

Fine structure of triplet centers in room temperature irradiated 6H-SiC

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Abstract. In non-annealed 6H-SiC samples that were electron irradiated at room temperature, a new EPR signal due to a $S=1$ defect center with exceptionally large zero-field splitting ($D = +652 \cdot 10^{-4} \text{ cm}^{-1}$) 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.

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. 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. It is quite intuitive that the omnipresent vacancies introduced by radiation are compensated by the creation of interstitials. 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 electron paramagnetic resonance (EPR) spectra (see [2] and ref. 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 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 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 77K during irradiation, carbon split-interstitials CC_C (EI n spectra) are present without post-annealing [7]. The non-annealed samples also contain V_{Si}⁻ but no further paramagnetic defects. If electron irradiation is performed at room temperature EI n remains the dominant EPR spectrum, however, besides V_{Si}⁻ further spectra are observed. Some of them are well-known from irradiated p -type SiC. However, at least one spectrum (EI m) of unknown microscopic origin was not reported before and has the strongest fine structure observed so far in SiC for intrinsic defects.

Experimental details

The investigated sample belongs to a series of 6H-SiC samples from a commercial wafer and was n -type due to nitrogen donors ($1 \cdot 10^{18} \text{ cm}^{-3}$). The sample was irradiated at room temperature with 2 MeV electrons (dose $1 \cdot 10^{18} \text{ cm}^{-2}$) without any cooling so that during irradiation the sample was locally heated up to 300°C. After irradiation, the non-annealed sample was investigated with EPR under illumination with a halogen lamp at 12 K in order to minimize thermal effects onto the ZFS.

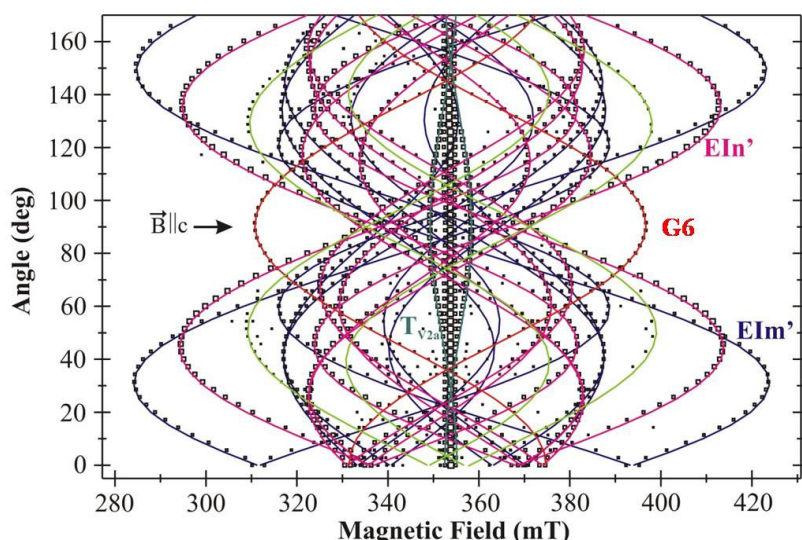


Figure 1: Angular dependence of room temperature electron irradiated 6H-SiC measured at 12 K under illumination (halogen lamp). The dots are the experimental EPR line positions, the full lines are determined from the spin-Hamiltonian parameters given in Table 1. For the labels of the triplet-lines see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

Field calibrations were done using the hyperfine (hf) lines 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 (FS) splitting. The spin state of one of them, the so-called T_{v2a} line with the smallest ZFS (below $20 \cdot 10^{-4} \text{ cm}^{-1}$) 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 Si vacancy [1-14] or an $S=3/2$ high-spin state [15-18]. The other three spectra labeled G6 [5], EIn' , and EIm' are clearly due to $S=1$ centers whereby at least the latter has not been reported before. This new spectrum is by far less intense than the dominating signal of the Si monovacancy, suggesting a defect concentration not considerably above $1 \cdot 10^{17} \text{ cm}^{-3}$. Note that without illumination all triplet centers vanish and only the isotropic signal of the negatively charged Si vacancy remains observable in the dark.

