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Signature of the Negative Carbon Vacancy-Antisite Complex

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Abstract. The negative carbon vacancy antisite complex is analysed by *ab initio* theory in view of the SI5 EPR-center. The complex occurs in a Jahn-Teller distorted ground state and a meta stable state. This and the calculated hyperfine structure agree nicely with the temperature dependent EPR spectra of SI5. An interpretation of the photo-EPR experiments is proposed.

Introduction

In SiC the silicon vacancy (V_{Si}) is a metastable defect [1, 2] that transforms in p-type and intrinsic material into the stable carbon vacancy-antisite complex (V_C-C_{Si}). However, direct evidence of the V_C-C_{Si} complex is scarce. Recently, the V_C-C_{Si} complex was suggested as a model for the P6/P7 center [3]. Our investigations, however, show that this identification has to be revised in favor of the earlier divacancy model [4]. In recent experiments on high purity semi-insulating (HPSI) and irradiated n-type 4H-SiC the SI5-center was identified as a highly abundant defect [5, 6] with a characteristic temperature dependent hyperfine (HF) signature. At low temperatures ($< 50\,\mathrm{K}$) the center possesses C_{1h}-symmetry and a large HF-tensor due to two Si-atoms, while at higher temperatures C_{3v}-symmetry and one large Si HF-tensor is observed. Photo-EPR experiments located the Fermi-level at $E_C - 1.1$ eV suggesting a negative charge state of the defect center [5, 6]. In this paper we report the theoretical identification of the SI5-center as the negative V_C-C_{Si} complex and the theoretical interpretation of the photo-EPR spectra. We revise the earlier tentative model of a divacancy [5, 7] that was suggested by the high symmetry of the previous high temperature EPR-spectra and the missing large Si HF-tensor.

Method

Our theoretical analysis of the negative carbon vacancy-antisite complex is based on *ab initio* supercell methods within the framework of the density functional theory and the local density approximation. Large supercells equivalent to 288 lattice sites were used to represent the complex in the 4H polytype. Its electronic properties and the relaxation were obtained with an efficient pseudopotential

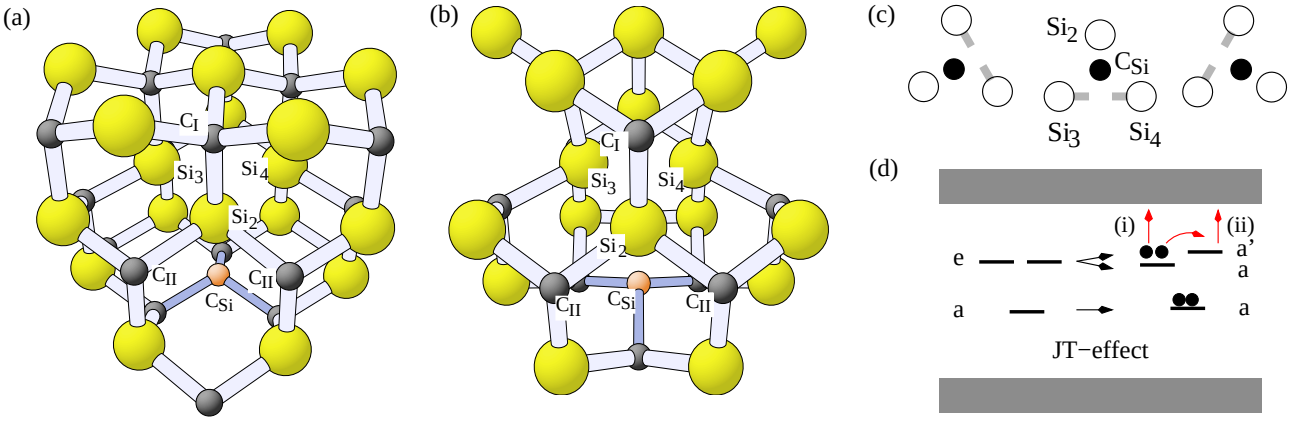

Fig. 1: The axial V_C-C_{Si} complex. Geometry of the complex at (a) cubic and (b) hexagonal sites. (c) equivalent orientations in the Jahn-Teller groundstate (view along c-axis). (d) defect levels, the direct and indirect ionization (path i and ii, respectively) are indicated by arrows.

method (for details cf. Ref. [8]). To assess the effect of the artifically low band gap we also included a scissors-operator in the calculation. The hyperfine values were than calculated using the all-electron PAW-method (for details cf. Ref. [9]). The photo excitation spectrum was assessed using the Δ-SCF approach.

