Divacancy in 4H-SiC

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Electron paramagnetic resonance and ab initio supercell calculations suggest that the P6/P7 centers, which were previously assigned to the photoexcited triplet states of the carbon vacancy-antisite pairs in the double positive charge state, are related to the triplet ground states of the neutral divacancy. The spin density is found to be located mainly on three nearest C neighbors of the silicon vacancy, whereas it is negligible on the nearest Si neighbors of the carbon vacancy.

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Divacancies are common defects in semiconductors comprised of neighboring isolated vacancies. For SiC, an unambiguous identification of this defect that has been predicted to be thermally stable [1–3] is so far missing. The P6/P7 centers were first observed by electron paramagnetic resonance (EPR) in heat-treated n-type 6H-SiC [4] and were later shown to be a common defect in as-grown n-type [5] and high-purity semi-insulating (HPSI) [6,7] SiC. Based on their symmetry (axial or C3v for P6 and monoclinic or C1h for P7), P6/P7 centers were suggested to be the divacancy [4]. In a study using magnetic circular dichroism of the absorption (MCDA), MCDA-detected EPR, and ab initio calculations [8], P6/P7 centers were instead assigned to the photoexcited triplet state of the carbon vacancy-carbon antisite pair in the doubly positively charged state VC1C2 vi. The formation of the center was suggested to be due to the migration of a nearest C neighbor into the silicon vacancy (VSi) [8]. The process VSi + VC → VC1C2 vi is theoretically predicted to have a low reaction barrier (≈1.7 eV) [2]) and can therefore be a dominating process. For SiC, so far there is no experimental evidence that the reaction VSi + VC → VC1C2 vi is important and that the divacancy is a common defect. In a previous EPR study of HPSI SiC substrates [7], a very stable center SI-5 was assigned to the divacancy. However, in a recent EPR study [9], a symmetry lowering of SI-5 from C3v to C1h and additional large hyperfine (hf) interactions with 29Si were observed that invalidated this model. Indeed, recent EPR studies [9] and supercell calculations [10] identify SI-5 as the carbon vacancy-carbon antisite pair in the negative charge state VC1C2 vi.

In this Letter, we present results from EPR studies and ab initio supercell calculations which confirm that P6/P7 are originating from the triplet ground states of the neutral divacancy in the C3v/C1h configurations.

Samples used in the study are N-doped n-type (concentration ≈1 × 1017 cm−3), Al-doped p-type (≈1 × 1018 cm−3), and HPSI 4H-SiC. In HPSI samples, the concentration of N is ≈1 × 1015 cm−3. The irradiation by 3 MeV electrons was performed at room temperature with a dose of 2 × 1018 cm−2. For some n-type samples, the irradiation was performed at 850 °C with doses of 2 × 1018 cm−2 and 1 × 1019 cm−2. EPR measurements were performed on Bruker ER200D and E580 X-band spectrometers. For light illumination, a Xenon lamp (150 W) was used in combination with a Jobin-Yvon 0.25 m grating monochromator and/or different optical filters.

The P6/P7 spectra can be detected after irradiation but are weak. The signals reach the maximum after annealing at ≈850 °C. In irradiated p-type 4H-SiC, the spectra can be detected only under illumination with light of photon energies > 1.1 eV. However, in heavily irradiated (1 × 1019 cm−2) n-type samples, the spectra can be detected in darkness in the whole temperature range of 4–293 K. Figure 1 shows the P6/P7 spectra measured in darkness at 8 K. We labeled the P6 spectra according to Ref. [11] and the corresponding C1h spectra as P7b and P7′ b. The g value for P6/P7 is 2.003; the axially symmetric D and anisotropic E values of the fine structure parameter...
The axial ($C_{3v}$) and monoclinic ($C_{1h}$) configurations of the divacancy are illustrated in Figs. 3(a) and 3(b), respectively. For $P6b$ and $P6’b$, the best fits to the inner hf structures are obtained with the hf tensors of 3 Si atoms on the bonds along the $c$ axis, labeled $S_{6h}$, and 6 Si atoms in the plane, labeled $S_{6i}$ [see Fig. 3(a)]. The simulation of the $P6b$ and $P6’b$ lines and their hf structures are plotted in Fig. 2(a). The simulation includes the following hf interactions with: (i) 3 $C_i$ nearest neighbors of $V_{Si}$, (ii) 3 $S_{6h}$ and 6 $S_{6i}$ second neighbors of $V_{Si}$, and (iii) 3 nearest $S_i$ neighbors of $V_C$. As can be seen in $\times 10$ scale spectra in Fig. 2(a), the simulation describes perfectly the observed spectra, not only the intensity of the hf lines but also their detailed superhyperfine structures.

