Electron paramagnetic resonance study of the HEI4/SI5 center in 4H-SiC

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Keywords: semi-insulating SiC, defect, deep level, EPR.

Abstract. We present new electron-paramagnetic-resonance (EPR) data on the HEI4/SI5 center in 4H-SiC. So far, the SI5 (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 4H-SiC. The artificially created SI5 center, which we had preliminary called HEI4, was found to be identical with the SI5 center in as-grown SiC. A high-intensity HEI4/SI5 spectrum of irradiated SiC revealed clear hyperfine structures of 29Si and 13C, which enabled us to identify the origin of this center as a carbon antisite-vacancy pair in the negative charge state (CSi–VC–). We assessed its electronic levels using photo-EPR.

Introduction

In high-purity semi-insulating (HPSI) 4H-SiC, special defects labeled SI to SI9 (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 SI5 center is one of the most abundant and the most stable centers among them. The SI5 center was characterized by an electron spin (S) of 1/2, a C3v symmetry, and two hyperfine (HF) structures due to 29Si (nuclear spin I = 1/2, natural abundance = 4.7%) or 13C (I = 1/2, 1.1%) [2]. Its origin was tentatively assigned to a divacancy (VSi–Vc) [2,3]. However, the analysis of SI5’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 Vc-Vsi. In this report, we present more complete EPR data on the SI5 center by taking advantage of the artificial creation of this center by electron irradiation. The SI5 center in irradiated SiC, which had been called HEI4 in our recent paper [4], revealed complete HF structures of 29Si and 13C, with a new conclusion that this center originates from a negatively charged carbon antisite-vacancy pair (CSi–VC–). This conclusion was also confirmed by first principles calculations [5].

Formation of the HEI4/SI5 center by electron irradiation

Substrates used in this study were commercial nitrogen (N)-doped n-type 4H-SiC(0001) wafers (room-temperature carrier concentration = 1017 /cm3). So far the SI5 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 SI5 center. If the irradiation was done at room temperature to the above n-type substrates, the created defects were mostly Si vacancies (the Vsi and T2a centers) [6]. If the irradiation temperature was raised above 350°C, both Vsi and T2a signals disappeared in the dark; instead, the HEI4 (SI5) signal appeared in addition to unidentified EPR signals which we
EPR results and discussion

A typical $HEI4/SI5$ 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, $HEI4$ [4], is identical with the $SI5$ 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 $SI5$ at 77K [2] and $HEI4$ at 80 K; $g_\parallel = 2.0048$ and 2.0049, $g_\perp = 2.0030$ and 2.0032, $A_\parallel$(HF2’) = 40.7 and 43.2 MHz, $A_\perp$(HF2’) = 31.8 and 34.2 MHz, $A_\parallel$(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 ($A_\parallel = 8.0$ 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 ($A_\parallel = 2.2$ 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 $HEI4/SI5$ 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 $HEI4/SI5$ 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 $HEI4/SI5$ center ($C_{3v}$ symmetry) measured at 100 K under illumination.](image)
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.

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 (CSi$^{-}$-$V_C^-$) for the origin of the HEI$^4$/SI$^5$ center. A carbon antisite (CSi$^{-}$) 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 $EI5$ ($V_C^-$) and HEI1 ($V_C^+$) [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$_{1,3}$ 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 CSi$^{-}$-$V_C^-$ in large super cells could excellently reproduce the observed HF parameters of the HEI$^4$/SI$^5$ center [5]. According to the calculations, the CSi$^{-}$-$V_C^-$ pair involves a large Jahn-Teller distortion, and the CSi$^{-}$ 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 $V_C$. 

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**Fig. 2.** Temperature dependence of the HEI$^4$/SI$^5$ spectrum measured for $B \parallel c$. 

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In the last place, we mention a photo-EPR study. In the dark, the HEI4/SI5 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 HEI4/SI5 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 HEI4/SI5 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 HEI4/SI5 EPR center by taking advantage of irradiated n-type 4H-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 “SI5” or “HEI1” (alphabets + number), instead of the original labels (“SI-5” or “HEI1”, respectively).

Fig. 3. The HEI4/SI5 center ($C_{1h}$ symmetry) measured at 30 K under illumination.