slight misalignment. For such small hf splittings, the second-order effect on the energy is small and forbidden transitions should have less effect on the hf structure. The intensity ratio of each pair of the strong hf lines and the main line varies between $\sim 8.8\%$ and 9.6% , which correspond to the hf interaction between the electron spin and the nuclear spins of two ²⁹Si nuclei (or one ²⁹Si at two equivalent Si sites, to be more precise). The intensity ratio between the weak pair and the main line has a maximum of 3.9% , which could correspond to the hf interaction between the electron spin and the nuclear spin of one ²⁹Si nucleus. The angular variation in the splitting of these hf lines can be followed for some EPR lines at low fields and is shown in Fig. 9. Similar data could not be obtained for other EPR lines due to severe overlapping with each other. With limited data, only two principal *A* values can be determined from one loop in the angular dependence with **B** rotating in the (11 $\bar{2}$ 0) plane. (The

FIG. 6. (Color online) Low-field lines of EI4 in (a) 4H- and (b) 6H-SiC. The inner hf structures due to the interaction with a number of Si and C sites are indicated.

determination of the third principal value, A_{yy} , requires data of hf splittings of two other EPR lines which could not be clearly distinguished from other lines.) The fits give the principal values for three hf structures (in the unit of 10^{-4} cm^{-1}): (i) $A_1=10$ and $A_2=11$, (ii) $A_1=10$ and $A_2=13$, and (iii) $A_1=13$ and $A_2=15$. For all the three hf structures, the third principal A value is also in the range $8 \times 10^{-4} - 15 \times 10^{-4} \text{ cm}^{-1}$. For these parameters, the uncertainty can be as high as $\sim 2 \times 10^{-4} \text{ cm}^{-1}$ due to possible mixture of the data points from different angular dependences.

Following one-electron linear combination of atomic orbitals approximation, the hf tensor can be decomposed into isotropic (a) and anisotropic (b) parts. Here $a=(A_{\parallel}+2A_{\perp})/3$ is the Fermi contact term, which determines the spin density in the s orbital and $b=(A_{\parallel}-A_{\perp})/3$ determines the spin density on the p orbital. In the case of the EI4 center, the hf tensors are nearly axial along the principal z axis so $A_{\perp}$ is replaced by $(A_{xx}+A_{yy})/2$ and $A_{\parallel}=A_{zz}$. For the large-splitting Si hf of the EI4 center in 4H-SiC we obtain: $a=69 \times 10^{-4} \text{ cm}^{-1}$ and $b=9 \times 10^{-4} \text{ cm}^{-1}$. Using the atomic parameters given by Morton and Preston¹⁸ the spin densities on the $3s$ and $3p$ orbitals of the Si_1 atom are estimated to be 4% and 23%, respectively. The total spin density on the Si_1 atom then becomes 27%. For the EI4 center in 6H-SiC, the corresponding spin densities are determined as 4%, 20%, and 25%. For the hf interaction with one ^{13}C , the a and b values

FIG. 7. (Color online) Parts of the EI4 EPR spectra for different angles between $\mathbf{B}$ and $\mathbf{c}$ in the $(1\bar{1}00)$ plane with the double pair of ^{13}C hf lines indicated. One of the two main lines for $\theta=0^\circ$, two of the six main lines for $\theta=40^\circ$, and two of the four main lines for $\theta=90^\circ$ are shown.

are $a=23 \times 10^{-4} \text{ cm}^{-1}$ and $b=9 \times 10^{-4} \text{ cm}^{-1}$ which correspond to the spin densities of 0.6% and 8% on the $3s$ and $3p$ orbitals, respectively. The total spin density on the ^{13}C atom is 9%.

We studied the EI4 EPR signal intensity as a function of measurement temperature in order to obtain information about the ground and excited states. The measured temperature dependence is shown for 4H-SiC as black circles in Fig. 10. The decreasing signal intensity with increasing measurement temperature confirms that the $S=1$ EI4 center corresponds to a ground state. If we consider a system with a triplet (E_T , with two electrons occupation) and a higher lying singlet (E_S , which can also accommodate two electrons) with the energy separation between the states, ΔE , the intensity of the EPR signal can be described as

FIG. 8. (Color online) The measured angular dependence of the ^{13}C hf splitting for $\mathbf{B}$ rotating in the $(1\bar{1}00)$ plane (rings). Considering both allowed and forbidden transitions, one $\mathbf{A}$ tensors could be estimated from fitting with the measured data. The simulated angular dependence of the allowed and forbidden lines using the observed parameters is shown as solid and dashed loops, respectively.

