Electron paramagnetic resonance study of carbon antisite-vacancy pair in *p*-type 4*H*-SiC

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Abstract. Carbon antisite-vacancy pair ($C_{Si}V_C$) is a fundamental defect in SiC, and is theoretically predicted to be very stable in *p*-type materials; however, this pair was found only in the from of a negatively charged state (i.e., the *SI*5 center = $C_{Si}V_C^-$) in *n*-type and semi-insulating 4*H*-SiC, and yet, its presence has not been shown in *p*-type SiC. In this report, we present the first EPR observation on positively charged $C_{Si}V_C$ pairs in *p*-type 4*H*-SiC. By carefully examining *p*-type samples after electron irradiation, we found a pair of new defects with C_{3v} and C_{1h} symmetries. They correspond to "*c*-axial" pairs (C_{3v}) and "basal" pairs (C_{1h}) of $C_{Si}V_C^+$, respectively. The positively charged pairs are characterized by a strong ^{13}C hyperfine interaction due to a dangling bond on a carbon antisite (C_{Si}), which is successfully resolved for the *c*-axial pairs.

Introduction

Antisite-vacancy (AV) pairs are one of the fundamental defects in compound semiconductors, because they are metastable/stable counterparts of monovacancies. In SiC, silicon vacancy [Fig. 1(a)] can be converted into carbon AV pairs [Fig. 1(b)]. Recently, their negatively charged state ($C_{Si}V_C^-$) was assigned to the origin of the *SI*5 center in *n*-type and semi-insulating (SI) 4*H*-SiC [1]. In these substrates, the carbon AV pair plays an important role on the SI property of SiC [1]. This pair should be also important in *p*-type substrates, because theoretical studies [2,3] predicted that the pair is more stable in *p*-type SiC (i.e., in the form of a positively charged state) rather than in *n*-type SiC. However,

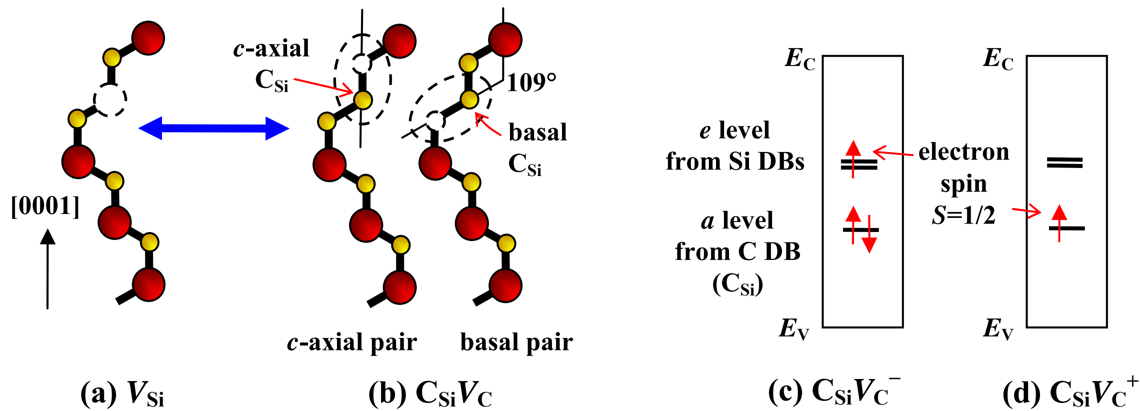

Fig. 1. Basic features of carbon AV pairs ($C_{Si}V_C$) in 4*H*-SiC. Atomic models of (a) silicon vacancy (V_{Si}) and (b) its counterpart, $C_{Si}V_C$ pair. They can be transformed into each other. As shown in (b), the carbon AV pair exhibits two different orientations and has a set of three silicon dangling bonds (DBs) and one carbon DB. These DBs generate two gap levels as shown for (c) negative charge state or (d) positive charge state (in the valence band, another *a* level is generated and is doubly occupied) [1,4]. Depedening on the charge state, an electron spin has a quite different nature.

contrary to the theoretical predictions, stable positively charged AV pairs have not been found yet. In this report, we present the first experimental data on positively charged carbon AV pairs ($C_{Si}V_C^+$) in *p*-type 4*H*-SiC using electron paramagnetic resonance (EPR). The pair possesses four dangling bonds (DBs) of either Si or C [Fig. 1(b)], which generate two electronic levels (*a* and *e*) in the gap [1,4]. In its negative charge state [Fig. 1(c)], an electron spin (S = 1/2) occupies the doubly-degenerate *e* level mainly due to Si DBs, resulting in strong hyperfine (HF) interactions due to ^{29}Si isotopes (nuclear spin I = 1/2, natural abundance = 4.7%) [1]. On the contrary, in its positive charge state, an electron spin should be strongly localized on a C_{Si} atom, generating a strong HF interaction due to a ^{13}C isotope (I = 1/2, natural abundance = 1.1%). We here show this ^{13}C HF signature for *c*-axial carbon AV pairs [c.f., the left hand side one of Fig. 1(b)].

