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## Identification of the Carbon Antisite-Vacancy Pair in 4H-SiC

T. Umeda,<sup>1</sup> N. T. Son,<sup>2</sup> J. Isoya,<sup>1</sup> E. Janzén,<sup>2</sup> T. Ohshima,<sup>3</sup> N. Morishita,<sup>3</sup> H. Itoh,<sup>3</sup> A. Gali,<sup>4</sup> and M. Bockstedte<sup>5,6</sup>

<sup>1</sup>University of Tsukuba, Tsukuba 305-8550, Japan

<sup>2</sup>Linköping University, S-581 83 Linköping, Sweden

<sup>3</sup>Japan Atomic Energy Agency, Takasaki 370-1292, Japan

<sup>4</sup>Budapest University of Technology and Economics, Budafoki út 8., H-1111, Budapest, Hungary

<sup>5</sup>Universität Erlangen-Nürnberg, Staudtstrasse 7/B2 D-91058 Erlangen, Germany

<sup>6</sup>Universidad del País Vasco, E-20018 San Sebastián, Spain

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The metastability of vacancies was theoretically predicted for several compound semiconductors alongside their transformation into the antisite-vacancy pair counterpart; however, no experiment to date has unambiguously confirmed the existence of antisite-vacancy pairs. Using electron paramagnetic resonance and first principles calculations we identify the *SI5* center as the carbon antisite-vacancy pair in the negative charge state ( $C_{Si}V_C^-$ ) in 4H-SiC. We suggest that this defect is a strong carrier-compensating center in *n*-type or high-purity semi-insulating SiC.

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Vacancies are one of the most simple and fundamental point defects in crystals. However, in a compound material, the vacancies are not simple defects, as is generally expected. For instance, in an *AB* compound material, during the diffusion of the *A* vacancy one of its nearest neighbors, a *B* atom, can move into the vacant lattice site forming a pair of a *B* antisite and a *B* vacancy. The antisite-vacancy (AV) pairs are the counterpart of the isolated vacancies in compound materials, and can be energetically stable or metastable defects with respect to the vacancies. AV complexes in III-V semiconductors have already been studied. Theoretical studies [1–3] predicted that the arsenic AV complex is more stable than the Ga vacancy in *p*-type GaAs. A recent paper [4], however, has shown that none of the detected electron paramagnetic resonance (EPR) centers can be associated with the AV complex in GaAs. Also, theoretical calculations [5] have indicated that the nitrogen AV complex can appear in *p*-type GaN but no experimental evidence has supported this assertion so far. In these materials, the stability order of the cation vacancies and their anion AV counterparts depends on the Fermi level ( $E_F$ ): in *p*-type material, the anion AV complex is more stable than the cation vacancy, whereas in *n*-type material the cation vacancy is more stable. For a certain  $E_F$  position both configurations are equally stable. Mutual transformations of AV complex and the cation vacancy can then be induced, e.g., when irradiation induced compensation centers anneal out and change the  $E_F$  position. In this sense, the cation vacancy and the anion AV counterparts form a bistable defect pair. In silicon carbide (SiC), carbon is more electronegative than silicon, i.e., the Si vacancy is the cation vacancy. As for the III-V semiconductors, a similar bistability was theoretically predicted between the carbon AV complex ( $C_{Si}V_C$ ) and the isolated Si vacancy depending on  $E_F$  [6,7]: in *n*-type SiC, the latter vacancy is more stable, whereas in *p*-type, semi-insulating (SI) materials, the former AV pair is more stable. The

*P6/P7* EPR centers were associated with the excited triplet states of  $C_{Si}V_C^{2+}$  based on experiments and calculations for SiC [8,9]. Recent EPR measurements have shown, however, that the *P6/P7* centers originate from the triplet ground states of the neutral divacancy [10]. To the best of our knowledge, no experimental evidence unambiguously shows the existence of an AV complex as a fundamental defect in a compound semiconductor.