FIG. 9. The measured angular dependence of the splitting of the hf structures in the range 9–16 G (rings). The magnetic field was rotated in the (11 $\bar{2}$ 0) plane, from $\mathbf{B} \parallel \mathbf{c}$ to $\mathbf{B} \parallel [1\bar{1}00]$. Two principal values for each of three $\mathbf{A}$ tensors could be estimated from fitting with the measured data. The solid loops show the part of the angular dependence that could be simulated using these values.

$$I(T) \propto \{N / [\exp(-\Delta E/k_B T)]\} f(T), \quad (2)$$

where N is the total defect concentration on the two levels and $f(T) = [1 - \exp(-\delta/k_B T)] / [1 + \exp(-\delta/k_B T)]$ is the population difference between the Zeeman splitting levels with $M_S = 0$ and $M_S = \pm 1$. At microwave frequency ~ 9.5 GHz, $\delta \sim 0.04$ meV. The best fit with the measured intensities gives $\Delta E = 15$ meV. Here we assumed that spin-orbit transitions can occur between the ground-state triplet and the excited state singlet mediated by phonons, which is principally allowed by symmetry for this defect. The detailed study of spin-orbit transitions is beyond the scope of this paper. The assumption of direct absorption of phonons in this process is reasonable because the obtained energy difference (15 meV) is smaller than the highest-energy phonons (~ 120 meV). The deviation at low temperatures can be due to other effects (in addition to the effect of the Boltzmann distribution), such as Orbach process, that influence on the EPR intensity at low temperatures. Nevertheless, this experimental study indicates

FIG. 10. (Color online) The dependence of the EI4 EPR signal intensity on the measurement temperature (circles) for 4H-SiC. The best fit (solid curve) using Eq. (2), for a triplet ground state and a higher lying singlet state, gives energy difference $\Delta E = 15$ meV between the states.

FIG. 11. (Color online) The dependence of the EPR intensities of predominant intrinsic defects in HPSI 4H-SiC irradiated with 2 MeV electrons on annealing temperature. The intensity scale on the y axis is not the same for the different EPR centers and only shows the annealing behavior of individual defects.

that the ground state of the defect is a triplet and that a singlet excited state is closely above the ground state.

B. Annealing study

In previous annealing studies on as-grown HPSI 6H-SiC the EI4 center was thermally stable up to at least 1200 °C.¹⁰ In irradiated samples, however, the annealing behavior is different. Figure 11 shows the intensities of the prominent EPR spectra in a HPSI 4H-SiC sample, irradiated with 2 MeV electrons to a dose of 2×10^{18} cm⁻², after annealing at different temperatures. Since the optimum conditions for detection of these EPR defects are different (for detection of some defects such as V_{Si} and the divacancy illumination is required), absolute comparison in intensity between spectra is not relevant. Therefore, the EPR intensity of each defect is calibrated to its own maximum and plotted in Fig. 11. Thus, the plot shows only the change in intensity of each defect with annealing temperature. In the whole studied temperature range (up to 1000 °C), the signal of V_{Si} is steadily decreased. The signal of V_C^+ is also decreased with a similar rate up to ~ 800 °C and is then slightly increased at temperatures above ~ 900 °C. At the same time as the signal of V_{Si} decreases the $C_{Si}V_C$ signal increases (Fig. 11). The transformation from V_{Si} to $C_{Si}V_C$ has been previously predicted by theoretical calculations.¹⁹ This process seems to be dominating in the temperature range below 600 °C. In this temperature range, the signals of the EI4 center and the neutral divacancy²⁰ slightly increase. With further increasing annealing temperature the EI4 signal increases drastically and reaches a maximum at annealing temperature ~ 750 °C. Above ~ 800 °C, it rapidly decreases and approaches the intensity level before annealing while an opposite annealing behavior is observed for the divacancy (Fig. 11). This suggests a possible transformation from the EI4 defect to the divacancy. It is interesting to notice that when the divacancy signal rapidly increases the V_C^+ signal does not change or even slightly increases. This indicates that the formation of the divacancy in this temperature range may be dominantly governed by the transformation from the EI4 defect and not by the interaction between V_{Si} and V_C .

