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The silicon vacancy in SiC

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ABSTRACT

The isolated silicon vacancy is one of the basic intrinsic defects in SiC. We present new experimental data as well as new calculations on the silicon vacancy defect levels and a new model that explains the optical transitions and the magnetic resonance signals observed as occurring in the singly negative charge state of the silicon vacancy in 4H and 6H SiC.

1. Introduction

The isolated silicon vacancy (V_{Si}) is one of the basic intrinsic defects in SiC. Due to the existence of inequivalent Si lattice sites there are in 4H SiC two V_{Si}, one hexagonal (h) and one quasi-cubic (k); while in 6H SiC there are three V_{Si}, one hexagonal (h) and two quasi-cubic (k_1 and k_2), each of them having several different charge states in the band gap. The reported photoluminescence (PL) and magnetic resonance signals attributed to V_{Si} are not conclusive concerning the origin, site, charge state etc of this defect.

We will here present (1) new experimental data as well as (2) new calculations on the V_{Si} defect levels and (3) a new model that explains the optical transitions and the magnetic resonance signals observed as occurring in the singly negative charge state of the silicon vacancy (V_{Si}^-) in 4H and 6H SiC.

2. Experimental and calculations

Optical spectroscopy. The samples have been investigated using Fourier transform infrared spectroscopy (FTIR) absorption. We have also measured the PL using a single monochromator and a multichannel CCD detector. In the PL experiments the samples were excited with a Ti:Sapphire laser at 752.5 nm.

Magnetic resonance. Optical detection of magnetic resonance (ODMR) experiments were performed on a modified X-band (~9.23 GHz) Bruker spectrometer. The UV multi-lines of an ion Ar laser were used for excitation. For resonance excitation, a tuneable Ti:Sapphire laser was used. Electron paramagnetic resonance (EPR) experiments were carried out on an X-band E580 Elexsys spectrometer. The sample temperature could be regulated between 5 K and room temperature.

Calculations. The calculations have been carried out in a large 576-atom supercell using the Γ-point for k-point sampling. We could describe the localized defect states accurately. The Γ-point was needed to maintain the degenerate states, while the charge density was convergent in this large supercell at the same time. We have used density functional theory within local density approximation for the Hamiltonian which gives reliable order of the one-electron defect levels.

3. Previous results

There are two main no-phonon PL lines V1 and V2 in 4H SiC and three V1, V2 and V3 in 6H SiC that are related to V_{Si} [1,2], see Fig. 1. For both polytypes V1 has a high temperature companion V1′. No V2′ or V3′ lines have been observed. All PL lines are also visible in absorption. The lines were reported not to split in magnetic field [2]. At low temperatures two ODMR signals (T_{V1a}, T_{V1b} and so on) could be detected via each PL line. All ODMR signals were reported to be triplets ($S=1$) with isotropic g values

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close to 2. By selective excitation in each line, only the "a" ODMR signal of that line could be detected [1]. The polarization dependence of several of the lines was not conclusive. Later it was unambiguously shown that the T_{V2a} signal in 4H SiC had S=3/2 [3,4] and that it could be detected by EPR in darkness in some samples [5]. In addition, another EPR center with negligible zero-field splitting and S=3/2 was reported as V_{Si}^- in Ref. [6].

4. The model

In the V_{Si}, four C dangling bonds point to the vacant site. The bonds are too localized to overlap. Instead, the C atoms relax outwards and basically keep the C_{3v} symmetry independently of its charge state or its site in 4H SiC. The dangling bonds form two a_1 (degeneracy 2 if spin is included) levels and one e (degeneracy 4 if spin is included) level. The first a_1 level is resonant with the valence band not far from the top of it, while the remaining a_1 and e levels are very close (a_1 below e) at around 0.5–0.7 eV above the valence band edge in the neutral charge state increasing to about 0.9 eV in the singly negative charge state V_{Si}^-. In V_{Si}^-, there are five electrons distributed among the a_1, a_1 and e one-electron levels, (Fig. 2). The possible multiplets are listed in Table 1. If there are two electrons in the lowest a_1 level resonant with the valence band, one electron in the next a_1 level and two electrons in the e level, the electronic configuration can be denoted as $a_1^2a_1^1e^2$.

