Electron paramagnetic resonance study of the *HEI*4/*SI*5 center in 4H-SiC

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Abstract. We present new electron-paramagnetic-resonance (EPR) data on the *HEI*4/*SI*5 center in 4*H*-SiC. So far, the *SI*5 (SI-5) center has been observed only in as-grown SiC substrates; however, we found that it can be created by electron irradiation to commercial *n*-type 4*H*-SiC. The artificially created *SI*5 center, which we had preliminary called *HEI*4, was found to be identical with the *SI*5 center in as-grown SiC. A high-intensity *HEI*4/*SI*5 spectrum of irradiated SiC revealed clear hyperfine structures of ^{29}Si and ^{13}C, which enabled us to identify the origin of this center as a carbon antisite-vacancy pair in the negative charge state (C_{Si}-V_C^-). We assessed its electronic levels using photo-EPR.

Introduction

In high-purity semi-insulating (HPSI) 4*H*-SiC, special defects labeled *SI*1 to *SI*9 (SI-1 to SI-9) [1] were found by means of electron paramagnetic resonance (EPR) spectroscopy [2]. It is believed that these defects are related to the compensation of undesired residual carriers in HPSI materials. The *SI*5 center is one of the most abundant and the most stable centers among them. The *SI*5 center was characterized by an electron spin (*S*) of 1/2, a C_{3v} symmetry, and two hyperfine (HF) structures due to ^{29}Si (nuclear spin I = 1/2, natural abundance = 4.7%) or ^{13}C (I = 1/2, 1.1%) [2]. Its origin was tentatively assigned to a divacancy (V_{Si}-V_C) [2,3]. However, the analysis of *SI*5's HF structures [2] have revealed only 12-13% of the wave function for this center (11% on three C atoms and 1.5% on three Si atoms), which is too small for a divacancy in either the positive or negative charge state with an electron spin located at dangling bonds of V_C-V_{Si}. In this report, we present more complete EPR data on the *SI*5 center by taking advantage of the artificial creation of this center by electron irradiation. The *SI*5 center in irradiated SiC, which had been called *HEI*4 in our recent paper [4], revealed complete HF structures of ^{29}Si or ^{13}C, resulting in a new conclusion that this center originates from a negatively charged carbon antisite-vacancy pair (C_{Si}-V_C^-). This conclusion was also confirmed by first principles calculations [5].

Formation of the *HEI*4/*SI*5 center by electron irradiation

Substrates used in this study were commercial nitrogen (N)-doped *n*-type 4*H*-SiC(0001) wafers (room-temperature carrier concentration = 10^{17} /cm^3). So far the *SI*5 center has not been reported in any irradiated SiC and subsequently annealed samples. We found that the temperature during the irradiation is the key factor to yield the *SI*5 center. If the irradiation was done at room temperature to the above *n*-type substrates, the created defects were mostly Si vacancies (the V_{Si}^- and T_{v2a} centers) [6]. If the irradiation temperature was raised above 350°C, both V_{Si}^- and T_{v2a} signals disappeared in the dark; instead, the *HEI*4 (*SI*5) signal appeared in addition to unidentified EPR signals which we

labeled *HEI*5/6 (S = 1/2). Further increasing the irradiation temperature up to 800°C, EPR spectrum was strongly dominated by the *HEI*4/*SI*5 signal. Although we performed a similar experiment on *p*-type substrates, the formation of the *HEI*4/*SI*5 center was not observed. In the following study, we will analyze the *HEI*4/*SI*5 EPR spectra of *n*-type 4*H*-SiC irradiated with 2-4×10^{18} e/cm^2 at 800-850°C. All spectra shown in this paper were measured under photo excitation by a 100-W Halogen lamp.

