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Divacancy model for P6/P7 centers in 4H- and 6H-SiC

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Abstract. Electron paramagnetic resonance (EPR) studies of the P6/P7 centers in 4H- and 6H-SiC are reported. The obtained principal values of the hyperfine tensors of C and Si neighbors are in good agreement with the values of the neutral divacancy ($V_CV_{Si}^0$) calculated by *ab initio* supercell calculations. The 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 ($V_CC_{Si}^{2+}$), are related to the triplet ground states of the C_{3v}/C_{1h} configurations of $V_CV_{Si}^0$.

Introduction

The P6/P7 spectra were first observed in heat treated n-type 6H-SiC substrates by electron paramagnetic resonance (EPR) under photo-excitation [1]. Based on their symmetry (C_{3v} and C_{1h} for the P6 and P7 centers, respectively), the spectra were suggested to be related to the excited state of the C_{3v}/C_{1h} configurations of the divacancy [1], i.e. the close pair of the carbon and silicon vacancy. The P6/P7 spectra were also detected in as-grown, n-type 6H-SiC by optical detection of magnetic resonance (ODMR) [2]. In a study using magnetic circular dichroism of the absorption (MCDA), MCDA-detected EPR and *ab initio* calculations [3], the center was instead assigned to the excited triplet state of the carbon vacancy-antisite pairs in the doubly positively charged state, $V_CC_{Si}^{2+}$. The center was also found to be a common defect in high-purity semi-insulating (HPSI) 4H- and 6H-SiC substrates [4,5]. The formation of the center was suggested to be due to the migration of a nearest C neighbor into the silicon vacancy (V_{Si}) [3]. The process ($V_{Si} \rightarrow V_CC_{Si}$) is theoretically predicted to have a low migration barrier (~1.7 eV [3] and ~2.5 eV [6]), and can therefore be a dominating process. It is common in other semiconductors that the single vacancies interact with each other to form the divacancies. For SiC, so far there is no evidence that the process $V_{Si} + V_C \rightarrow V_CV_{Si}$ is an important one and that the divacancy is a common defect. The divacancy in SiC is predicted to be a very stable defect [6-8], but it has not so far been experimentally identified.

In a previous EPR study of HPSI SiC substrates [5], 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. Recent experiments [9] and *ab initio* supercell calculations [10] suggest SI-5 to be the carbon vacancy-carbon antisite pair in the negative charge state, $V_CC_{Si}^-$.

In this work, we present new EPR data on the P6/P7 centers in 4H- and 6H-SiC including the hf interactions with C and Si neighbor atoms. Comparing the EPR data with the parameters obtained by *ab initio* supercell calculations of the neutral divacancy, the P6/P7 centers are attributed to the ground triplet states of the neutral divacancy in the axial/non-axial configurations, respectively.

Experiment

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

Results and discussion

The P6/P7 spectra can be detected after irradiation but are very weak. The signals reach the maximum after annealing at ~850 °C. In irradiated p-type 4H-SiC the spectra can only be detected under illumination with light of photon energies ≥1.1 eV. In heavily irradiated (1×10^{19} cm^{-2}) n-type samples, the spectra can be detected in completely dark for the whole temperature range 4-293 K. Figure 1 shows the P6/P7 spectra observed at 8 K in dark.

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; in 4H-SiC the axially symmetric D and anisotropic E values of the fine structure parameter (in unit of 10^{-4} cm^{-1}) deduced from the fits to the angular dependences are: D(P6b) = D(P7b) = 447, D(P6'b) = 436, D(P7'b) = 408, E(P7b) = 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. In Ref. 13 the P6 and P6'(also P6'') family spectra were attributed to $V_CC_{Si}^{2+}$ and $V_CC_{Si}(Si_CC_{Si})$ complex defects, respectively. In our samples, we did not observe the P6'c and P6'' spectra.