Results and discussion

The EPR triplet spectra were analyzed with the usual effective spin-Hamiltonian including the Zeeman and FS terms resulting in the electronic g -tensor, the isotropic part D (ZFS) and the anisotropic part E of the FS. The spectra are characterized by a wide range of FS splittings. The nearly axial spectrum with $D = -405 \cdot 10^{-4} \text{ cm}^{-1}$ should be equivalent 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 and ZFS as already reported for the so-called EIn center in a 6H-SiC sample belonging to the same series. In addition, it is very similar to the so-called W1 spectrum [5]. With the prime, we denote the slightly elevated temperature present 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. Here, in the non-annealed irradiated samples, the $EI3$ center is observed, whereas, after moderate annealing the slightly different $EI3'$ center appears instead. A possible explanation could be that the two centers are due to the same defect center but within different charge states. The occurrence of one of them for a given annealing temperature could be explained by Fermi level arguments. 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 FS tensor and the crystal c -axis (cf. Table 1). This supports our assumption 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 hf splitting due to a single ^{13}C nucleus, the EIn center has recently been attributed to $(CC)_C$ in the twofold positive charge state [7], stable for Fermi levels lying in the lower

Table 1: Averaged g -tensor, D ($\pm$ for unknown sign), corresponding anisotropy E and angle Θ of the FS tensor given with respect to the c -axis for the defects of Fig. 1. The g -tensor for EIn was corrected by second order effects (see Fig. 2) due to the strong ZFS and is therefore considerably smaller than that originally reported in Ref. [7]. The D value in [7] was also corrected because of earlier measurements in an uneligible plane with respect to the B -field.

center	$\bar{g}$	D [10^{-4}cm^{-1}]	E [10^{-4}cm^{-1}]	Θ [$^\circ$]	T [K]
G6[5,6]	2.0034	± 397	0	0	100
W1[5,6]	2.0016	± 559	7	46	100
EI3' [4]	2.0063	± 538	-	46	77
EI3 [4]	2.0063	± 559	-	46	77
EIn [7]	2.0013	+558	5	46	10
EIn'	2.0013	+558	7	46	12
Elm'	2.0018	+652	-8	59	12

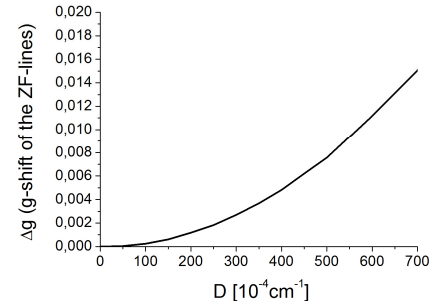


Figure 2: Non-linear second order shift of the (center of gravity of the) FS-lines dependent on D . Without non-linear correction the g -tensor would be too high by Δg .

half of the fundamental gap. Given the very large difference in the g -tensors, however, we cannot attribute the EI3/EI3' spectra unambiguously to the same microscopic model. The triplet spectrum labeled Elm' shows the strongest FS observed so far in SiC for an intrinsic defect. 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. This allows us to determine the sign of the ZFS 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 ZFS exceeds by far that of the spin-spin coupling [19]. The same holds in the case of the EIn/EIn' spectrum showing that the FS of the triplet spectra is dominated by spin-orbit coupling. For the G6 spectrum, in contrast, we found an inverted phase of the low-field line suggesting a negative sign of D and by this a dominating spin-spin contribution. In the Elm' spectrum, the intense low-field EPR absorption line with nearly isotropic g -tensor around 2.0013 allows the observation of resolved hf satellite lines ($\sim 41\text{MHz}$) due to three or four Si 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 mobile $(\text{CC})_{\text{C}}$, this annealing behavior suggests vacancy clusters like $\text{V}_{\text{C}}\text{V}_{\text{Si}}\text{V}_{\text{C}}$ or even larger aggregates as *initial* defects created via low temperature irradiation. In the literature, several $S=1$ spectra with considerably smaller ZFS ($|D|=180 \cdot 10^{-4} \text{cm}^{-1}$ [23,24] and $276 \cdot 10^{-4} \text{cm}^{-1}$ [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 ZFS 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 Si and C [26]. A comparatively large second-order spin-orbit coupling that enters the FS of the vacancy clusters is the consequence.

In room temperature electron irradiated 6H-SiC, a so far unknown EPR signal due to an $S = 1$ triplet center with exceptionally large ZFS ($D = +652 \cdot 10^{-4} \text{cm}^{-1}$) has been observed under illumination. The positive sign of D demonstrates that the spin-orbit contribution to the ZFS

exceeds by far that of the spin-spin interaction. A principal axis of the FS tilted by 59° against the crystal c-axis as well as the high ZFS 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 (CC)C split-interstitials, this annealing behavior suggests vacancy clusters like the VCVSiVC trimer to cause the Elm' spectrum. To confirm or refine our tentative model, theoretical calculations of the ZFS are highly recommended for future work.