HF-signature and excitation scheme of V_C-C_{Si}

In the carbon vacancy-antisite complex, the vacancy and the antisite can occupy neighboring cubic or hexagonal sites. When both sites are cubic or hexagonal the complex is aligned with the c-axis of the crystal and possesses a lower non-degenerate and a higher doubly degenerate level (a- and e-level, respectively) within the band gap. In the following we address the axially aligned complexes as the HF-signature of the other non-axial configurations has so far not been identified in the EPR-spectra. In the negative charge state the e-level is occupied by one electron giving rise to a Jahn-Teller distortion that lowers the symmetry to C_{1h}. In the Jahn-Teller ground state (JT) the spin density is mainly localized on two silicon dangling bonds of V_C (on Si_3 and Si_4 in Fig. 1) with antibonding character. Besides this configuration we have found a metastable (MT) configuration with the spin density mainly located at one dangling bond (on Si_2 in Fig. 1). It has only a slightly higher energy (by 0.02 eV) and will not be relevant at sufficiently low temperatures. In both states three rotationally equivalent (with respect to the c-axis) configurations exist with a different orientation of the respective dangling bond(s) (cf. Fig. 1c). The thermal motion of the atoms may induce a continuous switching between the equivalent configurations and a reorientation of the respective dangling bond(s). This leads to temperature dependent HF-tensors as seen for the SI5-center. The calculated HF-tensors of the states JT and MT are listed in Table 1 together with the experimental values obtained at 30 K (C_{1h}-symmetry) and at 100 K (C_{3v}-symmetry). We considered the direct ligands of V_C and the carbon neighbor as shown in Fig. 1a,b. For the configuration JT we find large HF-tensors on the two vacancy neighbors Si_3 and Si_4 and a much smaller one on Si_2 as expected from an inspection of the spin density. This finding nicely agrees with the HF-tensor for two Si atoms deduced from the EPR spectrum at 30 K. Note, that the difference between the calculated HF-tensors of the cubic and hexagonal complexes is smaller than the expected accuracy. A qualitative destinction between the two sites should be possible from the HF-tensors of the third and fourth neighbor shell. With the available experimental data for the SI5-center these HF-tensors could not be resolved and it is well possible that both sites contributed

	V_C-C_{Si} (k), JT			V_C-C_{Si} (h), JT				SI5 30K, Ref. [6]		
	$A_\perp$, $A_\parallel$ [mT]			$A_\perp$, $A_\parallel$ [mT]				$A_\perp$, $A_\parallel$ [mT]		
Si_2	0.3	0.3	0.1	0.8	0.8	0.3	Si (2×)	10.16	10.04	12.9
$Si_{3,4}$	10.8	10.9	13.8	11.2	11.3	14.2	C (2×)	1.3	1.3	1.8
C_{Si}	0.5	0.5	0.5	0.4	0.4	0.4				
C_{II}	1.3	1.3	1.7	1.4	1.4	1.7				
	V_C-C_{Si} (k), MT			V_C-C_{Si} (h), MT				SI5 100K, Ref. [6]		
	$A_\perp$, $A_\parallel$ [mT]			$A_\perp$, $A_\parallel$ [mT]				$A_\perp$, $A_\parallel$ [mT]		
Si_2	15.9	15.9	20.3	15.8	15.8	20.1	Si (1×)	6.38	6.38	8.02
$Si_{3,4}$	2.7	2.7	3.6	3.2	3.3	4.3	C (1×)	1.77	1.77	2.22
$\langle Si_{2-4} \rangle$	7.2	7.6	8.6	7.5	7.9	8.9				
C_{Si}	0.1	0.1	0.1	0.2	0.2	0.2				
C_I	0.9	0.9	1.3	1.3	1.3	1.7				