Experiment

We prepared a series of irradiated *p*-type 4*H*-SiC samples. Boron doped *p*-type 4*H*-SiC substrates (room temperature carrier concentration = 10^{15} /cm^3) were irradiated by 3-MeV electrons at around 800 ºC with a dose of 2×10^{18} e/cm^2 or higher. With the same irradition to *n*-type 4*H*-SiC samples [1], carbon AV pairs (the *SI*5 center) were dominantly formed, so that we expected a similar situation in the *p*-type samples. EPR spectra were measured by a Bruker E500 X-band spectrometer. Most of measurements were done at room temperatures where EPR intensities were considerably reduced as compared to those at low temperatures. To gain sufficient signal intensities, we used 1.5-mm thick samples. All measuremtns shown here were carried out in the dark (in the thermal equilibrium).

Results and discussion

Figure 2(a) shows a typical EPR spectrum of our *p*-type samples measured at 150 K, where the well-known *EI*5/*EI*6 EPR signals (from positively charged carbon vacancies, V_C^+) are dominant, as reported previously in Ref. [5]. Examining the same samples carefully at room temperature with a very low microwave power (0.1 μW), three new EPR signals were detected as shown in Fig. 2(b). We labeled them "*HEI*9" (there are two minor types, "*a*" and "*b*", as is seen in the figure, and we call a set of them "*HEI*9"), "*HEI*10", and "*HEI*11". These new signals were easily saturated even by a low microwave power, and disappeared under a normal power of 1 mW [see dashed line in Fig. 2(b), where only the *EI*5/6 signal is observed]. Due to this saturation effect, it was difficult to detect them at low temperatures (< 200 K), because longer spin relaxation times at lower temperatures make the signal saturation being much easier. With this reason, they might have not been found so far. But, they were formed as easily as for V_C^+ in *p*-type irradiated SiC: e.g., spin densities were 3×10^{17} /cm^3 for V_C^+ (*EI*5/6) and 3×10^{17} /cm^3 for the new centers (*HEI*9/10/11) after 2×10^{18} e/cm^2 irradiation. Thus, we speculate that they are also major defects in many *p*-type 4*H*-SiC samples and probably in

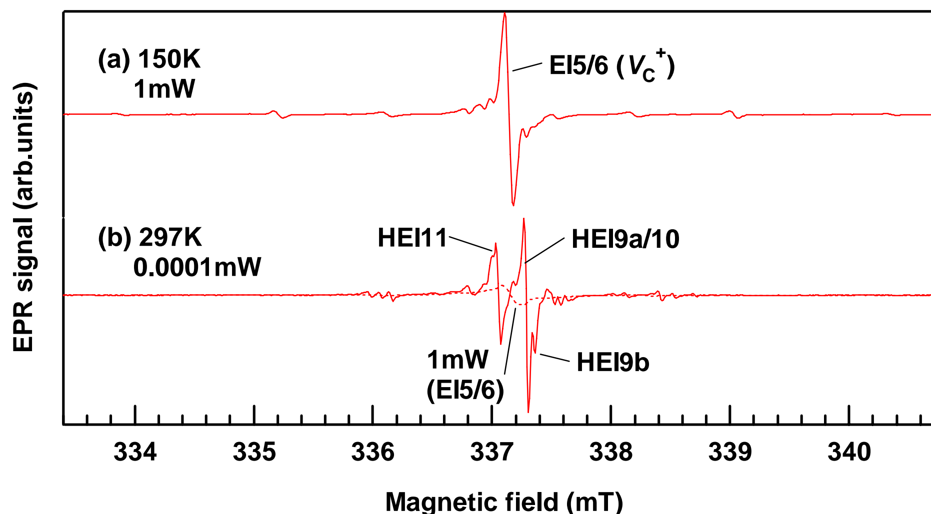

Fig. 2. EPR spectra of irradiated *p*-type 4*H*-SiC measured at 150 and 297 K using microwave powers of 1 mW or 0.1 μW. Vertical scales are different for (a) and (b).

semi-insulating substrates. The coexistence of V_C^+ and the new centers in the dark indicates that their electronic levels are located at similar positions in the gap. We believe that they are related to positively charged carbon AV pairs ($C_{Si}V_C^+$), which will be supported by the following EPR analyses.

