



Vacancy clusters created via room temperature irradiation in 6H-SiC

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ABSTRACT

In non-annealed 6H-SiC samples that were electron irradiated at low temperature, a new EPR signal due to a $S=1$ defect center with exceptionally large zero-field splitting ($D=+652 \times 10^{-4} \text{ cm}^{-1}$, $E=-8 \times 10^{-4} \text{ cm}^{-1}$) has been observed under illumination. A positive sign of D demonstrates that the spin-orbit contribution to the zero-field splitting exceeds by far that of the spin-spin interaction. A principal axis of the fine-structure tilted by 59° against the crystal c -axis as well as the exceptionally high zero-field splitting D can be qualitatively understood by the occurrence of additional close-lying defect levels in defect clusters resulting in comparatively large second-order spin-orbit coupling. A tentative assignment to vacancy clusters is supported by the observed annealing behavior.

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1. Introduction

Since dopant atoms hardly diffuse into SiC, other methods like ion implantation are the preferred doping methods, but result in various radiation-induced defects, which make doping ineffective. High temperature annealing is required to reduce these unwanted by-products. Valuable information of the annealing process can be gained from the non-annealed samples, which provide good insight in the conditions before the annealing process. It is quite intuitive that the omnipresent vacancies introduced by the radiation are compensated by the creation of interstitials. It is common consensus that mobile split-interstitials, either intrinsic ones like the carbon split-interstitial (CC_C) or those including dopants, e.g. (NC_C), play a central role in the beginning of the annealing process [1]. In spite of their importance, these defects are discussed controversially, and some of them could still not conclusively be assigned to experimentally observed electron paramagnetic resonance (EPR) spectra (for an overview, see Ref. [2] and references therein). The situation is complicated, since the centers can appear in different charge and spin states. The observability of the various defect states depends, thus, strongly on the background doping and details of the annealing history, determining the energetic position of the Fermi level. In some cases (see e.g. the $\text{EI3/EI3}'$ [3,4]) the various triplet centers differ only in the zero-field splitting (ZFS), whereby low-temperature EPR measurements are required to obtain the 'true' value. Otherwise, the ZFS is considerably reduced by thermal effects (see e.g. the D7 spectrum in 6H-SiC [5,6]).

In this work, we show that the occurrence of the spectra depends not only on the background doping (p -type [3,4] or n -type [7]) and details of the post-radiation annealing [8]. It turns out that the kind of defects critically depends on the conditions under which the irradiation itself was performed: In n -type 6H-SiC samples cooled to 77 K during irradiation, carbon split-interstitials CC_C (so-called Eln spectra) are present without any post-annealing treatment [7]. The non-annealed samples also contain V_{Si} but no further paramagnetic defects. If the electron irradiation is performed at room temperature the Eln remains the dominant EPR spectrum, however, besides V_{Si} further spectra are observed. Some of them are well-known from irradiated p -type SiC, whereby differences between p - and n -type materials can be mostly explained by Fermi level arguments. However, at least one of the spectra (labeled Elm) of unknown microscopic origin was not reported in the literature before. The new triplet spectrum has the strongest fine-structure constant ($D=+652 \times 10^{-4} \text{ cm}^{-1}$) observed so far in SiC for intrinsic defects.

2. Experimental details

The sample investigated in this work belongs to a series of 6H-SiC samples from a commercial wafer and was n -type due to nitrogen donors ($1 \times 10^{18} \text{ cm}^{-3}$). The sample was irradiated at room temperature with high-energy electrons (2 MeV) without any cooling so that during irradiation the sample was locally heated within the range of 200–300 °C. The dose of irradiation was about $1 \times 10^{18} \text{ cm}^{-2}$. After irradiation, the non-annealed sample was investigated with electron paramagnetic resonance (EPR). The EPR measurements were performed on a homemade X-band (9.87 GHz) spectrometer with a cylindrical TE_{011} cavity and a He gas flow cryosystem. A 100 kHz field modulation in

