

Identification of divacancies in 4H-SiC

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Abstract

The P6/P7 centers in 4H-SiC were studied by electron paramagnetic resonance (EPR) and ab initio supercell calculations. The hyperfine coupling constants of C and Si neighbors obtained by EPR are in good agreement with the calculated values for the neutral divacancy, $V_C V_{Si}^0$. Our results suggest that the P6/P7 centers, which were previously assigned to the photo-excited triplet states of the carbon vacancy–carbon antisite pairs in the double positive charge state ($V_C C_{Si}^{2+}$), are related to the triplet ground states of the C_{3v}/C_{1h} configurations of $V_C V_{Si}^0$.

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PACS: 61.72.Ji; 76.30.Mi; 71.15.Mb; 61.72.Bb

Keywords: Divacancies; Electron paramagnetic resonance; Ab initio calculations

1. Introduction

One of the most common intrinsic defects observed by electron paramagnetic resonance (EPR) and optically detected EPR in as-grown n-type [1] and high-purity semi-insulating (HPSI) [2,3] SiC substrates are the P6/P7 centers [4]. These centers were first observed by Vainer and Il'in [4] in 6H-SiC substrates, which were heated up to 2000 °C and quenched. Based on their symmetry (C_{3v} and C_{1h} for the P6 and P7 centers, respectively), the centers were suggested to be the divacancy [4], i.e. the close pair of the carbon and silicon vacancy. In a study using magnetic circular dichroism of the absorption (MCDA), MCDA-detected EPR (MCDA-EPR) and ab initio calculations [5], the centers were instead assigned to the excited triplet state of the carbon vacancy–carbon antisite pairs in the doubly positively charged state, $V_C C_{Si}^{2+}$. The divacancy is predicted

by theory [6–8] to be a very stable defect, but has not been experimentally identified so far. In a previous EPR study of semi-insulating SiC substrates [3], a very stable center, SI-5, was assigned to the divacancy based on the observed hyperfine (hf) interactions. This assignment was later supported by calculations [8]. However, in recent EPR studies [9] the symmetry lowering of SI-5 from C_{3v} to C_{1h} and additional large hf interactions with ^{29}Si were observed, that invalidated this model. Both experiments [9] and supercell calculations [10] suggest SI-5 to be the carbon vacancy–carbon antisite pair in the negative charge state, $V_C C_{Si}^-$.

In this work, we present new EPR data on the P6/P7 centers including the hf interactions with C and Si atoms in the first and second neighbor shells. The obtained hf coupling constants are in good agreement with the values determined by ab initio supercell calculations, suggesting that the P6/P7 centers are originating from the triplet ground states of the neutral divacancy in the C_{3v}/C_{1h} configurations.

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2. Experiment

Starting materials used in the study are N-doped n-type (concentration $\sim 1 \times 10^{17} \text{ cm}^{-3}$), Al-doped p-type ($\sim 1 \times 10^{18} \text{ cm}^{-3}$) and HPSI 4H-SiC wafers. In HPSI samples, the concentration of N is $\sim 4 \times 10^{15} \text{ cm}^{-3}$ [11]. The irradiation by 3 MeV electrons was performed at room temperature with a dose of $2 \times 10^{18} \text{ cm}^{-2}$. For some n-type samples, the irradiation was performed at 850°C with doses of 2×10^{18} and $1 \times 10^{19} \text{ cm}^{-2}$. 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.

3. Results and discussion

In our irradiated n-type, HPSI and p-type samples, typical P6/P7 type EPR spectra [2,5,12,13] were detected. Fig. 1(a) shows as an example the spectra in irradiated n-type 4H-SiC measured for the magnetic field \mathbf{B} along the c -axis at 77 K under illumination with light of photon energies between ~ 1.1 and ~ 1.7 eV. The P6/P7 signals can be detected after irradiation but very weak. The spectra reach their maximum after annealing at about 850°C . The P6/P7 spectra can also be detected in dark (the sample was kept inside the cryostat in completely dark for 1 day

before measurements) at temperatures close to room temperature (at 77 K, the spectra were not observable in dark) in both n-type or HPSI samples irradiated with a dose of $2 \times 10^{18} \text{ electrons/cm}^2$. In heavily irradiated ($1 \times 10^{19} \text{ electrons/cm}^2$) n-type samples, the P6/P7 spectra can be detected in dark for the whole temperature range 4–293 K. In irradiated p-type material, however, these spectra can only be detected under illumination by light with the photon energy larger than ~ 1.1 eV. The appearance of the P6/P7 centers in dark strongly suggested that they originate from the ground triplet state rather than the photoexcited positively charged (+2) state [5]. Fig. 1(b) shows the P6/P7 spectra measured in dark at 8 K. At this low temperature, the low-field lines of P6/P7 spectra are weaker than the corresponding high-field lines. The low-field P6/P6' lines even almost disappear. This indicates that the fine structure parameters D of all the P6/P6' and P7/P7' centers are positive ($D > 0$).