Angular dependences of the central lines of *HEI*9/10/11 are shown in Figs. 3(a) to (c), which reveal C_{3v} symmetry for *HEI*9 and C_{1h} symmetry for *HEI*10 and *HEI*11. Their g tensors were determined as summarized in Table I. They show simialr principal g values: $g_{\|}$ (g_{ZZ}) ≈ 2.002 and $g_{\perp}$ (g_{XX} and g_{YY}) ≈ 2.003-2.004. The main (||) principal g axis is parallel to the *c* axis for *HEI*9, while for *HEI*11 the axis is aligned nearly with a basal bond (θ = 109°). For *HEI*10, we found an intermediate situation between the former and the latter cases. From these results we speculate that a pair of the C_{3v} center (*HEI*9*a*/*b*) and the C_{1h} center (*HEI*10 and/or *HEI*11) corresponds to a common "pair"-type defect. For instance, it is well known that divacancies ($V_{Si}V_C$) exhibit a pair of *P*6(C_{3v}) and *P*7(C_{1h}) EPR spectra, which originate from *c*-axial pair (C_{3v}) and basal pair (C_{1h}) of $V_{Si}V_C$, respectively [6]. By analogy, we assign *HEI*9(C_{3v}) to *c*-axial $C_{Si}V_C^+$ pairs. This assignment can be confirmed by their HF interactions. It is also reasonable to consider that their minor types (*a* and *b*) correspond to two inequivalent configurations (*kk* and *hh* [6]) in 4*H*-SiC.

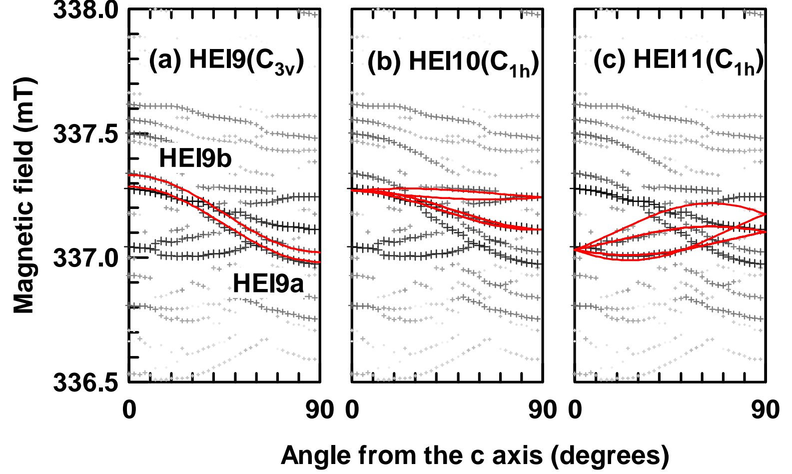

Fig. 3. Angular maps of EPR spectra for (a) *HEI*9*a*/*b*, (b) *HEI*10, and (c) *HEI*11. Magnetic field was rotated from [0001] to [-1100]. Symbols express experimental data (larger and draker symbols represent larger peaks) and solid lines are fitting results.

The *HEI*9*a*/*b* centers show strong HF interactions with nuclear spin(s) of I = 1/2, as shown in Fig. 4. For *HEI*9*b*, an intensity ratio for the HF lines *b* to the main line was estimated to be 2%, which suggests the contribution of one ^{13}C atom (1.1%) rather than one ^{29}Si atom (4.7%) (Note that the contribution of two nuclei is inconsistent with the observed C_{3v} symmetry). In addition, if we assigned one ^{29}Si atom to the origin of the HF lines *a* (see Fig. 4), the main line of *HEI*9*a* would take only 4% of the observed main line of "*HEI*9*a*/10", which is quite inconsistent with the observed intensity ratio of *HEI*9*a*:*HEI*10 in EPR spectra at other magnetic-field angles. Accordingly, we conclude that the observed HF interactions of *HEI*9*a*/*b* are due to one ^{13}C atom. Table I shows the principal values of the ^{13}C HF tensor ($A_{\perp}$ and $A_{\|}$). By using the standard isotropic and anisotropic HF constants of ^{13}C (A_{iso} = 134.77 mT and A_{aniso} = 3.83 mT), we find that an electron spin of *HEI*9*a* (*HEI*9*b*) is distributed on a *c*-axial carbon DB by 55 (58) % [2*s*-orbital density = 3 (4) % and 2*p*-orbital density = 52 (54) %]. Therefore, the *HEI*9 centers are strongly localized on a *c*-axial C

Table 1. Spin-Hamiltonian parameters for the new EPR centers in *p*-type 4*H*-SiC. θ expresses the angle between the main principal g axis and the *c* axis.