Group III-V semiconductors are widely used in optoelectronic devices. SiC is a promising wide-gap semiconductor for high-power, high-frequency, and high-temperature electronics. The SiC research is rapidly expanding thanks to the availability of high-quality SiC single crystals [11]. Recently, high-purity semi-insulating (HPSI) SiC grown by physical vapor transport [12] or high-temperature chemical vapor deposition [13] has become available. As for semi-insulating GaAs [14] or *p*-type GaN [15], deep electronic levels of native defects are believed to be responsible for the SI properties of HPSI SiC materials. Yet, in contrast to the situation in GaAs or GaN, where either the *EL2* center (arsenic antisite) or vacancy-dopant complexes facilitate the SI properties [1,14], the responsible native defects in HPSI SiC have yet to be identified [16–18]. Hence, it is an important task to identify the defects that could account for the SI properties. The *SI5* EPR center was first detected in some *n*-type and HPSI 4H-SiC substrates in a series of other EPR centers, labeled *SI1-SI9* [16]. In this Letter, we identify the *SI5* EPR center as the negatively charged carbon AV complex ( $C_{Si}V_C^-$ ) in 4H-SiC by EPR and first principles theory. We also show that this complex is an important compensating center in HPSI SiC samples with acceptor levels at around 1.1 eV below the conduction band edge.

The *SI5* EPR center with  $C_{3v}$  symmetry was observed in as-grown 4H-SiC substrates at 77 K [16]. Its concentration in these HPSI samples was insufficient to resolve all the hyperfine (HF) lines in detail. Therefore, we enhanced the

concentration of  $SI5$  centers in  $n$ -type SiC samples by electron irradiation of 3 MeV [19]. Our starting substrates were commercial  $n$ -type 4H-SiC (N concentration  $\sim 10^{17} \text{ cm}^{-3}$ ). EPR spectra were measured by Bruker X-band EPR or pulsed electron nuclear double resonance (ENDOR) spectrometers, with or without illumination by a 100 W halogen lamp with a filter (transparent above 0.6 eV) or by a 150 W xenon lamp with a monochromator. The uncertainty of the photon energy induced by the wide-opened slits of the monochromator is about 0.06 eV [20].

We first report a characteristic temperature dependency of the  $SI5$  EPR signal: at low temperatures [LT spectrum at 30 K, Fig. 1(a)], the signal has  $C_{1h}$  (low) symmetry while at high temperatures [HT spectrum at 100 K, Fig. 1(b)], it shows  $C_{3v}$  (higher) symmetry. The transformation between the LT and HT spectra occurs at  $\sim 50$  K. This behavior of the  $SI5$  center was also found in the as-grown HPSI samples in Refs. [10,16]. Similar transitions were also found for  $HEI1$  ( $V_C^-$ ) [20] and  $EI5$  ( $V_C^+$ ) [21] EPR centers. By analogy, we conclude that the HT ( $C_{3v}$ ) spectrum of the  $SI5$  center corresponds to a thermal average of the three symmetrically equivalent  $C_{1h}$  configurations. In the LT spectrum [Fig. 1(a)], one strong HF splitting (HF1) and four weak HF splittings (HF2-5) due to nuclear spins  $I = 1/2$  were observed. To identify the sources of HF2-5, we performed pulsed-ENDOR measurements for the magnetic field  $\mathbf{B} \parallel \mathbf{c}$  ([0001]) with the Mims sequence [21]. The ENDOR signals were observed at 37.5 MHz for  $^{13}\text{C}$  ( $I = 1/2$ , natural abundance 1.1%), 26.1 MHz for  $^{29}\text{Si}$  ( $I = 1/2$ , 4.7%), 16.1 MHz for  $^{13}\text{C}$ , and 11.9 MHz for  $^{29}\text{Si}$ , which agreed with the observed HF splittings of HF2-5 (37.2, 26.3, 15.4, and 10.4 MHz, respectively). For HF1, its intensity ratio to the central line (0.09/1) suggests that HF1 originates from two  $^{29}\text{Si}$  nuclei ( $^{29}\text{Si} \times 2$ ). The wave function of the LT  $SI5$  center is strongly localized on these two Si atoms. In the HT configuration [Fig. 1(b)], four HF structures (HF1'-4') with  $I = 1/2$  were detected. Only the high-intensity spectrum of Fig. 1 enabled us to detect the HF lines of HF1' and HF3'. Led by the intensity ratios of HF1' and HF3' to the central line (0.050:1 and 0.014:1, respectively), we assigned HF1' and HF3' to the

