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Divacancy and its identification: Theory

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Abstract. Only recently the well-resolved hyperfine structure of the P6/P7 EPR center has been experimentally observed. Based on the calculated hyperfine tensors we assign the P6/P7 center to the high spin state neutral divacancy, which is the ground state in agreement with the experiment. We propose a mechanism to explain the loss of divacancy signal at high temperature annealing in semi-insulating SiC samples. We discuss the possible correlation between the divacancy and some photoluminescence centers.

Introduction

The divacancy (V_C-V_{Si}), the close pair of a carbon vacancy and a silicon vacancy, was considered as the origin of the thermally very stable D_I photoluminescence center or of the Z_1/Z_2 DLTS centers in 6H-SiC [1]. Although the divacancy was indeed found to be a very stable defect by theory [2], no correlation between the divacancy and the D_I or Z_1/Z_2 centers could be established. The P6/P7 centers were first observed in 6H-SiC by electron paramagnetic resonance (EPR) under photo-excitation by Vainer and Il'in [3] and were tentatively assigned to the excited state of the divacancy. Later, based on a combined experimental and theoretical study the P6/P7 EPR centers with C_{3v}/C_{1h} symmetry were reassigned to the paramagnetic excited state of the double positively charged carbon vacancy-antisite complex ($(V_C$-$C_{Si})^{2+}$) in n-type 6H-SiC [4]. This reassignment of the P6/P7 centers was based on the observation of a weak hyperfine (HF) structure assigned to the interaction with one ^{13}C nucleus (I=1/2, 1.1% natural abundance). In recent EPR studies by Son and co-workers on P6/P7 centers, however, this HF structure was shown to be due to the HF interaction with three ^{13}C ligands instead of one in 6H and 4H-SiC [5]. Hence, the $(V_C$-$C_{Si})^{2+}$-model can no longer be valid and instead the model of a divacancy was suggested. In the present paper we confirm this model by a theoretical analysis based on *ab initio* supercell methods.

Method

The defect was represented by large supercells including up to 256 atoms. First the atomic structure was obtained using the pseudopotential method as outlined in Refs. [6] and [7] and then the HF tensors were calculated by the all electron PAW method [8]. Calculations were preformed with a scissors-operator to assess the effect of the LSDA band gap failure on the calculated ionization energies. Within the expected accuracy the scissor-correction does not affect the calculated HF tensors.

Neutral divacancy: electronic structure and its hyperfine signature

In V_C-V_{Si} the three C-dangling bonds and three Si-dangling bonds create six defect levels. In the axial configuration possessing C_{3v} symmetry two a_1 levels fall in the valence band while two, double degenerate e-levels lie in the gap. The lower e-level is formed by the dangling bonds of the C-ligands of V_{Si} below the midgap while the higher e-level is due to the Si-ligands of V_C above the midgap. In the neutral charge state of V_C-V_{Si} six electrons occupy the two resonances and the lower e-level. We found that the S=1 state is the ground state of the neutral divacancy, which hence is Jahn-Teller stable conserving the symmetry. The calculated (+/0) and (0/-) levels are at about 0.5 eV and 1.4 eV above the valence band edge, respectively. If the Fermi-level of the SiC sample is in this range then the EPR signal of the neutral divacancy should be detectable in the dark.

In 4H-SiC two configurations with C_{3v} symmetry (P6b, P6'b) and two configurations with C_{1h} symmetry have been detected by EPR [5]. Since detailed experimental information is available for the defects aligned along the c-axis possessing the C_{3v} symmetry we show here the calculated hf constants for these defects in Table 1. As expected from the analysis of the electronic structure the spin density is mainly localized on the C-ligands of V_{Si} and their neighbors while the contribution of the V_C-ligands is negligible. In the C_{1h} configurations the largest hf constant was found on one ^{13}C ligand, about 10 MHz higher than that of C_I (cf. Fig 1), while the other two C-atoms of V_{Si} have a few MHz smaller hf-constants. The hyperfine signals of these C-ligands of the non-axial centers were not resolved for all the angles in the experiment, nevertheless, when the magnetic field was at ∼70 degrees from the c-axis, the hf constant of one C is about 9 MHz larger than that of the other two C atoms, which also supports our model. For the axial and non-axial configurations the electronic structure and the overall localization of the spin density are very similar, except for a small splitting due to the symmetry lowering from C_{3v} to C_{1h}. For the axial-configurations the small difference between the cubic and hexagonal sites can be distinguished clearly, therefore, we assign P6b and P6'b to the C_{3v} configurations of the neutral divacancy at the hexagonal and cubic site, respectively.

Divacancy: a step in the formation of large vacancy aggregates?