The annealing behavior of the EI4 defect in the irradiated HPSI sample is quite different from that in the as-grown HPSI 6H-SiC sample.⁹ In the as-grown HPSI 6H-SiC containing low concentration of the silicon vacancy, no increase in the EI4 signal was detected.⁹ This suggests that the formation of the EI4 defect is related to the migration and annealing out of V_{Si} and not V_{C} . This is also in line with the annealing behavior of V_{C} , which becomes mobile at rather high temperatures (~ 1100 °C).²¹

C. Defect model

The observation of (i) large-splitting hf structure of one ^{29}Si along the c axis, (ii) the hf structures of four to five Si atoms, and (iii) the hf structure of one ^{13}C atom indicates that the EI4 center may involve more than one carbon vacancy (possibly two V_{C}) and one C antisite. The hf structures of three Si atoms (one with large hf splitting and the other two equivalent with the splitting in the range of 9–16 G) and one C atom may come from the $\text{C}_{\text{Si}}V_{\text{C}}$ pair. As shown in the annealing study, the $\text{C}_{\text{Si}}V_{\text{C}}$ defect is formed at rather low temperatures. When its concentration reaches a certain level, the interaction between $\text{C}_{\text{Si}}V_{\text{C}}$ and V_{C} can occur to form the $V_{\text{C}}\text{-C}_{\text{Si}}V_{\text{C}}$ defect. The close pair of $\text{C}_{\text{Si}}V_{\text{C}}$ and V_{C} defects, where C_{Si} is a common neighbor of both V_{C} , were studied by combined tight-binding and *ab initio* calculations by Gerstmann *et al.*²² and they found that the formation energy of the $V_{\text{C}}\text{C}_{\text{Si}}V_{\text{C}}$ complex strongly depends on the Fermi level and can be comparable or slightly higher than that of the $\text{C}_{\text{Si}}V_{\text{C}}$ defect and is smaller than the formation energy of the divacancy in all the range of the Fermi level. In their calculations, only the positive charge state of the complex with the electron spin $S=1/2$ was investigated. Looking for the possible defect model for the EI4 center, we performed *ab initio* calculations of different defects including the far-distance $V_{\text{C}}V_{\text{C}}$ pairs and different $\text{C}_{\text{Si}}V_{\text{C}}$ related defects to find a model that can have a stable spin $S=1$ triplet ground state and can explain the observed hf structures of the EI4 defect.

D. Computational methodology

We performed calculations using a 576-atom 4H-SiC supercell with Γ -point sampling of the Brillouin zone. This large supercell ensures the convergent charge and spin densities even for multivacancy defects and monitoring the degeneracy of the single-particle levels in the fundamental band gap. We applied local-density approximation within density-functional theory (DFT-LDA).^{23,24} The geometry was optimized by VASP code^{25,26} while the hyperfine tensors were determined by CPPAW code²⁷ using projector augmented wave methodology²⁸ and plane-wave cutoff of 30 Ry. The technical convergence for the relative stabilities is about 10 meV and for the calculated hyperfine tensors it is well within 1%. This method was proven to be very successful in identification of defects in 4H-SiC.^{11,20,29,30} We investigated the conversion between the relevant defect multivacancy defect configuration and the divacancy. We applied the nudged elastic band method implemented in the VASP code.³¹ We applied more than ten images in order to obtain the transition state. In our investigations we also considered charged defects. In

that case we applied the charge correction of 0.65 fraction of the Makov-Payne monopole term³² as has been suggested by Lany and Zunger recently.³³ This raises the total energy of single charged defects by about 0.08 eV in our 4H-SiC supercell. For the relevant configuration of the multivacancy defects we calculated the $(+|0)$ and $(0|-)$ occupation levels which provides the stability window of the neutral defect as a function of the position of the Fermi level. While DFT-LDA suffers from the self-interaction error which may influence the accuracy of the calculated occupation levels, we believe that the provided numbers can reveal the stability of the neutral defect in a semiquantitative manner.