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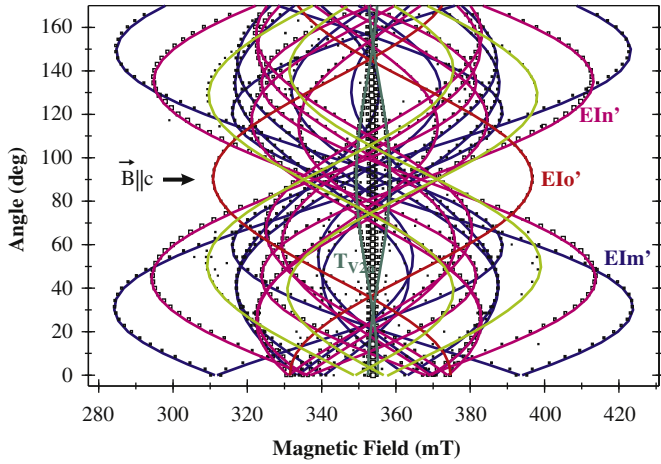


Fig. 1. (Color online) Angular dependence of room temperature electron irradiated 6H-SiC measured at 12 K under illumination (white light, halogen lamp). The dots are the experimental EPR line positions, the full lines are determined from the spin-Hamiltonian parameters given in Table 1. For the labels of the triplet-lines see also Table 1, for that of V_{Si} and T_{v2a} see text. All remaining lines belong to other orientations of these defects.

combination with lock-in detection has been applied for signal improvement. During the EPR measurements, the sample was cooled down to 12 K in order to minimize thermal effects onto the ZFS. Furthermore, the sample was illuminated with the white light of a halogen lamp (150 W). Field calibrations were done using the hyperfine satellites of the N donors as a marker for an accurate g -factor determination.

Under illumination, our measurements show a set of EPR-lines which can be attributed to six different centers. Fig. 1 shows the angular dependence of these lines. The apparently isotropic lines at around 353 mT arise from the negatively charged Si vacancy V_{Si} with total spin $S=3/2$ [9,10] and the nitrogen donors. The remaining part of the EPR-spectra consists of four EPR-lines showing a clearly resolved fine-structure splitting. The spin state of one of them, the so-called T_{v2a} line with the smallest ZFS (below $20 \times 10^{-4} \text{ cm}^{-1}$) has been subject to a controversial discussion in the literature. It is more or less accepted that the V_{Si} related center is either an $S=1$ triplet state of the neutral silicon vacancy [11–14] or an $S=3/2$ high-spin state [15–18]. The other three spectra labeled EIo' , EIn' , Elm' are clearly due to $S=1$ defect centers whereby at least the latter has not been reported in the literature before. Without illumination the signals of the triplet centers, the T_{v2a} center and the signals of the N donors vanish. Only the isotropic signal of the negatively charged silicon vacancy remains.

3. Results and discussion

The EPR triplet spectra were analyzed with the usual effective spin-Hamiltonian including the Zeeman and fine-structure terms

$$H = \mu_B \vec{B} \cdot \underline{\underline{g}} \cdot \vec{S} + \vec{S} \cdot \underline{\underline{D}} \cdot \vec{S} = \mu_B \vec{B} \cdot \underline{\underline{g}} \cdot \vec{S} + D[S_z^2 - \frac{1}{3}S(S+1)] + E(S_x^2 - S_y^2)$$

resulting in the electronic g -tensor and the isotropic part D (zero-field splitting) and the anisotropic part E of the fine structure. The spectra are characterized by a wide range of fine-structure splittings. The nearly axial spectrum EIo' ($D = -405 \times 10^{-4} \text{ cm}^{-1}$) is similar to the G6 spectrum reported in Ref. [5]. However, it is less intense and thus not in the main scope of this work. A further triplet spectrum labeled EIn' shows exactly the same g -tensor as already reported for the so-called EIn center in a 6H-SiC sample