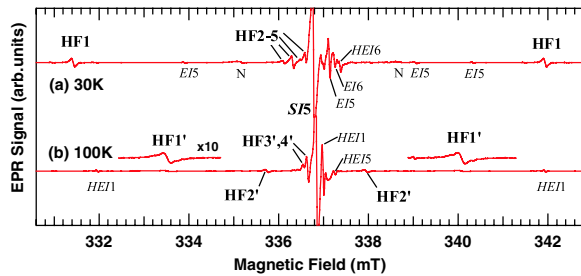


FIG. 1 (color online).  $SI5$  EPR spectra in irradiated 4H-SiC (dose:  $2 \times 10^{18} \text{ e/cm}^2$ ) measured at (a) 30 K and (b) 100 K for  $\mathbf{B} \parallel \mathbf{c}$ , 9.452 GHz, under illumination by a 100 W halogen lamp. Other weaker EPR signals of  $EI5/6$ ,  $HEI1$ ,  $HEI5/6$ , and N donors are also indicated.

interaction with one  $^{29}\text{Si}$  and one  $^{13}\text{C}$  nucleus, respectively. We also correct the previous assignment of HF2' ( $^{13}\text{C} \times 3$ ) [16]:  $^{13}\text{C} \times 1$  or  $^{13}\text{C} \times 2$  are more likely, as its intensity ratio to the central line is estimated to be 0.018:1. The model of the negatively charged divacancy for this center proposed in Refs. [9,16] is obsolete as it only accounts for the HF2' and HF4' lines detected in the HPSI SiC samples and not for the new additional HF1' and HF3' lines. The divacancy model further predicted that the largest HF splitting would originate from one  $^{13}\text{C}$  atom at low temperatures [9] and not from two  $^{29}\text{Si}$  atoms (HF1) now detected. Hence, we need a new model for the  $SI5$  center. Table I summarizes the spin-Hamiltonian parameters for both  $SI5$ -LT and  $SI5$ -HT configurations, which were determined by the angular-pattern simulations shown in Figs. 2(a) and 2(b). The HF parameters of the  $SI5$ -LT configuration and temperature dependence of the  $SI5$  center are very similar to those of the EPR center  $HEI1$  ( $V_C^-$ ) [20]. Our working model thus became the axial configuration of the negatively charged carbon AV complex ( $C_{Si}V_C^-$ ). The theoretical analysis below demonstrates this.

We carried out first principles calculations on the  $C_{Si}V_C^-$  defect and its HF interaction based on the density functional theory and the local spin density approximations (LSDAs). The complexes were represented by large supercells including up to 288 atoms. Firstly the atomic structure was obtained using the pseudopotential method as outlined