E. *Ab initio* results and discussion

Based on the orientation of the **D** tensor it was suggested^{1–3} that the EI4 center is originating from a far distance $V_{\text{C}}V_{\text{C}}$ pair [see Fig. 11(a)]. In that case, one V_{C} is at the hexagonal site while the other is at the cubic site. In our calculations the two isolated vacancies are more stable than the $S=1$ spin state of this multivacancy defect. The calculated spin density is equally localized on three Si dangling bonds in this far distance $V_{\text{C}}V_{\text{C}}$ pair. These findings are contradictory to the measured stability and spin-density distribution of the EI4 EPR center, so this defect can be disregarded as a model for the EI4 center. Our annealing experiment shows that the EI4 center transforms to divacancy, thus the combination of the $\text{C}_{\text{Si}}V_{\text{C}}$ pair and V_{C} defect may be considered as a feasible candidate.

It is worthwhile to summarize here the present knowledge about the diffusion of single vacancies and the creation of multivacancy defects. In high-purity SiC samples the carbon-vacancy EPR signal (V_{C}^+) starts to anneal out at about 1100 °C while the silicon-vacancy-related $\text{T}_{\text{V}2\text{a}}$ EPR signal already anneals out above 850 °C. This suggests that the silicon vacancy diffuses faster than the carbon vacancy at the Fermi-level position characteristic for these high-purity SiC samples. *Ab initio* calculations predicted³⁴ that the negatively charged silicon vacancy has a lower energy barrier than that of the neutral or positively charged carbon vacancy. Particularly, the double negatively charged Si vacancy has about 2.5 eV energy barrier for long-range diffusion and also for conversion from Si vacancy to negatively charged $\text{C}_{\text{Si}}V_{\text{C}}$ pair while the barrier energy for diffusion is 4.1 eV and 3.5 eV for the single positively charged and neutral V_{C} defect, respectively. Putting all these data together we may conclude that V_{C} was in neutral or in its single positive charged state while V_{Si} was in its single or double negatively charged state in the experimental conditions, where V_{Si} is mobile and converted to the $\text{C}_{\text{Si}}V_{\text{C}}$ pair during the diffusion at lower anneal temperatures than for which V_{C} starts to move. In this scenario V_{Si} approaches V_{C} at some temperatures and they can form new multivacancy clusters that are most probably neutral. V_{Si} can approach V_{C} as a $\text{C}_{\text{Si}}V_{\text{C}}$ pair during the diffusion. Several configurations may occur. We studied the neutral complexes of the $\text{C}_{\text{Si}}V_{\text{C}}$ pair and V_{C} by *ab initio* supercell calculations.

One class of configurations is when $\text{C}_{\text{Si}}V_{\text{C}}$ approaches V_{C} by its V_{C} part [see Fig. 12(b)]. In this case one Si atom is a common neighbor of both V_{C} , making the $S=1$ state about

FIG. 12. (Color online) The defect configurations considered by our *ab initio* calculations. The clusters are cut from the 576-atom supercell showing the optimized geometry of the defects. (a) The far distance V_C - V_C pair. Next, different configurations of V_C and $C_{Si}V_C$ pair: (b) V_C approached by V_C part of $C_{Si}V_C$ pair; (c) V_C approached by C_{Si} part of $C_{Si}V_C$ pair where $C_{Si}V_C$ pair is off-axis and the symmetry is C_1 ; (d) V_C approached by C_{Si} part of $C_{Si}V_C$ pair where $C_{Si}V_C$ pair is off-axis and the symmetry is C_{1h} ; (e) V_C approached by C_{Si} part of $C_{Si}V_C$ pair where $C_{Si}V_C$ pair is on-axis and the symmetry is C_{1h} . The small and large balls depict the carbon and silicon atoms, respectively. The dotted lines guide the eyes to find the vacant sites in the complex. The grey lobes are the isosurfaces of the calculated spin density for $S=1$ ground-state systems.