belonging to the same series. However, with $D = 558 \times 10^{-4} \text{ cm}^{-1}$ it provides a 18% larger ZFS. By this it is very similar to the so-called W1 spectrum originally reported in Ref. [5]. With the prime, we denote the slightly elevated temperature required for the occurrence of the centers (200 °C instead of 77 K during irradiation within the sample) as already used in the case of the $EI1/EI1'$ ($S=1/2$) and $EI3/EI3'$ ($S=1$) centers in p -type SiC. It is important to note here that all members of the $EI3/EI3'$ and EIn/EIn' family show with 46° exactly the same angle between the principal axis of the fine-structure tensor and the crystal c -axis (cf. Table 1). This suggests that all the $S=1$ spectra with $\theta=46^\circ$ originate from the same or at least a similar microscopic structure. Based on the resolved hyperfine splitting due to a single ^{13}C nucleus, the EIn center has recently been attributed to a $(\text{CC})_C$ carbon split-interstitial in the two-fold positive charge state [7], stable for Fermi levels lying in the lower half of the fundamental gap. The observability of the $2+$ charge state in the nominally n -type-doped material could be a consequence of a strong shift of the Fermi level towards midgap in the sample irradiated during cooling (77 K). Assuming that under illumination at room temperature, a local heating to 200 °C is sufficient to shift back the Fermi level towards the conduction band, the EIn' center could be related to the corresponding neutral charge state. In p -type SiC, the situation is vice versa: in the non-annealed irradiated samples, the neutral charge state ($EI3$) is supported, whereas, after moderate annealing, the Fermi level is shifted back towards the valence band making positively charged states ($EI3'$) more probable. Given the very large difference in the g -tensors we cannot attribute the $EI3/EI3'$ spectra unambiguously to the same microscopic model.

The triplet spectrum labeled Elm' shows the strongest fine-structure constants observed so far in SiC for an intrinsic defect ($D = 652 \times 10^{-4} \text{ cm}^{-1}$, $E = -8 \times 10^{-4} \text{ cm}^{-1}$). Since the triplet spectra arise under illumination only, we cannot distinguish between ground states or excited states. However, we can take advantage of a partial occupation inversion within the Zeeman-levels that is induced by illumination. The inversion manifests itself in an inverted phase of the high-field line with respect to the low-field line (see Fig. 2). This allows us to determine the sign of the zero-field splitting by comparing the phase of the low-field line with that of the well-defined absorption line of the N donors. The same phase and, consequently, a positive sign of D demonstrate that the spin-orbit contribution to the zero-field splitting exceeds by far that of the spin-spin coupling [19]. The same holds in the case of the EIn' spectrum as well as for the EIn spectrum [7] showing that the fine structure of these triplet spectra is dominated by spin-orbit coupling. For the EIo' spectrum in contrast the inverted phase of the low-field line suggests a negative sign of D and by this a dominating spin-spin contribution. Only the Elm' spectrum

Table 1

Averaged g -tensor, zero-field splitting D ($\pm$ in case of unknown sign), corresponding anisotropy E and angle θ of the fine structure tensor given with respect to the crystal c -axis for the defects observed in Fig. 1.

Center	$\bar{g}$	D (10^{-4} cm^{-1})	E (10^{-4} cm^{-1})	θ (deg)	T (K)
W1 [5,6]	2.0016	± 559	7	46	100
G6 [5,6]	2.0034	± 397	0	0	100
EI3' [4]	2.0063	± 538	–	46	77
EI3 [4]	2.0063	± 559	–	46	77
EIn [7]	2.0013	± 481	5	46	10
EIn'	2.0013	± 558	7	46	12
Elm'	2.0018	± 652	–8	59	12
EIo'	2.0025	–405	0	1	12

Note that the g -tensor for EIn was corrected by second-order effects due to the strong zero-field splitting and is therefore considerably smaller than that originally given in Ref. [6].