Figures 2(a) and 2(b) show the detailed hf structure of the low-field lines P6b and P6'b in HPSI 4H- and 6H-SiC, respectively. From the intensity ratio between the two outer hf lines and the main lines of ~3.3-3.4 %, which is approximately the natural abundance of three ^{13}C nuclei (I=1/2, 1.11%), these hf lines are assigned to the hf interaction with three nearest C neighbors (labeled C_I). Using a field modulation amplitude of 0.01 mT, the two inner hf structures can be well-resolved for the P6'b line in 4H-SiC [Fig. 2(a)]. 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 simulation of the P6b and P6'b lines and their hf structures includes the hf interactions with following atoms: (i) 3 C_I for the outer hf, (ii) 3 Si_{IIa} (on the bond along the *c* axis) and 6 Si_{IIb} (in the basal plane) for the two inner hf, (iii) 3 nearest Si_I neighbors of V_C for the unresolved shoulders. As can be seen in ×10 scale spectra in Figs. 2(a) and 2(b), the simulation fits perfectly the observed spectra, not only the intensity of the hf lines but also their detailed superhyperfine structures. The C_I hf structure was also detected at some other directions and the C_I hf tensors of the P6b and P6'b

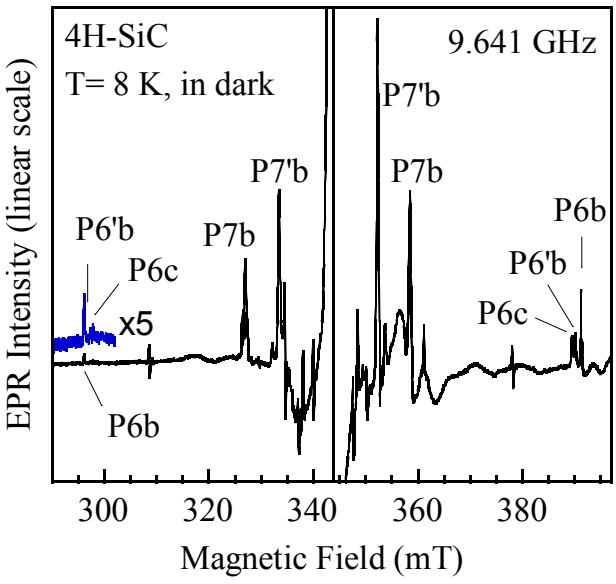

Fig. 1: EPR spectra of the P6/P7 centers in electron-irradiated and annealed n-type 4H-SiC measured for ***B*** || ***c*** at 8 K in dark.