EPR results and discussion

A typical *HEI*4/*SI*5 spectrum and an angular dependence of the resonant fields measured at 100 K are shown in Figs. 1(b) and (a), respectively. The central strong signal, *HEI*4 [4], is identical with the *SI*5 signal: in both cases, the same C_{3v} symmetry, g values, and HF structures [HF2' and HF4' in Fig. 1(b)] are observed. We have checked that spin-Hamiltonian parameters are in good agreement between *SI*5 at 77K [2] and *HEI*4 at 80 K; $g_{\|}$ = 2.0048 and 2.0049, $g_{\perp}$ = 2.0030 and 2.0032, $A_{\|}$(HF2') = 40.7 and 43.2 MHz, $A_{\perp}$(HF2') = 31.8 and 34.2 MHz, $A_{\|}$(HF4') = 11.8 and 11.7, $A_{\perp}$(HF4') = 12.7 and 11.8 MHz, respectively. In Fig. 1, new HF structures (HF1' and HF3') are clearly observed, that were too weak to be detected in HPSI samples. The HF1' structure shows the largest HF splitting ($A_{\|}$ = 8.0 mT, $A_{\perp}$ = 6.4 mT, axial symmetric around a basal Si-C bond). Its relative intensity to the total spectrum is approximately 5%, suggesting that the HF1' splitting originates from one ^{29}Si atom. Furthermore, we reassign the HF2' splitting ($A_{\|}$ = 2.2 mT, $A_{\perp}$ = 1.8 mT, *c*-axial) due to one ^{13}C atom, instead of three ^{13}C atoms in the previous assignment [2]. The HF3' and HF4' splittings were nearly isotropic and would be related to outer atoms of the relevant center; hence we focus only on HF1' and HF2'. The angular dependence of HF1' indicates that the relevant Si atom is most likely one of three Si neighbors of a carbon vacancy (V_C) [e.g., Si_3 atom in the inset of Fig. 1(b)], and the HF1' ^{29}Si interaction is caused by a Si dangling bond pointing to the V_C. Using the LCAO (linear combination of atomic orbitals) analysis [4] on HF1' and HF2', an electron-spin distribution is estimated to be 18%+5% on one Si atom + one C atom. This result is quite different from the previous one: 11%+1.5% on three C atoms + three Si atoms [2]. Therefore, the divacancy model is not appropriate and a new model is necessary.

We also found that the *HEI*4/*SI*5 spectrum is strongly temperature dependent, as shown in Fig. 2. As the temperature decreases, the HF1' lines vanish due to the broadening and the HF2' splitting becomes smaller. The HF3' and HF4' lines are almost unchanged. But, near 55 K, all HF lines are broadened and vanish. Further decreasing the temperature, the *HEI*4/*SI*5 spectrum shows completely different HF structures (HF1-5) as well as a different symmetry (C_{1h}).

The EPR spectrum and angular dependence of this C_{1h}-symmetric phase are shown in Figs. 3(b)

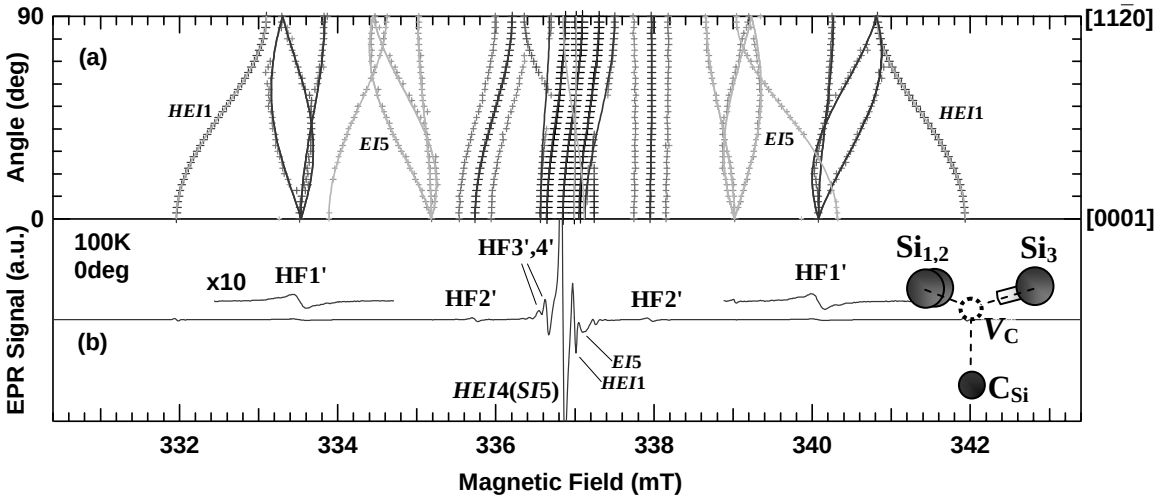

Fig. 1. The *HEI*4/*SI*5 center (C_{3v} symmetry) measured at 100 K under illumination.

and (a), respectively. One very strong HF interaction (HF1) and four weak HF splittings (HF2-5) are observed. The relative intensity of HF1 indicates that it originates from HF interactions of two ^{29}Si atoms. They can be identified as two Si neighbors of a V_C [e.g., $Si_{1,2}$ atoms in the inset of Fig. 3(b)] based on the determined HF tensor of HF1. The atomic model shown in Fig. 3(b) satisfies the observed C_{1h} symmetry with respect to the (11-20) plane. The LCAO analysis revealed that an electron spin is strongly localized on the two Si atoms by 31%+31%. For other HF structures (HF2-5), we confirmed by pulsed-ENDOR measurements that they originate from either ^{29}Si or ^{13}C.