0.4 eV higher in energy than the singlet state. Since the temperature dependence of EI4 EPR center clearly shows the $S=1$ ground state this configuration is not an appropriate candidate. Another class of configurations is when $C_{Si}V_C$ approaches V_C by its C_{Si} part, where C_{Si} and the approached V_C are not immediate neighbors. Within this class the complexes can form either C_1 [Fig. 12(c)] or C_{1h} [Fig. 12(d)] symmetry. According to the calculations the singlet and triplet states are equally stable (within 0.01 eV) for the C_1 symmetry configuration while the $S=1$ state is significantly more stable than the $S=0$ state by about 0.04 eV for the C_{1h} symmetry configuration. The EI4 spectrum exhibits C_{1h} symmetry, so the C_{1h} symmetry configuration depicted in Fig. 12(d) may explain its features. The gray lobes in this figure show the spin-density distribution localized strongly on a single Si dangling bond and less on C_{Si} in the $C_{Si}V_C$ part of the com-

plex. This configuration seems to be a promising candidate for the EI4 EPR center since the largest hyperfine interaction was measured on single Si and C atoms. In this particular configuration the $C_{Si}V_C$ part of the complex is in off-axis configuration. It is possible to approach V_C by an on-axis $C_{Si}V_C$ pair with exhibiting C_{1h} symmetry [Fig. 12(e)] where the resulting complex is similar to the previous one. Indeed, the calculations suggest that this complex also has a $S=1$ ground state (which is stable over the singlet state by about 0.4 eV). The spin density is mainly localized on a single C_{Si} but also partly on *two* Si dangling bonds in the approached V_C part of the complex [see the gray lobes in Fig. 12(e)]. Thus, this complex may be detected in SiC but it is not responsible for the EI4 EPR center. Finally, we note that it cannot be disregarded that the C_1 symmetry configuration depicted in Fig. 12(c), which has a very similar spin-density distribution to that of the C_{1h} symmetry configuration depicted in Fig. 12(d), can be detected by EPR without any excitation. In summary, the configuration depicted in Fig. 12(d) shows the features (symmetry and spin-density distribution) that may explain the experimental findings about the EI4 EPR center, thus we investigated this configuration of the V_C - $C_{Si}V_C$ complex in detail.

Despite that the V_C - $C_{Si}V_C$ complex has a relatively low symmetry, the combination of the single-particle orbitals coming from the approached V_C and from $C_{Si}V_C$ can form near degenerate states because both isolated defects possess defect levels at very similar energies in the fundamental band gap. That is the source of the stabilization of the high spin ground state. The detailed spin-density distribution of the V_C - $C_{Si}V_C$ complex is shown in Fig. 13. The largest localization can be found on a single Si dangling bond which points near parallel to the c axis of the crystal. The spin density is also well localized on the off-axis C_{Si} dangling bond pointing to the vacant site. The direction of the $\mathbf{g}$ tensor and the $\mathbf{D}$ tensor is largely influenced by these dangling bonds making their largest component off-axis. Those atoms that cause larger hyperfine splitting than 10 G, in addition to the single Si and the C_{Si} mentioned above, are denoted by numbers 2–4. Experimentally, we found the sets of 2-2-1 Si atoms in this region which is in good agreement with the observed data (see Table I). The dark (blue colored) atoms exhibit hyperfine splitting close to 5 G and could be the main cause of the innermost detectable hf structure, shown in Fig. 6. Overall, the calculated hyperfine tensors are in good agreement with the resolved hyperfine data and the calculations consistently yield the unresolved hyperfine constants.

The EI4 EPR center may be identified by the particular C_{1h} configuration of the V_C - $C_{Si}V_C$ complex shown in Fig. 13. We found that the $(+|0)$ and $(0|-)$ occupation levels are at about 1.6 eV and 2.0 eV above the valence band, respectively, which shows that this defect is indeed neutral at the position of the Fermi level where the isolated V_C is neutral and the isolated V_{Si} is negatively charged.³⁴ This is in line with the scenario we gave above about the possible formation routes of the EI4 center. The calculated binding energy of this complex with respect to the isolated carbon and silicon vacancies is over 3 eV favoring the complex formation, which explains the stability of this complex. According to the experimental finding, this complex should transform to