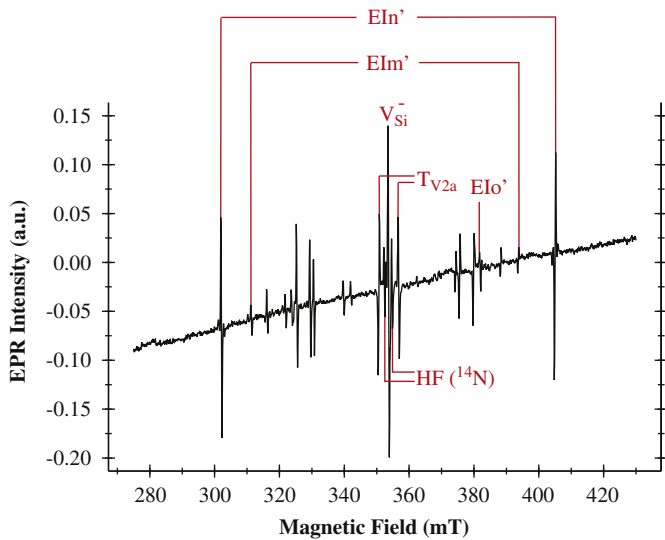


Fig. 2. Intensity of the EPR spectra [arb. u.] of room temperature electron irradiated 6H-SiC measured at 12 K under illumination with light from a halogen lamp recorded for $\theta=63^\circ$ (compare Fig. 1, resonance lines labeled according Table 1). HF(^{14}N) is the hyperfine split EPR lines of the nitrogen donors. For the labels V_{Si}^- and T_{V2a} , see text. All remaining lines belong to other defect orientations of these defects. The high-field lines of EIn' and Elm' are both inverted with respect to their low-field lines, which have the same phase as the nitrogen donor lines. For the EIo' spectrum the situation is vice versa, suggesting $D < 0$.

shows a negative anisotropy contribution E to the fine structure. Moreover, the intense low-field EPR absorption-line with nearly isotropic g -tensor around 2.0013 allows the observation of resolved hyperfine satellite lines (~ 41 MHz) due to three or four silicon ligands.

Already after low-temperature annealing ($T=150^\circ\text{C}$ [8]), the Elm' spectrum has vanished and, instead, the well-known P6/P7 spectra [20–22] appear. Assuming recombination with the mobile $(\text{CC})_{\text{C}}$ split-interstitials, this annealing behavior suggests vacancy clusters like $V_{\text{C}}V_{\text{Si}}V_{\text{C}}$ or even larger aggregates as initial defects created via low-temperature irradiation. In the literature, several $S=1$ spectra with considerably smaller ZFS ($|D|=180 \times 10^{-4} \text{ cm}^{-1}$ [23,24] and $|D|=276 \times 10^{-4} \text{ cm}^{-1}$ [23–25]) have already been attributed to multi-vacancies. Our tentative assignment of the Elm spectrum to vacancy trimers, however, is supported by an angle of 59° between the principal axis of the D -tensor and the crystal c -axis: neglecting lattice relaxation around the complexes, all trimer complexes in the material provide a symmetry axis $109^\circ/2=54.5^\circ$ to the crystal c -axis. Qualitatively, the exceptionally high zero-field splitting D can be understood by the occurrence of additional close-lying defect levels. This results in wave functions that are strongly perturbed by spin–orbit coupling—an effect that already occurs for the rather light elements silicon and carbon [26]. A comparatively large second-order spin–orbit coupling that enters the fine-structure of the vacancy clusters is the consequence.

4. Summary

In 6H-SiC samples that were electron irradiated at room temperature, a so far unknown EPR signal due to an $S=1$ triplet

center with exceptionally large zero-field splitting ($D=+652 \times 10^{-4} \text{ cm}^{-1}$) has been observed under illumination. The positive sign of D demonstrates that the spin–orbit contribution to the zero-field splitting exceeds by far that of the spin–spin interaction. A principal axis of the fine-structure tilted by 59° against the crystal c -axis as well as the exceptionally high zero-field splitting D can be understood by the occurrence of additional close-lying defect levels in defect trimers resulting in a large second-order spin–orbit coupling. A tentative assignment to vacancy clusters is supported by the observed annealing behavior: already after low-temperature annealing, the Elm' spectrum has vanished and the well-known P6/P7 spectra of the divacancy appear, instead. Assuming recombination with mobile $(\text{CC})_{\text{C}}$ split-interstitials, this annealing behavior suggests vacancy clusters like the $V_{\text{C}}V_{\text{Si}}V_{\text{C}}$ trimer to cause the Elm' spectrum. To confirm or refine our tentative model, theoretical calculations of the zero-field splitting are highly recommended for future work.

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