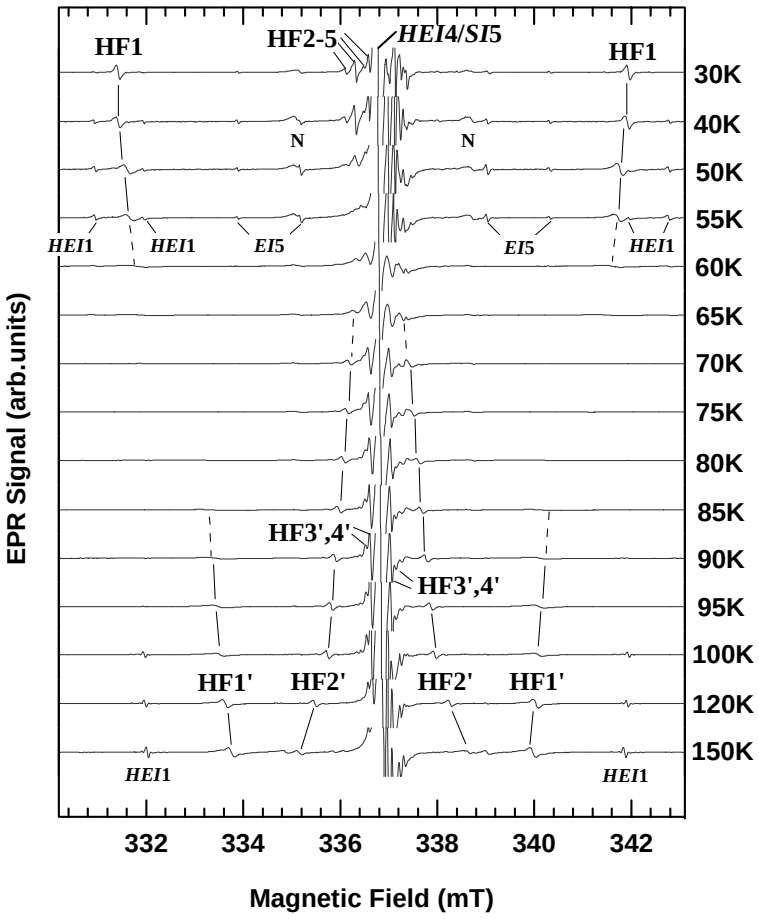

Fig. 2. Temperature dependence of the *HEI*4/*SI*5 spectrum measured for **B** || *c*.

Accordingly, our EPR data reveal that (1) the *HEI*4/*SI*5 center is not coupled with impurities, (2) it should involve a V_C, (3) it is most likely to a single negative charge state because of S=1/2 and its presence in irradiated *n*-type samples, but (4) it should be different from a simple V_C^- (the *HEI*1 center [4]), (5) its wave function distributes mainly on two Si atoms of a V_C in the low-temperature C_{1h} phase, and (6) the *HEI*4/*SI*5 center transforms into a C_{3v} configuration at higher temperatures.

To take all these into account, we propose the *c*-axial negatively charged carbon antisite-vacancy pair (C_{Si}-V_C^-) for the origin of the *HEI*4/*SI*5 center. A carbon antisite (C_{Si}) is located at the *c*-axial neighbor of a V_C, as shown in the insets of Figs. 1(b) and 3(b). Naturally, this model is consistent with the results (1) to (4). The result (5) is also reasonable, because this situation (electron-spin distribution = 31%+31% on two Si neighbors of V_C^-) is quite similar to that for a simple V_C^- (*HEI*1) [4] where the electron-spin distribution was found to be 30%+30% on two Si neighbors of V_C^-. The result (6) can be interpreted by a thermally activated reorientation. A similar phenomenon was already observed for *EI*5 (V_C^+) and *HEI*1 (V_C^-) [4] where the defects exhibited a C_{1h} symmetry at low temperatures but a C_{3v} symmetry at high temperatures. The thermally activated reorientation rapidly moves an electron spin among the $Si_{1\text{-}3}$ atoms. As a result, it generates a C_{3v} average state, and also causes the lifetime broadening effect (< 100 K) and the motional narrowing effect (> 100 K) on the HF1' ^{29}Si line (see Fig. 2). It is worthy to note that first principles calculations for C_{Si}-V_C^- in large super cells could excellently reproduce the observed HF parameters of the *HEI*4/*SI*5 center [5]. According to the calculations, the C_{Si}-V_C^- pair involves a large Jahn-Teller distortion, and the C_{Si} atom forms a sp^2-like structure with a non-bonding orbital. But, this orbital is occupied by two electrons and hardly contributes to ^{13}C HF interaction. Therefore, an electron spin is distributed mainly on the V_C side, resulting in the large ^{29}Si HF interactions, as observed in the experiment. The calculations [5] predicted that the HF2' ^{13}C interaction is generated from a second nearest neighbor C atom of V_C.