The angular dependences of the $C_i$ hf splitting of $P6b$ and $P6’b$ with $B$ rotating in the $(1120)$ plane are shown in Fig. 3(c). These hf tensors have $C_{1h}$ symmetry and their principal values obtained from the fit are given in Table I. The hf interactions with the nearest $C_{ia}$ and $C_{ib}$ neighbors of $P7b$ were also observed for some crystal directions as shown in Fig. 3(d). The $C_{1h}$ hf tensor has $C_{1h}$ symmetry and is similar to that observed for the nearest $C_i$ neighbors of $P6b/P6’b$. The principal values of the $C_i, C_{ia}$, and $C_{ib}$ hf tensors are given in Table I. The hf structures of $P7b$ detected at some directions between 60°–90° show to be similar to that of $P7b$ [Fig. 2(b)]. The broad inner hf lines of $P7b$ and $P7’b$ are unresolved, corresponding to splitting of 0.3–0.46 mT or ~9–13 MHz. Their intensity ratios correspond to the interaction with nine Si atoms.

The observation of the $P6/P7$ spectra in dark at low temperatures confirms that these centers are related to the ground triplet state. From the above analysis of the hf

![FIG. 1. EPR spectrum of $P6/P7$ centers measured for $B \parallel c$ in irradiated and annealed (850 °C) n-type 4H-SiC at 8 K in dark.](image)

![FIG. 2 (color online). EPR spectra of $P6/P7$ centers observed in irradiated and annealed (850 °C) HPSi 4H-SiC at 77 K under illumination (photon energies ~1.1–1.7 eV), showing hf structures of (a) $P6b/P6’b$ lines at $B \parallel c$ and (b) $P7b/P7’b$ lines at ~70° from the $c$ axis.](image)

![FIG. 3 (color online). Si and C neighbors of the divacancy in (a) axial ($C_{3v}$) and (b) monoclinic ($C_{1h}$) configurations. Angular dependence with $B$ rotating in the (1120) plane of the hf splitting of (c) $C_i$ nearest neighbors of $P6b/P6’b$ and (d) $C_{ia}$ and $C_{ib}$ nearest neighbors of $P7b’$. For $P6b$ and $P6’b$, a misalignment of 1.5° off the (1120) plane toward the [1100] direction was taken into account in the simulation.](image)
interactions, the neutral divacancy appears to be the most probable model for the P6/ P7 centers.

We have performed \textit{ab initio} supercell calculations of the neutral divacancy in 4H-SiC using supercells containing 256 lattice sites. For the optimization of the geometry, we employed pseudopotential methods, namely, the SIESTA code with double-$\zeta$ polarized basis set for both C and Si atoms [12] and the FHI-96SPIN plane wave code with a well-converged basis set (cutoff energy of 30 Ry) [13], to check the results. The calculations were based on the local spin density approximation (LSDA: Ceperley-Alder as parameterized by Perdew and Zunger) and norm-conserving Troullier-Martins pseudopotentials [12,13]. We found that the optimized geometries of the divacancies obtained by both codes practically agreed. The hf tensors were then calculated by all electron projector augmentation wave method using the above LSDA functional [14]. In the latter calculations, we applied a 30 Ry cutoff for the plane-waves basis set and one projector for each angular momentum in the projectors of C and Si atoms. This methodology has proven to be very successful in the study of $V_C$ in 4H-SiC [15]. We verified that the well-known band gap failure of the LSDA did not affect our results for the ionization energies beyond the expected accuracy by applying a scissors operator to open the LSDA band gap to the experimental value as suggested by Baraff and Schlüter [16]. With this \textit{ad hoc} correction, we assured also that the defect spin density is not tightly coupled to the energetic position of the conduction band states. We found the same hf tensors within the achievable accuracy. The obtained hf constants for different configurations are given in Table I. We found that the ground state of the neutral divacancy is a high spin state with $S = 1$. In the axial configurations, two doubly degenerate $e$ levels appear in the band gap: The first one is below the midgap arising from C dangling bonds of $V_{Si}$, while the second one is above the midgap arising from Si dangling bonds of $V_C$. In the neutral charge state, the lower $e$ level is occupied by two electrons with parallel spins making the defect Jahn-Teller stable. As a consequence, the spin density is mainly localized on the nearest carbon neighbors of $V_{Si}$, whereas the contribution of the dangling bonds at $V_C$ is almost negligible. In the off-axis $C_{lh}$ configurations, the situation is very similar apart from the small splitting of the degenerate $e$ levels due to the low symmetry. The calculated ( +0) and (0 ) levels are at $\sim$0.5 and $\sim$1.4 eV above the valence band, respectively. The neutral charge state with $S = 1$ is the ground state of the divacancy when the Fermi level is in this range.