Center	symmetry	g_{XX}	g_{YY}	g_{ZZ} ($g_{\|}$)	θ (deg.)	$A_{\perp}$ (mT)	$A_{\|}$ (mT)
*HEI*9*a*	C_{3v}	2.00408	2.00408	2.00228	0	2.3	8.3
*HEI*9*b*	C_{3v}	2.00380	2.00380	2.00195	0	3.7	9.9
*HEI*10	C_{1h}	2.00348	2.00258	2.00226	145		
*HEI*11	C_{1h}	2.00399	2.00345	2.00263	116		

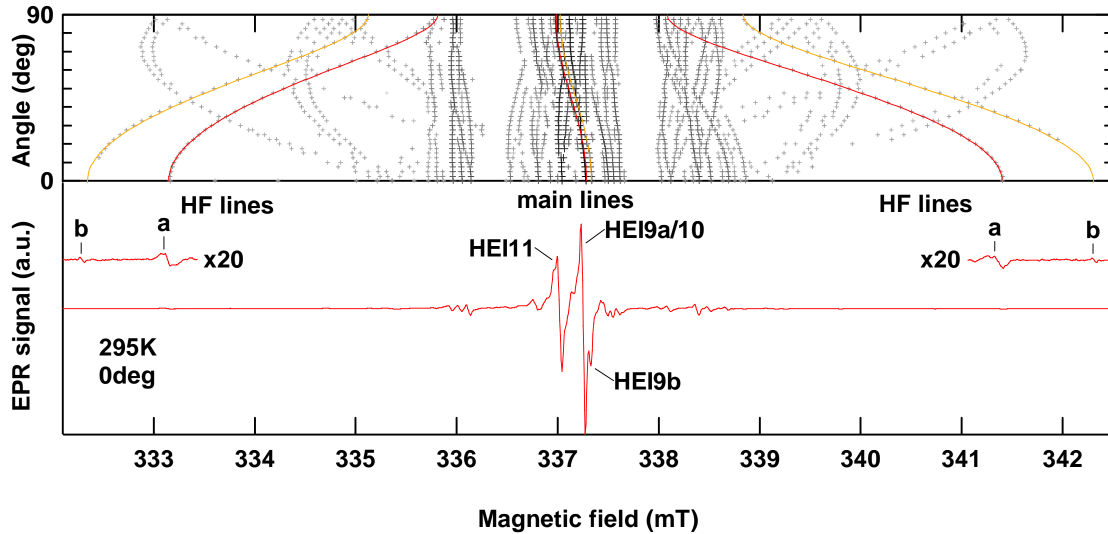

Fig. 4. Angular map of ^{13}C hyperfine interactions for *HEI*9*a*/*b*. Magnetic field was rotated from [0001] to [-1100]. EPR spectrum shown here was measured using a microwave power of 0.1 μW. Solid lines in the angular map indicate fitting results.

atom (i.e., *c*-axial C_{Si} atom in Fig. 1), identifying them as *c*-axial $C_{Si}V_C$ pairs in the positive charge state [c.f., Fig. 1(d)]. We should note that this positive charge state does not involve Jahn-Teller instability and hence C_{3v} symmetry is observed.

The basal pairs of $C_{Si}V_C^+$ will correspond to *HEI*10 and/or *HEI*11. For this case, there should be also two inequivalent configurations, *kh* and *hk* [6]. Likewise the *c*-axial pairs, we should observe a strong ^{13}C HF interaction due to a basal C_{Si} atom [c.f., Fig. 1(b)]. In the angular map of Fig. 4, one finds unidentified HF lines, a part of which may originate from the basal $C_{Si}V_C^+$ pairs.

Conclusion

Based on careful EPR analyses on irradiated *p*-type 4*H*-SiC, we have revealed for the first time stable positively charged carbon AV pairs ($C_{Si}V_C^+$). The *HEI*9*a*/*b* centers with C_{3v} symmetry were assigned to *c*-axial pairs of $C_{Si}V_C^+$. We also found two C_{1h}-symmetric centers (*HEI*10 and *HEI*11) similar to *HEI*9, which supposedly corresponds to basal pairs of $C_{Si}V_C^+$.

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