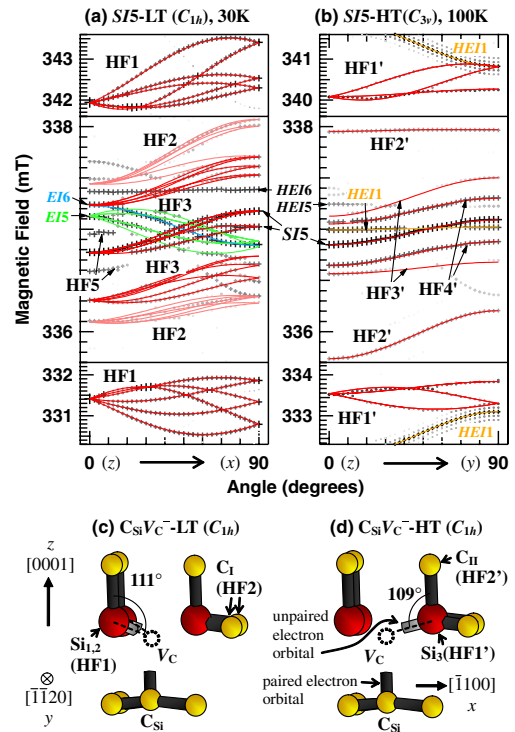


FIG. 2 (color online). Angular maps of the  $SI5$  center in the (a) LT and (b) HT configurations, measured for  $\mathbf{B}$  rotating in (a)  $(11\bar{2}0)$  and (b)  $(\bar{1}100)$  planes. The solid lines were calculated using the parameters in Table I and Refs. [20] ( $HEI1$ ) and [21] ( $EI5/6$ ). Respective atomic models are shown in (c) and (d).

TABLE I. Spin-Hamiltonian parameters of the *SI5* center and theoretical HF tensors for  $C_{Si}V_C^-$  in the LT and HT configurations. The spin-Hamiltonian is defined in Ref. [20], and  $\mathbf{g}$  is a  $g$  tensor and  $\mathbf{A}(i)$  is a HF tensor for an atom  $i$ . Principal values of  $\mathbf{A}$  are given in mT (1 mT = 28.02 MHz). Calculated values refer to the cubic and (in parentheses) hexagonal complex. The main ( $\parallel$ ) principal axes are expressed in the conventional polar angles of  $\theta$  and  $\phi$  of the coordinate system in Fig. 2. Labels and notation are given in the text and in Fig. 2.

	$X (\perp)$	$Y (\perp)$	$Z (\parallel)$	$\theta; \phi (^\circ)$
<b>EPR</b>				
<i>SI5</i> -LT ( $C_{1h}$ ) 30 K				
$\mathbf{g}$	2.003 72	2.002 59	2.005 34	10; 180
HF1, $\mathbf{A}(^{29}\text{Si} \times 2)$	10.16	10.04	12.99	111; $\pm 51$
HF2, $\mathbf{A}(^{13}\text{C} \times 2)$	1.3	1.3	1.8	
HF3, $\mathbf{A}(^{29}\text{Si} \times 2)$	0.9	0.9	1.1	
<i>SI5</i> -HT ( $C_{3v}$ ) 100 K				
$\mathbf{g}$	2.003 39	2.003 39	2.004 84	0
HF1', $\mathbf{A}(^{29}\text{Si} \times 1)$	6.38	6.38	8.02	109
HF2', $\mathbf{A}(^{13}\text{C} \times 1)^a$	1.77	1.77	2.22	0
<b>Theory</b>				
$C_{Si}V_C^-$ -LT ( $C_{1h}$ )				
$\mathbf{A}(\text{Si}_{1,2})$	10.8 (11.2)	10.9 (11.3)	13.8 (14.2)	108; $\pm 52$ (108)
$\mathbf{A}(C_{Si})$	0.1 (0.2)	0.1 (0.2)	0.1 (0.2)	
$\mathbf{A}(C_1 \times 2)$	1.3 (1.4)	1.3 (1.4)	1.7 (1.7)	
$C_{Si}V_C^-$ -HT ( $C_{1h}$ )				
$\mathbf{A}(\text{Si}_{1-3})$ avg.	7.2 (7.5)	7.6 (7.9)	8.6 (8.9)	
$\mathbf{A}(C_{II})$	0.9 (1.3)	0.9 (1.3)	1.3 (1.7)	

<sup>a</sup>We used  $^{13}\text{C} \times 1$  as the origin of HF2', as the calculation predicted this case rather than  $^{13}\text{C} \times 2$ .