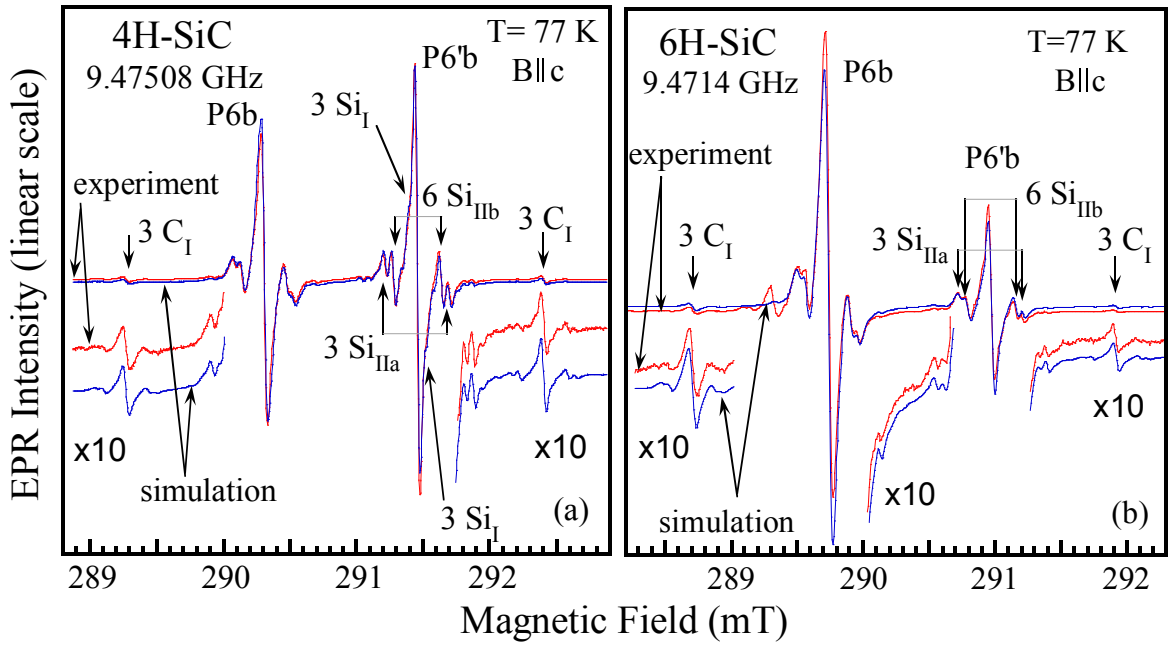

Fig.2: Part of the P6b and P6'b spectra in electron-irradiated and annealed (850 °C) HPSI (a) 4H- and (b) 6H-SiC recorded at 77 K for ***B*** || ***c*** showing hf structures of 3 nearest C_I and 3 Si_{IIa} and 6 Si_{IIb} in the second neighbor shell of V_{Si}. The simulations using the hf parameters and line width obtained from experiments are plotted for comparison. Detailed structures of hf lines can be seen in ×10 scale inserts of experimental and simulated spectra.

centers in 4H-SiC could be determined. Their principal values are summarized in Table 1. The angle between the principal *z*-axis of the C_I hf tensor of P6b and P6'b centers in 4H-SiC is 73°.

For the P7b and P7'b centers in both 4H-and 6H-SiC, the hf structure due to the interaction with three C_I 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 the experimental error, the inner hf interactions of P6b and P6'b are isotropic. Our observation of the P6/P7 signals at low temperatures in dark confirms that the centers are related to the triplet ground state but not the photo-excited state as previously suggested [1,3]. The observed hf interactions with the nearest and second neighbors suggest that these centers may be the divacancy in the neutral charge state, $V_CV_{Si}^0$.

The divacancy model for the P6/P7 centers is supported by recent *ab initio* supercell calculations of the neutral divacancy in 4H-SiC by Gali et al [11]. As can be seen in Table 1, the calculated hf parameters for Si and C neighbors of the divacancy are in good agreement with the values obtained by EPR. Comparing the calculated hf parameters of three C_I neighbors of $V_CV_{Si}^0$ in the hexagonal-

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. The calculated values for the neutral divacancy of C_{3v} symmetry at the hexagonal (hh) and cubic (kk) sites in 4H-SiC from Ref. 11 are given for comparison. The angle between the principal z-axis of the ***A*** tensor and the *c* axis is 73° for all the centers. The number of equivalent atoms is shown in parentheses.

Center	P6b			$(V_{Si}V_C)^0$ (hh) [11]			P6'b			$(V_{Si}V_C)^0$ (kk) [11]		
	A_{xx}	A_{yy}	A_{zz}	A_{xx}	A_{yy}	A_{zz}	A_{xx}	A_{yy}	A_{zz}	A_{xx}	A_{yy}	A_{zz}
C_I (×3)	53	50	110	55	56	116	47	45	104	49	49	110
Si_{IIa} (×3)	12	12	12	9	9	9	13	13	13	10	10	9
Si_{IIb} (×6)	9	9	9	9	9	8	10	10	10	10	10	9
Si_I (×3)	3	3	3	3	4	5	3	3	3	1	1	2

hexagonal (hh) and cubic-cubic (kk) configurations with the experimental values of the P6b and P6'b centers in 4H-SiC, we assign P6b and P6'b to the axial (C_{3v}) configuration of the neutral divacancy at the hexagonal and cubic lattice site, respectively. The calculated (+/0) and (0/–) levels of the neutral divacancy are at ~0.5 eV and ~1.4 eV above the valence band, respectively [11]. The neutral charge state with S=1 is the ground state of the divacancy when the Fermi-level is in this range.

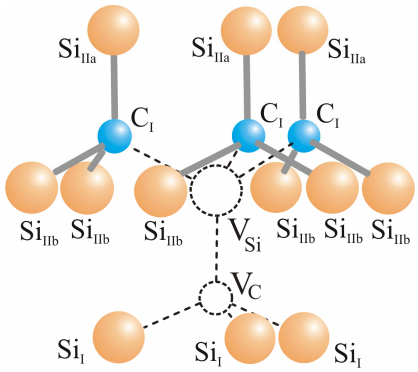

Fig. 3: Carbon and silicon neighbors of a divacancy in axial symmetry.

Conclusion

Based on the EPR observation and *ab initio* supercell calculations we identified the P6/P7 centers in 4H- and 6H-SiC to be related to the ground triplet state of the neutral divacancy, $V_CV_{Si}^0$, in the axial/non-axial (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} (~59-60%) whereas it is negligible on the nearest Si neighbors of V_C. The vacancy model for the 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.

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