Using on-axis samples we obtained more accurate fine structure parameters D and E for the P7 type center compared to that in our previous work using off-axis samples [12]. We name the P6 spectra according to the labels used in Ref. [13] and labelled the corresponding C_{1h} spectra as P7b and P7'b. The g -value for P6/P7 centers is 2.003; D and E values (in unit of 10^{-4} cm^{-1}) deduced from the fits to the angular dependences are, $D(\text{P6b}) = D(\text{P7b}) = 447$, $D(\text{P6'b}) = 436$, $D(\text{P7'b}) = 408$, $E(\text{P7b}) =$

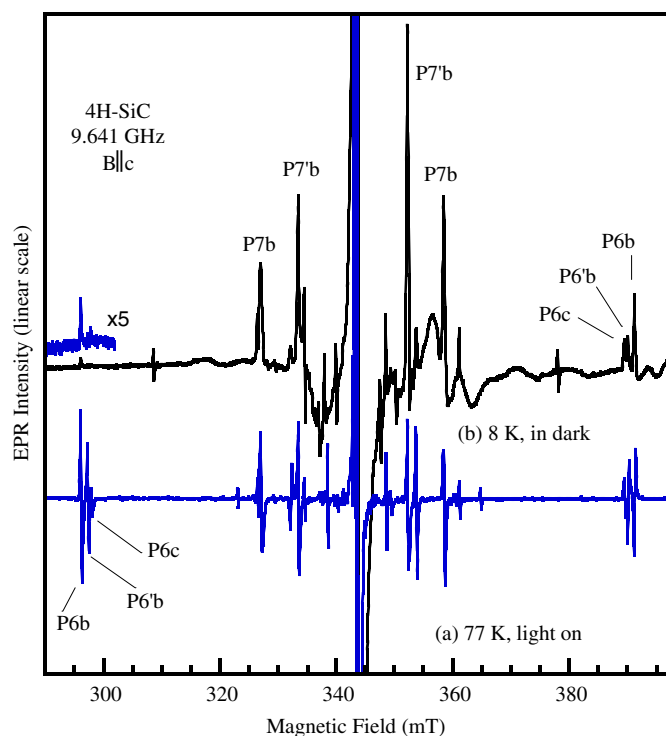


Fig. 1. EPR spectra of the P6/P7 centers in electrons irradiated and annealed (850°C) n-type 4H-SiC measured for $\mathbf{B} \parallel c$ (a) at 77 K under illumination with light of photon energies between ~ 1.1 and ~ 1.7 eV and (b) at 8 K in dark.