in Ref. [7] and then the HF tensors were calculated with the all-electron projector augmentation wave method [20,21]. Calculations were performed with and without a scissors-operator (cf. Ref. [7] and references therein) to assess the effect of the LSDA band gap failure on the calculated HF tensors. The values obtained with and without the correction agree to within their accuracy. In 4*H*-SiC, there are two inequivalent substitutional sites, called cubic (*k*) and hexagonal (*h*) lattice sites. In the cubic (hexagonal) AV complex aligned with the *c* axis (axial complexes), the vacancy and antisite occupy neighboring *k*(*h*) sites. The calculated HF tensors of these two AV complexes are summarized in Table I. The negatively charged axial  $C_{Si}V_C^-$  complexes undergo a Jahn-Teller distortion, due to the occupation of the degenerate *e* level by one electron within the band gap. As shown in Fig. 2, two distinct configurations were obtained with the major part of the spin density being located either at  $\text{Si}_{1,2}$  [LT configuration, Fig. 2(c)] or at  $\text{Si}_3$  [HT configuration, Fig. 2(d)]. Both configurations exhibit  $C_{1h}$  symmetry consistent with the experiment. The LT configuration was found to be energetically favored (by 0.02 eV) over the HT configuration, verifying the low-temperature HF signature. Moreover, the

calculated HF tensors of  $\text{Si}_{1,2}$  for the *k* and *h* sites are in good agreement with the experimental ones (HF1 in Table I) regarding both the principal values and axes. The next largest HF interactions were found on the first C neighbors of  $\text{Si}_3$  [ $C_1$  in Fig. 2(c)], which also agree with the experimental values for HF2 (Table I). Additional measurable HF interactions were found on the first neighbor C and second neighbor Si atoms of  $\text{Si}_{1,2}$  atoms, which might account for the not fully resolved lines HF3-5 of the EPR spectrum. According to our calculations, the other HF interactions are weaker, in particular, for  $C_{Si}$  (see Table I). Its dangling bond mainly contributes to the doubly occupied localized *a* level below the paramagnetic *e* level. For the HT configuration, the calculations predicted that an unpaired electron is localized on one Si atom ( $\text{Si}_3$ ), similar to the HT spectrum. Again, the calculated HF tensor of  $C_{Si}$  is negligible. The HF2' interaction observed for *SI5*-HT most likely arises from the  $C_{II}$  ligand of  $\text{Si}_3$  [see Fig. 2(d)]. The  $C_{3v}$  symmetry should originate from a motional average over the three different orientations of the HT configuration. We simulated this average by taking the spatial average of the main HF tensors of symmetrically equivalent atoms ( $\text{Si}_{1-3}$ ). The calculated principal values of the average Si tensor are shown in Table I as " $\mathbf{A}(\text{Si}_{1-3})$ avg." Within the limits of this approximation, these values reproduce well the experimental observation at 100 K. For both the LT and HT configurations, the difference between the calculated HF tensors of the cubic and hexagonal complexes is below the expected accuracy. Qualitatively, the two complexes are distinguishable by the HF tensors of the third and fourth neighbor shells. These could not be resolved experimentally, and it is likely that both complexes contributed to the *SI5* spectrum. The above experimental and theoretical arguments consistently explain both the LT and HT spectra, and we therefore identify the *SI5* center as the axial  $C_{Si}V_C^-$  complex.

In the present study we observe only the axial complex, but the basal complex should also exist, like for  $V_{Si}V_C$  (*P6/P7* centers) [8,10]. This phenomenon occurs for the EPR centers which are sensitive to light illumination. For example, it was reported that in some irradiated *n*-type SiC samples, the *P6* (*c*-axial complex) signal was present but the *P7* (basal complex) signal was completely absent [22]. As for HPSI SiC [16], the *SI5* signal in the irradiated samples was strongly enhanced by illumination. Our photo-EPR measurements on an irradiated sample (dose:  $4 \times 10^{18} e/cm^2$ ) suggested that its  $E_F$  is located at about 1.1 eV below the conduction band edge ( $E_C$ ) [20]. In the same sample, we observed a significant photo enhancement of the *SI5* signal just above  $1.1 \pm 0.06$  eV. Thus, the majority of the  $C_{Si}V_C$  complexes exist in a nonparamagnetic doubly negatively charged state ( $C_{Si}V_C^{2-}$ ). This is consistent with the previous photo-EPR data on HPSI and *n*-type SiC [16] that indicated a dominance of the *SI5* level (singly negatively charged level) in the range from  $E_C - 1.2$  eV to  $E_C - 1.5$  eV. First principles calcu-