References

- [1] U. Gerstmann, E. Rauls, Th. Frauenheim, and H. Overhof, Phys. Rev. B Vol. 67 (2003), p. 205202
- [2] N.T. Son, Mt. Wagner, C.G. Hemmingsson, L. Storasta, B. Magnusson, W.M. Chen, S. Greulich-Weber, J.-M. Spaeth, and E. Janzén, in *Silicon Carbide, Recent Major Advances*, ed. by W.J. Choyke, H. Matsunami, G. Pensl, Springer Berlin, Heidelberg 2004, 461-492, ISBN 3-540-40458-9.
- [3] N.T. Son, W.M. Chen, J.L. Lindström, B. Monemar, and E. Janzén, Mat. Sci. Eng. B Vol. 61-62 (1999), p. 202
- [4] N.T. Son, P.N. Hai, and E. Janzén, Mat. Sci. Forum Vol. 353-356 (2001), p. 499
- [5] N.M. Pavlov, M.I. Iglitsyn, M.G. Kosaganova, V.N. Solomatin, and Yu.V. Baranov, Sov. Phys. Solid State Vol. 13 (1972), p. 2363
- [6] N.M. Pavlov, M.I. Iglitsyn, M.G. Kasaganova, and V.N. Solomatin, Sov. Phys. Semicond. 9 845 (1975).
- [7] M.V.B. Pinheiro, E. Rauls, U. Gerstmann, S. Greulich-Weber, J.-M. Spaeth, and H. Overhof, Mat. Sci. Forum Vol. 527-529 (2005), p. 551
- [8] M.V.B. Pinheiro, E. Rauls, U. Gerstmann, S. Greulich-Weber, and J.-M. Spaeth, Phys. Rev. B Vol. 70 (2004), p. 245204
- [9] J. Schneider and K. Maier, Physica B Vol. 185 (1993), p. 199
- [10] T. Wimbauer, B.K. Meyer, A. Hofstaetter, A. Scharmann, and H. Overhof, Phys. Rev. B Vol. 56 (1997), p. 7384
- [11] E. Sörman, N.T. Son, W.M. Chen, O. Kordina, C. Hallin, and E. Janzén, Phys. Rev. B Vol. 61 (2000), p. 2613
- [12] Mt. Wagner, N.Q. Thinh, N.T. Son, W.M. Chen, E. Janzén, P.G. Baranov, E.N. Mokhov, C. Hallin, and J.L. Lindström, Phys. Rev. B Vol. 66 (2002), p. 155214
- [13] N.T. Son, Z. Zolnai, and E. Janzén, Phys. Rev. B Vol. 68 (2003), p. 205211
- [14] P.G. Baranov, A.P. Bundakova, I.V. Borovykh, S.B. Orlinskii, R. Zondervan, and J. Schmidt, JETP Lett. Vol. 86 (2007), p. 202
- [15] N. Mizuochi, J. Isoya, S. Yamasaki, H. Takizawa, N. Morishita, T. Ohshima, and H. Itoh, Phys. Rev. B Vol. 66 (2002), p. 235202
- [16] N. Mizuochi, J. Isoya, S. Yamasaki, H. Takizawa, N. Morishita, T. Ohshima, and H. Itoh, Phys. Rev. B Vol. 72 (2005), p. 235202
- [17] E. Janzén, A. Gali, P. Carlsson, A. Gällström, B. Magnusson, and N.T. Son, Mat. Sci. Forum Vol. 615-617 (2009), p. 347
- [18] J. Isoya, T. Umeda, N. Mizuochi, and T. Ohshima, Mat. Sci. Forum Vol. 615-617, (2009), p. 353
- [19] G.D. Watkins, Phys. Rev B Vol. 12 (1975), p. 4383
- [20] V.S. Vainer and V.A. Il'in, Sov. Phys. Solid State Vol. 23 (1981), p. 2126
- [21] Th. Lingner, S. Greulich-Weber, J.-M. Spaeth, U. Gerstmann, E. Rauls, Z. Hajnal, Th. Frauenheim, and H. Overhof, Phys. Rev. B Vol. 64 (2001), p. 245212
- [22] N.T. Son, P. Carlsson, J. ul Hassan, E. Janzén, T. Umeda, J. Isoya, M. Bockstedte, N. Morishita, T. Ohshima, and H. Itoh, Phys. Rev. Lett. Vol. 96 (2006), p. 055501
- [23] I.V. Ilyin, M.V. Muzafarova, E.N. Mokhov, P.G. Baranov, S.B. Orlinskii, and J. Schmidt, Physica B Vol. 340-342 (2003), p. 128
- [24] I.V. Ilyin, M.V. Muzafarova, E.N. Mokhov, and P.G. Baranov, Semicond. Sci. Technol. Vol. 22 (2007), p. 270
- [25] W.E. Carlos, N.Y. Garces, and E.R. Glaser, Phys. Rev. B Vol. 74 (2006), p. 235201
- [26] U. Gerstmann, A.P. Seitsonen, F. Mauri, and J. von Bardeleben, Mat. Sci. Forum Vol. 615-617 (2009), p. 357