FIG. 13. (Color online) The suggested defect model for the EI4 center in the 4H-SiC crystal structure. The cluster is cut from the 576-atom supercell showing the optimized geometry of the defect. The carbon (silicon) atoms are depicted as the smallest (largest) balls. The dotted lines guide the eyes to find the vacant sites in the complex. The grey lobes are the isosurfaces of the calculated spin density. The atoms most important for the detected hf structure are indicated by 1–4 which should read as Si_{1–4} atoms. The C_{Si} atom binds to three other C atoms in the middle of the figure, having the Si₃ and Si₄ atoms as its second neighbors. The Si_{2–4} atoms have hyperfine splitting larger than 10 G while the other dark (blue) balls show those Si and C atoms that have hyperfine splitting of about 5 G.

divacancy after higher temperature anneal, thus this issue must be studied for unambiguous identification of this defect. We find a transition route where the migrating C_{Si} atom can jump from its original position in the V_C-C_{Si}V_C complex to the vacant site of the approached V_C, resulting in the divacancy complex. The transition state and other important configurations during this conversion are shown in Fig. 14. The migrating C_{Si} first temporarily binds to the Si atom possessing the largest hyperfine interaction in the V_C-C_{Si}V_C complex beside the two neighbor C atoms and two originally low-coordinated Si atoms of the approached V_C part of the complex, releasing one neighbor C atom [Fig. 14(b)]. The bonds between Si atoms and the migrating C_{Si} keep the total energy of the system relatively low. Then the migrating C_{Si} wanders to the side of the approached V_C by releasing the Si atom in the C_{Si}V_C part of the complex [Fig. 14(c)] and during this action one finds the transition state shown in Fig. 14(d). The migrating C atom leaves a V_{Si} behind, near to the V_C which was originally part of the C_{Si}V_C pair. The migrating C atom goes further to the nearest vacant site without any barrier energy [Fig. 14(e)] and finally forms the divacancy [Fig. 14(f)]. The calculated energy barrier of this process is about 3.1 eV which is larger than the migration barrier energy of V_{Si} but smaller than the migration barrier energy of V_C at the

FIG. 14. (Color online) The suggested model of the transition from EI4 center to the off-axis divacancy. The clusters are cut from the 576-atom supercell showing the calculated geometry of the defects using the nudged elastic band method. The small and big balls depict the C and Si atoms, respectively. (a) Starting configuration: optimized V_C-C_{Si}V_C defect, (b) migrating C_{Si} in the C_{Si}V_C part of the complex, (c) migrating C_{Si} toward the approached V_C part of the defect, (d) transition state, (e) migrating C atom toward the nearest vacant site, (f) final configuration: optimized divacancy. The dotted lines guide the eyes to find the vacant sites in the complex. The arrow indicates the movement of the migrating atom.

relevant charge states. The reverse process has more than 4.7 eV energy barrier, which is a higher energy than that for migration of V_C, thus the reverse process is not likely to occur. These findings are very consistent with the experimental data: at lower temperature anneal (<750 °C) V_C is stable and the migrating V_{Si} can form the V_C-C_{Si}V_C complex with V_C while at higher temperature anneal the complex can transform directly to a divacancy which remains stable. This result implies that the immediate V_CC_{Si}V_C complex, studied by Gerstmann *et al.*,²² may not form since the V_C-C_{Si}V_C complex can transform directly to a divacancy.

IV. SUMMARY

Using electron-irradiated HPSI 4H- and 6H-SiC samples, we were able to observe a strong signal of the EI4 EPR center, including an additional large-splitting hf structure due to the interaction with one Si, a smaller-splitting hf structure due to the interaction with one C atom, and other hf structures related to the interaction with a number of Si atoms. Based on the observed hf structures, defect symmetry and annealing behavior, together with results from supercell calculations, we suggest that the defect corresponding to the EI4 EPR center in 4H- and 6H-SiC is a neutrally charged complex consisting of a carbon antisite-vacancy pair in off-axis configuration and another carbon vacancy at the third-nearest-neighbor site of the antisite, (V_C-C_{Si}V_C)⁰, with both vacancies and the antisite in the (11 $\bar{2}$ 0) or equivalent plane.

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