As can be seen in Table I, the principal values and the direction of the symmetry axis of the hf tensors of nearest C neighbors obtained from EPR are in good agreement with the calculated values for the neutral divacancy. Even small differences in the hf tensors of P6b and P6' are also observed by EPR and calculations. Therefore, we assign P6b and P6' to the axial $C_{3v}$ configurations of the neutral divacancy at the hexagonal ($h$) and cubic ($k$) sites, respectively. Since the $C_{1h}$, $C_{3v}$, and $C_{4h}$ hf tensors were not determined for P7b, an unambiguous identification of individual $C_{1h}$ configurations is not possible. Using the linear combination of atomic orbital analysis, the spin density on a nearest C neighbor is determined as: $\sim$1.8%--1.9% on the $s$ orbital and $\sim$18%--19% on the $p$ orbital for P6b, P6', and P7b. The total spin density on the three nearest C neighbors of the neutral divacancy is $\sim$60% for the $C_{3v}$ configuration (P6b/P6') and $\sim$62% for the $C_{1h}$ configuration (P7b). The spin localization on the three nearest Si neighbors of $V_C$ ($Si_i$ or $Si_{ia}$ and $Si_{ib}$) is negligible ($\sim$1%).

In the previous annealing studies [11,17], the annealing characteristic of the Si vacancy ($T_{V_{2a}}$ center) and P6'/P7 centers was interpreted in terms of the theoretically predicted transformation of $V_{Si}$ into $V_C$/$C_{Si}$. The reidentification of the P6'/P7 centers with the divacancy demands a reinterpretation of its annealing behavior. Although a full analysis is beyond the scope of the present Letter, we briefly discuss here our annealing experiments performed for two sets of as-grown HPSI 4H-SiC samples: (i) No. 1 with strong signals of $V_{Si}$ ($T_{V_{2a}}$ center), Si-5 (i.e., $V_C$/$C_{Si}$ center [9,10]), and $V_C^+$ (E15 center [7]); (ii) No. 2 with
that the annealing characteristics of sample sets No. 1 and No. 2 are shown in Figs. 4(a) and 5. The annealing temperature dependences of EPR centers in the signal can be detected in dark or under illumination. The formation of the Si vacancy \( V_Si \) and a weak \( V_C \) signal was detected in dark. Since the heating/cooling time varied with temperature, the annealing is not isochronal. In both sample sets, the signals of \( V_C \), TV, and \( P6b/P6'b \) signals were detected under illumination (photon energies \( \sim 1.1-1.7 \) eV) whereas the SI-5 signal was detected in dark.

In summary, based on EPR observation and \textit{ab initio} supercell calculations, we identified the \( P6b/P7 \) centers in 4H-SiC to be related to the ground triplet state of the neutral divacancy in the \( C_{3v}/C_{1h} \) configurations and assigned the \( P6b \) and \( P6'b \) axial centers to the \( C_{3v} \) configuration at the hexagonal and cubic site, respectively. The spin density is found to be located mainly on three nearest C neighbors of \( V_Si \), whereas it is negligible on the nearest Si neighbors of \( V_C \). The vacancy model for \( P6/P7 \) centers also implies that the interaction between \( V_Si \) and \( V_C \) to form divacancies is significant and the divacancy is a common defect in SiC. Annealing studies suggest that the formation of the divacancy is governed mainly by diffusion of \( V_C \) and \( V_Si \).

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\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig4.png}
\caption{(color online). Annealing temperature dependence of EPR centers in as-grown HPSI 4H-SiC samples with (a) strong signals of TV (or \( V_Si \)), SI-5 (i.e., \( V_CC_{Si} \)) and \( V_C \), (b) strong TV and SI-5 and weak \( V_C \) signals. The \( V_C^+ \), TV, and \( P6b/P6'b \) signals were detected under illumination (photon energies \( \sim 1.1-1.7 \) eV) and the SI-5 signal was detected in dark.}
\end{figure}

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