Table 1: HF-tensors of V_C-C_{Si}^- in comparison with those of the SI5-center. The atoms are labeled according to Fig. 1. Angular braces refer to configurational averages (cf. text).

to the SI5-spectrum. The carbon antisite (C_{Si}) possesses a much smaller HF-tensor than the second carbon neighbors of the vacancy, since the C_{Si} dangling bond mainly contributes to the fully occupied non-degenerate a-level. This explains the fact that this HF-interaction was not resolved in the experiment. Instead a HF-interaction with two C-atoms was found, which most likely originated from the second carbon neighbors of the vacancy as suggested by the agreement with the tensors C_{II}. For the MT state we find a large HF-tensor on Si_2 and smaller ones on Si_3 and Si_4 as suggested by the spin density of the e-levels. As for configuration JT only much smaller HF-tensors are found for C_{Si} and the other ligands of the complex. Qualitatively, these findings agree with the SI5-spectrum measured at 100 K. In particular only one large Si HF-interaction is observed. The experimentally observed HF-interaction with one C-atom cannot be explained by the antisite but most likely arises from the carbon neighbor C_I of Si_2. For a more quantitative comparison the motional reorientation is important. We approximately included this effects by taking the average of the respective Si HF-tensors for the three equivalent reorientations. The principal values were calculated for the averaged HF-tensor and are denoted by angular braces in Table 1. The averaged Si HF-tensor indeed agrees well with the experimental one.

In HPSI-SiC [5] and irradiated n-type SiC [6], the SI5-signal could be significantly enhanced by illumination. As a function of the photon energy [6] the SI5-signal (at 77 K) increased in three steps with thresholds at 0.65 eV, 0.9 eV and 1.1 eV. Experimentally the Fermi-level was located at $E_C - 1.1$ eV. The photo-EPR experiments suggest that the concentration of V_C-C_{Si}^{2-} should dominate over V_C-C_{Si}^-. The calculated ionization level (-|2-) of $E_C - 1.1$ eV ($E_C - 0.9$ eV) of the cubic (hexagonal) complex as obtained for the largest supercell agrees with this conclusion within the limited accuracy of the calculation. We analyzed the photo ionization of the V_C-C_{Si}^{2-} using the approximate Δ-SCF approach. V_C-C_{Si}^{2-} displays a similar Jahn-Teller effect as V_C-C_{Si}^-. Illumination can directly ionize the complex (path (i) in Fig. 1d), thus recovering the paramagnetic state. Alternatively an excited state of the complex and a subsequent ionization of this state could occur (path (ii) in Fig. 1d). In the excited state each of the split e-levels is occupied by one electron. Due to the Frank-Condon shifts of this excited state with respect to the vertical transition a broader band of excitation energies occurs with

an optical line shape governed by the Huang-Rhys factors. To estimate the effect we also calculated the zero-phonon transition including relaxations of the excited state. For the direct vertical ionization of the Jahn-Teller ground state we obtain 1.4 eV (1.5 eV) for the hexagonal (cubic) complex. These values are 0.3 eV higher than the experimentally deduced upper threshold but still within the expected accuracy for such approximate calculations (cf. e.g. [3]). For the vertical internal transition we obtain excitation energies of 0.9 eV (1.3 eV). The zero phonon transition energy amounts to 0.6 eV (0.6 eV). For both the vertical and the zero-phonon transition a second photon of the same energy can ionize the excited defect state. The ionization energies of the metastable configuration are lower by 0.2-0.3 eV. We obtain 1.1 eV for the direct ionization of the hexagonal complex. The exciation energy of the indirect process amounts to 0.7 eV (vertical transition) and 0.3 eV (zero-phonon line). Our results suggest an interpretation of the lower thresholds as the indirect ionization of the complex. The direct ionization of V_C-C_{Si}^{2-} should account for the highest threshold.

Conclusion

In conclusion, the present theoretical analysis of the negative axial carbon vacancy-antisite complex provides an identification of the SI5 EPR-center with this complex. A Jahn-Teller effect underlies the temperature dependent HF-signature. Based on our calculations we propose an interpretation of the observed photo-EPR thresholds.

Acknowledgments

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