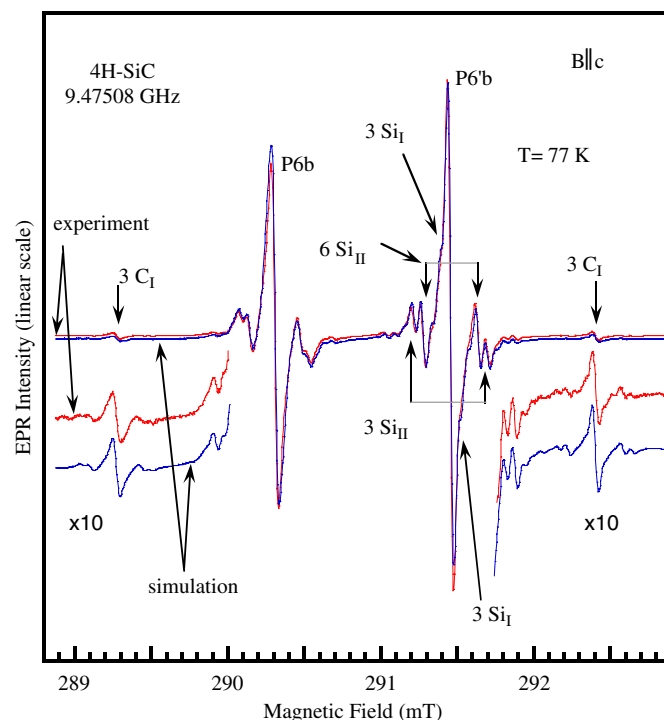


Fig. 2. Low-field lines of the P6b and P6'b spectra in irradiated and annealed HPSI 4H-SiC measured under illumination with light of photon energies between ~ 1.1 and ~ 1.7 eV for $\mathbf{B} \parallel c$, showing the hf interaction with three ^{13}C nuclei (in $\times 10$ scale). The hf interaction with nine Si atoms, of which three are along the c -axis, can be well-resolved (see text for details of the simulation).

90 and $E(P7'b) = 10$. The angle between the principal axis of the fine structure tensor and the c -axis for the P7b and P7'b centers is 70.5° and 71° , respectively.

Fig. 2 shows the detailed hf structure of the low-field lines P6b and P6'b. The same structure is also observed for corresponding high-field lines. For both P6b and P6'b, the intensity ratio between the two outer hf lines and the main lines is ~ 3.3 – 3.4% , which is approximately the natural abundance of three ^{13}C nuclei ($I = 1/2$, 1.11%). These hf lines are therefore assigned to the hf interaction with three nearest C neighbors (labeled C_1). Using a field modulation amplitude of 0.01 mT, the two inner hf structures can be well-resolved for the P6'b line (Fig. 2). Their intensity ratios agree well with the interaction with three and six ^{29}Si nuclei ($I = 1/2$, 4.7%). Fig. 3 shows the C and Si neighbors of a divacancy in axial symmetry. The number of C and Si neighbors is the same for the general case of a paired complex involving Si and adjacent C site. The hf interactions with following neighbor atoms may be distinguishable: 3 C_1 and 3 Si_1 in the nearest neighbor shells, 9 Si_{II} and 9 C_{II} atoms in the second neighbor shells, of which 3 Si_{II} and 3 C_{II} atoms on the bonds along the c -axis may have hf interactions different from that of the other 6 atoms in the basal plane (second neighbors C_{II} of V_C are not shown in Fig. 3). Among different alternatives, the best fits to the inner hf structures are the interactions with 3 and 6 Si atoms. The unresolved shoulders of the P6'b line can be well fitted by the interaction with 3 Si atoms. The simulation of the P6b and P6'b lines and their hf structures are plotted in Fig. 2. The simulation includes the hf interactions with following atoms: (i) 3 C_1 for the outer hf, (ii) 3 Si_{II} (on the bond along the c -axis) and 6 Si_{II} (in the basal plane) for the two inner hf, (iii) 3 nearest Si_1 neighbors of C site for the unresolved shoulders. The line-width at a half-maximum used in the fit is 0.04 mT. Below we show the identification of these hf structures based on the ab initio calculations of hf coupling constants. As can be seen in $\times 10$ scale spectra in Fig. 2 the simulation fits perfectly the observed spectra, not only the intensity of the hf lines but also their detailed superhyperfine structures. The C_1 hf structure was also detected at some other directions and the C_1 hf tensors of the P6b and P6'b centers could be determined. Their principal values are summar-

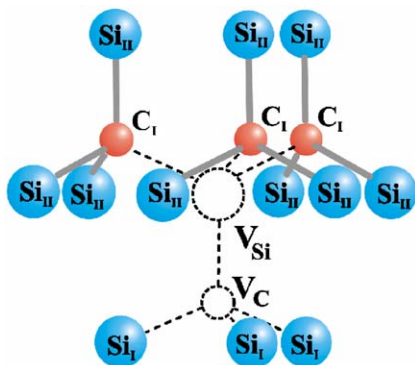


Fig. 3. Carbon and silicon neighbors of a divacancy in axial symmetry.