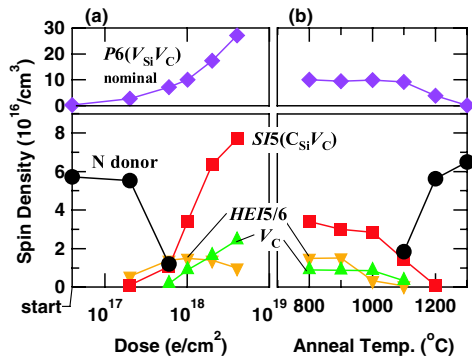


FIG. 3 (color online). Spin densities of defects and N donors in (a) electron radiation experiment (using six samples with different doses) and in (b) isochronal annealing experiment (using a single sample). At 70 K, N-donor and HEI5/6 signals were measured in the dark, whereas SI5, P6, and  $V_{\text{C}}$  signals were measured under illumination by a 100 W halogen lamp. Data for P6 are nominal, as its triplet spin system could have a nonequilibrium population by the photo excitation.

lations also support this view: the ionization levels  $(0|-)$  and  $(-|2-)$  as calculated in the largest cell (288 atoms) amount to  $E_{\text{C}} - 1.0$  eV and  $E_{\text{C}} - 0.9$  eV, respectively. Note that the precision of these values is limited due to the finite size of the supercells and errors of the exchange-correlation functional. Yet, energy increment between the  $-1$  and  $-2$  charged states is relevant, and both the levels can compensate the residual carriers. Accordingly,  $E_{\text{F}}$  is pinned at  $\sim E_{\text{C}} - 1.1$  eV or lower due to  $C_{\text{Si}}V_{\text{C}}$  in SiC.

To examine the role of the SI5 center in the carrier compensation, we carried out step-by-step irradiation and subsequent isochronal annealing experiments of  $n$ -type SiC samples as shown in Fig. 3. In the nonirradiated substrate, the EPR spectrum was dominated by the signal of the neutral N donors at the  $k$  site. This donor signal rapidly decreased with increasing electron dose, whereas the SI5 center, the P6 center, the unidentified HEI5/6 centers, and the C-vacancy centers (HEI1 and EI5) were formed [Fig. 3(a)]. However, the spin densities of  $V_{\text{C}}$  and HEI5/6 were lower than the total density of N donors. Figure 3(b) plots the spin density for an isochronal annealed (30 min in Ar ambient)  $n$ -type sample after the  $1 \times 10^{18}$ - $e/\text{cm}^2$  irradiation. The SI5 signal started to decrease after annealing at  $1100^{\circ}\text{C}$  alongside with the recovery of the N donor signal. Both observations suggest a correlation between the SI5 center and the compensation of the N donors. In contrast to our irradiated samples, HPSI substrates exhibited the SI5 signal even after annealing at  $1600^{\circ}\text{C}$  [10,16]. Its higher thermal stability in the HPSI samples could be due to a lower  $E_{\text{F}}$  position and the different abundances of other defects interfering with the annealing of SI5. Theoretical studies [7] predicted that the available annealing paths and their activation energies strongly depend on  $E_{\text{F}}$ , which should result in a lower thermal stability of SI5 at a higher  $E_{\text{F}}$  in the gap. Recent positron annihilation studies suggested the presence of

vacancy aggregates in HPSI SiC samples [23]. According to theory, such aggregates can dissociate and be a source of isolated vacancies and AV complex at high annealing temperatures [7,9,24]. Thus, vacancy defects as well as the SI5 center (carbon AV complexes) play an important role in the SI property of SiC.

In conclusion, our EPR analysis and first principles calculations identify the SI5 center in 4H-SiC with the fundamental AV complex in the negative charge state ( $C_{\text{Si}}V_{\text{C}}^{-}$ ). In  $n$ -type SiC this defect is singly or doubly negatively charged due to the compensation by residual carriers and plays an important role in facilitating the SI property in some HPSI SiC substrates.

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