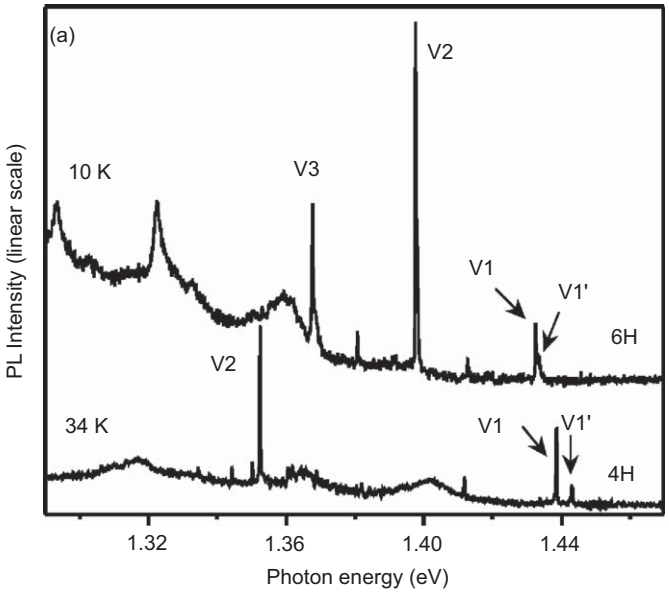

Fig. 1. Silicon vacancy related PL lines in 4H and 6H SiC (from Ref. [2]).

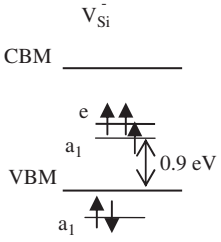

Fig. 2. The spins of the three electrons in the band gap in the singly negative charge state of the silicon vacancy line (S=3/2) in the ground state $^4A_2$.

Keeping the lowest a_1 level full yields the only configuration that allows a high-spin (S=3/2) multiplet state $^4A_2$, which is also expected to be the ground state. This is experimentally confirmed by the EPR observation of T_{V2a} in darkness.

The a_1 and e levels in the band gap are so close that it is relevant to consider also the T_d case when they have merged to a t_2 (degeneracy 6 if spin is included) level. The possible multiplets in that case are also listed in Table 1. The energy separation between the different multiplets originating from the same electronic configuration is expected to be 0.5–1 eV in the T_d case, which is only slightly smaller than the expected energy separation between different electronic configurations. The additional splitting of the multiplets induced by the hexagonal field going from T_d to C_{3v} symmetry will be much smaller.

In principle all multiplets with the same symmetry label in Table 1 will mix. For instance, there are two $^4A_2$ multiplets: $^4A_2(a_1^2a_1^1e^2)$ and $^4A_2(a_1^1a_1^2e^2)$. Interaction between them will increase their energy separation and thus lower the energy of the $^4A_2$ multiplet with the lowest energy. However, if the energy separation between the multiplets is large the effect will be small. In the same way low-lying doublets, (see Table 1), may be pushed down by interaction with higher-lying doublets of the same symmetry. As mentioned above, we find experimentally that the high-spin state is the ground state for V_{Si}^-.

5. Optical selection rules

An optical transition between an initial and final state having the same spin S is allowed if the direct product $\Gamma_{initial} \otimes \Gamma_d \otimes \Gamma_{final}$ contains A_1. In C_{3v} symmetry $\Gamma_{initial}$ and Γ_{final} are either A_1, A_2 or E. Γ_d is A_1 for light polarized parallel to the c axis and E for light

Table 1
Possible multiplets formed by the five electrons in V_{Si}^- in different electronic configurations in C_{3v} and T_d symmetry.

Electronic configuration		Possible multiplets
C_{3v}	T_d	
$a_1^2a_1^2e^1$		^2E
$a_1^2a_1^1e^2$		$^4A_2$, $^2A_2$, ^2E, $^2A_1$
$a_1^1a_1^0e^3$		^2E
	$a_1^2t_2^3$	$^4A_2$, $^2T_1$, ^2E, $^2T_2$
$a_1^1a_1^2e^2$		$^4A_2$, $^2A_2$, ^2E, $^2A_1$
$a_1^1a_1^1e^3$		^4E, ^2E, ^2E
$a_1^1a_1^0e^4$		$^2A_1$
	$a_1^1t_2^4$	$^4T_1$, $^2T_1$, ^2E, $^2T_2$, $^2A_1$
$a_1^0a_1^2e^3$		^2E
$a_1^0a_1^1e^4$		$^2A_1$
	$a_1^0t_2^5$	$^2T_2$

Table 2
Optical transitions between multiplets in C_{3v} symmetry.

ΔS=0	A_1	A_2	E
A_1	∥	0	⊥
A_2		∥	⊥
E			∥, ⊥

∥: allowed if polarized ∥c axis, ⊥: allowed if polarized ⊥c axis, 0: forbidden.