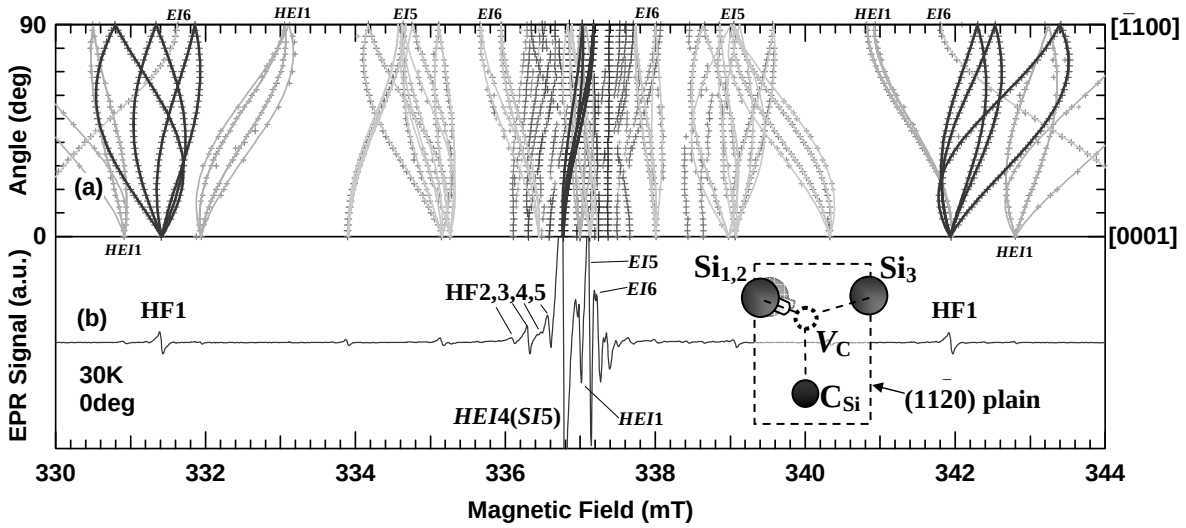

Fig. 3. The *HEI*4/*SI*5 center (C_{1h} symmetry) measured at 30 K under illumination.

In the last place, we mention a photo-EPR study. In the dark, the *HEI*4/*SI*5 signal was detectable but very weak. It was drastically enhanced by the photo excitation just above 1.1 eV. We found that this 1.1-eV threshold corresponds to an electron excitation from a defect at E_F (the Fermi level) to the conduction band edge (E_C) [4]. Namely, E_F of our sample is located at E_C – 1.1 eV in thermal equilibrium. At this condition, most of C_{Si}-V_C were stabilized into an EPR-inactive charge state most likely C_{Si}-V_C^{2-}. The illumination converted them to C_{Si}-V_C^-, which caused the enhancement on the *HEI*4/*SI*5 signal. Our photo-EPR data suggest that the C_{Si}-V_C pairs captured electrons from the N donors, forming the C_{Si}-V_C^{2-} levels at E_C – 1.1 eV. By looking the photo excitation data carefully, there were also weak enhancements on the *HEI*4/*SI*5 signal below the 1.1-eV threshold. They were found at 0.65 eV and 0.9 eV. The theoretical calculations [5] suggest that these thresholds are associated with the internal excitations of the C_{Si}-V_C pair.

Summary

We have studied hyperfine interactions of the *HEI*4/*SI*5 EPR center by taking advantage of irradiated *n*-type 4*H*-SiC substrates. The detailed EPR analysis revealed that this center originates from negatively charged C_{Si}-V_C pairs. They contributed to the compensation of the N donors in the irradiated *n*-type samples.

References

[1] We here use conventional notations such as "*SI*5" or "*HEI*1" (*alphabets* + number), instead of the original labels ("SI-5" or "HEI1", respectively).

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