Table 1

The principal values (in MHz) of the hf tensors of C and Si neighbors determined by EPR for the P6b and P6'b centers and calculated for the neutral divacancy of C_{3v} symmetry at the hexagonal (hh) and cubic (kk) sites in 4H-SiC

Experiment	P6b				P6'b			
	A_{xx}	A_{yy}	A_{zz}	θ	A_{xx}	A_{yy}	A_{zz}	θ
$C_1 (\times 3)$	53	50	110	73°	47	45	104	73°
$Si_{II} (\times 3)$	12	12	12		13	13	13	
$Si_{II} (\times 6)$	9	9	9		10	10	10	
$Si_I (\times 3)$	3	3	3		3	3	3	
Theory	$(V_{Si}V_C)^0$ (hh)				$(V_{Si}V_C)^0$ (kk)			
$C_1 (\times 3)$	55	56	116	73°	49	49	110	73°
$Si_{II} (\times 3)$	9	9	9		10	10	9	
$Si_{II} (\times 6)$	9	9	8		10	10	9	
$Si_I (\times 3)$	-3	-4	-5		-1	-1	-2	

θ is the angle between the principal z -axis of the A tensor and the c -axis. The number of equivalent atoms is shown in parentheses.

ized in Table 1. The angle between the principal z -axis of the C_1 hf tensor of P6b and P6'b centers is 73° .

For the P7b and P7'b centers, the hf structure due to the interaction with three C_1 atoms was also detected at some angles close to 70° with respect to the c -axis where the spectra are well separated from others. Within experimental error, the inner hf interactions of P6b and P6'b are isotropic. Their hf coupling constants are also given in Table 1. In our previous work [12] and also in Ref. [5], the signal-to-noise ratio was rather poor and weak hf lines were likely in the noise and not detectable. This leads to the incorrect assignment of the observed hf lines to the interaction with one ^{13}C nucleus [5,12]. Our observation of the P6/P7 signals at low temperatures in dark and the hf interaction with three C_1 neighbors rules out the model of $V_C C_{Si}$ for the P6/P7 centers. The most probable model for these centers is the divacancy in the neutral charge state, $V_C V_{Si}^0$.

In order to confirm this model, we have performed ab initio supercell calculations of the divacancy in 4H-SiC. Large supercells including up to 256 atoms were used. The optimized geometry was obtained using pseudopotential method as outlined in Refs. [14,15] and then the HF-tensors were calculated by the all electron PAW method [16]. Calculations were performed with a self-consistent scissors operator to assess the effect of the LSDA band gap failure on the calculated ionization energies. Since the detailed experimental information is available for the defects aligned with the c -axis possessing the C_{3v} symmetry we show here the calculated hf constants for these defects in Table 1. The calculated hf constants of the defects possessing C_{1h} symmetry will be published elsewhere. The divacancy forms six defect levels due to the three carbon dangling bonds of the V_{Si} part and to the three silicon dangling bonds of the V_C part. In the C_{3v} symmetry two a_1 and two doubly degenerate e levels are formed. The two fully occupied a_1 levels falls in the valence band. The two

doubly degenerate e levels appear in the band gap: the first one is below the midgap arising due to the carbon dangling bonds of V_{Si} while the second one is above the midgap arising due to the silicon dangling bonds of V_C . In the neutral charge state of the defect the deeper e level is occupied by two electrons with parallel spins making the defect Jahn–Teller stable. As a consequence, the ground state of the neutral divacancy is a high spin state with $S = 1$. The spin density is mainly localized on the carbon ligands of V_{Si} part and their near neighbor atoms while the contribution of the V_C part is almost negligible. The calculated (+/0) and (0/–) levels are at ~ 0.5 eV and ~ 1.4 eV above the valence band (E_V), 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 1, the principal values and the direction of the symmetry axis of the ^{13}C and ^{29}Si hf tensors obtained from EPR are in good agreement with the calculated values for the neutral divacancy. Even small differences in principal values of hf tensors of P6b and P6'b are also observed by EPR and calculations. Therefore, we assign P6b and P6'b to the C_{3v} configurations of the neutral divacancy at the hexagonal and cubic site, respectively.

In summary, we have identified the P6/P7 centers as the C_{3v}/C_{1h} configurations of the neutral divacancy, based on the electronic structure, including the hf structures of C and Si neighbors, obtained from EPR and determined by ab initio supercell calculations. Comparing the hf tensors obtained from experiments and calculations, we assign the P6b and P6'b centers to the C_{3v} configurations of the neutral divacancy at the hexagonal and cubic site, respectively.

Acknowledgements

Support from the Swedish Foundation for Strategic Research program SiCMAT, the Hungarian OTKA F-

038357, the grant no. 2005008 and SNIC021-03-20 from the Swedish National Supercomputer Center, and the German DFG (SiC-Research group and BO1851/2-1) is acknowledged.

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