According to earlier theoretical results [9] vacancy migration is favorable in n-type SiC. The silicon vacancy should start to diffuse at about 600-700 °C, which then can form a divacancy with the carbon vacancy. At higher temperatures the migration of the carbon vacancy should supplement this process. In p-type material the migration of vacancies is less favorable [9]. In heavily electron irradiated n-type SiC the formed defects can pin the Fermi-level below midgap. As a consequence, after annealing the EPR signal of the neutral V_C-V_{Si} can be detected in the

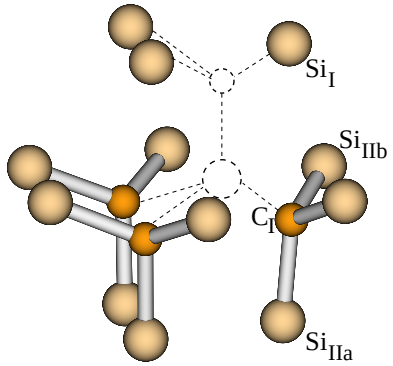

Fig. 1: The geometry of the axial $(V_C\text{-}V_{Si})^0$ complex (at hexagonal site).

	P6b, Ref. [5]			V_C(h)-V_{Si}(h)			P6'b, Ref. [5]			V_C(k)-V_{Si}(k)		
	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

Table 1: Principal values of HF-tensors in MHz of axial $(V_C\text{-}V_{Si})^0$ defects in comparison with those of P6-centers. The angle between the principal z-axis of the A-tensor of C_I and the c-axis is 73° for both centers in the experiment and in the calculations as well. The atoms are labeled according to Fig. 1.

dark even at 4 K [5]. This is consistent with the neutral divacancy model. In as-grown semi-insulating HPSI SiC samples the divacancy signal starts to drop at annealing temperatures above 1500-1600 °C. This can be explained either by dissociation of the divacancy or forming larger aggregates of vacancies [9, 10]. The diffusion of V_C should contribute to the formation of the aggregates. We have estimated the dissociation barriers of V_{Si}-$(V_C)_n$ defects (n=1-4) from the binding energy of additional carbon vacancies and the diffusion barrier of V_C. The dissociation barrier amounts to 7.5 eV. Thus, the kinetic formation of thermally stable vacancy aggregates is a feasible process to explain the annealing of V_C-V_{Si} in SiC. We also note that EPR signals associated with multivacancy centers were indeed proposed in heavily neutron irradiated Lely-grown SiC [11].

Divacancy: its excitation and possible correlation with photoluminescence centers

It was found that excitation of about 1.1 eV is needed to detect P6/P7 EPR signals in p-type SiC [5]. According to the theory if the Fermi-level was below the (+/0) level of the divacancy in the sample then excitation is required to make the divacancy neutral. We have calculated the vertical ionization energies within the ΔSCF-method. The energies of the (+)→(0) excitation to the S=1 ground state and to the S=0 excited state are obtained approximately and amount to 0.9 and 1.0 eV, respectively. These values are consistent with the experimental findings. The intensity of the P6/P7 EPR signal can be also increased under illumination or using magnetic circular dichroism under absorption in n-type SiC [4, 5]. In a theoretical analysis the calculation of the excitation energies of the neutral and the negatively charged divacancy

are not accessible within the present approach (the inclusion of configurational interaction is required), therefore we do not comment on the possible excitation mechanisms in these cases. Furthermore, photoluminescence centers (PL) were found in the infrared (IR) region associated with defects in SiC. The so-called UD-2 and V_C-C_{Si} PL centers were proposed to correlate with the P6/P7 EPR centers [12, 13]. In 4H-SiC four zero-phonon lines (ZPL) were detected for both PL centers (V_C-C_{Si}: ∼1.00-1.05 eV, UD-2: ∼1.10-1.15 eV). Assuming that free holes are injected during the PL process the V_C-C_{Si} and UD-2 PL centers might be related to the (+)→(0)(S=1) and to the (+)→(0)(S=0) transitions. Correlation studies between the P6/P7 EPR centers and these PL centers may reveal the possibility of the afore-mentioned processes.

Conclusion

In conclusion, the P6/P7 EPR centers can be identified as the axial/non-axial configuration of the neutral divacancy in SiC for the following reasons: the theory explains (i) that the S=1 state is the ground state (ii) the number of configurations and their symmetry (iii) the measured hyperfine tensors (iv) the appearance and disappearance of the P6/P7 signal in annealed SiC samples by the migration and aggregation of vacancies. We also provided excitation energies between the (+) and (0) states. The possible relation to the known PL centers and to the photo-excitation was discussed.

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