

Ligand hyperfine interaction at the neutral silicon vacancy in 4H- and 6H-SiC

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(Received 9 November 2001; revised manuscript received 25 July 2002; published 31 October 2002)

The silicon vacancy in its neutral charge state (V_{Si}) has been unambiguously identified in 4H- and 6H-SiC. This was achieved by observation of ligand hyperfine interaction with the four carbon atoms in the nearest-neighbor shell and the twelve silicon atoms in the next-nearest-neighbor shell surrounding the vacancy. The complete hyperfine tensors have been determined for the V_{Si}^0 center residing at all inequivalent lattice sites in the two polytypes. These are compared with the parameters previously obtained for the negatively charged silicon vacancy.

DOI: 10.1103/PhysRevB.66.155214

PACS number(s): 71.55.Cn, 76.70.Hb, 61.72.Ji, 61.80.Fe

I. INTRODUCTION

Research on SiC has made tremendous progress during the last decade. The great potential of SiC as a future material for high-power and high-frequency, microelectronic devices, which is due to its superior material properties compared to silicon (wider band gap, higher thermal conductivity, higher electric breakdown field), has been extensively described. Already now, devices such as SiC Schottky diodes are commercially available.

A lot of effort has been laid down to reduce the number of macrodefects in SiC, such as micropipes, because these are detrimental for devices. As the number of these defects is reduced, understanding and control of point defects is getting increasingly important. Impurities and intrinsic defects can both create problems by, e.g., introducing unwanted carrier traps or recombination channels or be beneficial, e.g., as dopants or to achieve semi-insulating behavior.

SiC exists in a wide variety of polytypes, each with a different crystal structure and unique physical properties (size of the band gap, carrier mobility, etc.). The best-studied polytypes are 3C-, 4H-, and 6H-SiC. These are also the technologically most relevant ones. 3C-SiC has cubic symmetry, whereas 4H- and 6H-SiC are hexagonal crystals. They vary in the stacking order of silicon-carbon bilayers, resulting in an increasing unit cell size from 3C- over 4H- to 6H-SiC. Whereas all silicon atoms in 3C-SiC have identical crystal surroundings (the same is true for all carbon atoms), there exist two inequivalent lattice sites in 4H-SiC and three such inequivalent sites in 6H-SiC. All silicon sites have an identical nearest-neighbor (NN) shell consisting of four tetrahedrally arranged carbon atoms. But the next-nearest-neighbor (NNN) shell arrangement differs for the so-called hexagonal (*h*) and quasicubic (*k*) lattice sites in 4H-SiC. The same is true for the hexagonal and the two quasicubic sites

k_1 and k_2 in 6H-SiC, k_1 and k_2 differ only in their third nearest neighbors. Point defects in these polytypes can occur at any of the inequivalent sites. The properties of these defects (like their positions in the band gap) typically depend on the site on which they reside. The silicon vacancy in SiC is interesting both scientifically, as one of the fundamental intrinsic defects, and technologically. It is known to exist in various charge states within the band gap, thus creating electrically active levels. Their influence on device performance has to be studied, because vacancies can be introduced into the material either during growth (especially at high growth rates) or during device fabrication steps such as ion implantation. In ion implantation, radiation damage is produced in addition to the desired incorporation of dopant atoms. In order to study the radiation damage separately, irradiation of SiC with high-energy particles (electrons,¹⁻¹⁰ protons,¹¹⁻¹³ and neutrons¹⁴⁻¹⁷) has been used. This is also an excellent approach to study intrinsic defects such as vacancies, antisites, interstitials and their associated complexes.

So far, the silicon vacancy in SiC has only been unambiguously identified in its negative charge state in electron paramagnetic resonance (EPR) experiments. This was achieved by observation of ligand hyperfine interaction (also called super hyperfine interaction) with ^{13}C atoms in the NN shell and ^{29}Si atoms in the NNN shell for the 3C,² 4H,¹⁶ and 6H polytypes.¹⁸ In other studies, a spin $S=1$ center was found in optically activated EPR (Ref. 19) experiments on Lely grown 6H-SiC and optically detected magnetic resonance (ODMR)⁷ experiments on electron irradiated 4H- and 6H-SiC. In EPR, ligand hyperfine interaction with both NN ^{13}C atoms and NNN ^{29}Si atoms was observed, but from the intensity ratios of the ^{29}Si signals to the central line the authors suggested the defect to be a distant vacancy pair. The ODMR experiments revealed a defect center with identical g

value and zero-field splitting, but the ratio of ^{29}Si signals to the central line was higher than in the EPR experiments, suggesting interaction with 12 Si atoms in the NNN shell. Due to low signal-to-noise ratio, no clear ligand hyperfine interaction with the ^{13}C atoms in the NN shell could be observed. Later on, the same signal as in Ref. 19 was found in EPR together with the known signal from the silicon vacancy in its negative charge state.¹² However, not even the ligand hyperfine interaction with the Si atoms in the NNN shell could be resolved in these studies, so the assignment of the signals to the neutral silicon vacancy was only possible by referring back to Ref. 7.

As described above, there remains a controversy about the chemical identity of the spin-1 defect. In this paper observation of the ligand hyperfine lines with ^{13}C atoms in the NN shell are reported also for this defect in 4*H*- and 6*H*-SiC in ODMR experiments. This observation removes the possibility of the defect being a complex defect like a close vacancy pair or a vacancy-impurity complex. Arguments are presented against the assignment of the defect to distant vacancy pairs, which was originally suggested when the lines were reported for the first time in EPR experiments.¹⁹ The defect is thus identified as the isolated silicon vacancy, presumably in the neutral charge state.

II. EXPERIMENTAL DETAILS

The natural abundance of ^{13}C with nuclear spin $I=1/2$ is only 1.1%. The more common isotope ^{12}C has nuclear spin $I=0$, therefore no hyperfine splitting can be observed for this isotope. This small amount of ^{13}C makes the observation of the ligand hyperfine lines extremely difficult, in particular, a quantitative fit of the observed line intensities proved impossible. Therefore, a 6*H*-SiC sample that was grown with a ^{13}C enriched precursor material was used in this study. A SIMS (secondary ion mass spectroscopy) measurement revealed a ^{13}C concentration of $(21.7 \pm 2)\%$. The uncertainty is due to the small size and the poor surface quality of the sample. This is consistent with the value of $(19.5 \pm 0.5)\%$ deduced from a best fit to the experimental data (to be presented below).

In addition, high-quality samples with the natural abundance of ^{13}C were used. These were free-standing epitaxial 4*H*- and 6*H*-SiC films grown by the technique of chemical vapor deposition (CVD). Both these samples and the ^{13}C enriched sample were irradiated with 2.5 MeV or 3 MeV electrons to a dose of $1 \times 10^{17} \text{ cm}^{-2}$. The ODMR setup consists of a modified Bruker EPR system working at X band (~ 9.3 GHz). A tuneable Ti:sapphire laser was used as excitation source, the resulting luminescence passed appropriate filters and was detected by a liquid-nitrogen-cooled Ge detector (model North Coast).

III. RESULTS

A. Hyperfine interaction with ^{13}C atoms in the NN shell

The ODMR signals reported here were observed via a photoluminescence (PL) band in the near infrared.⁷ It consists of sharp no-phonon (NP) lines and a broad phonon-

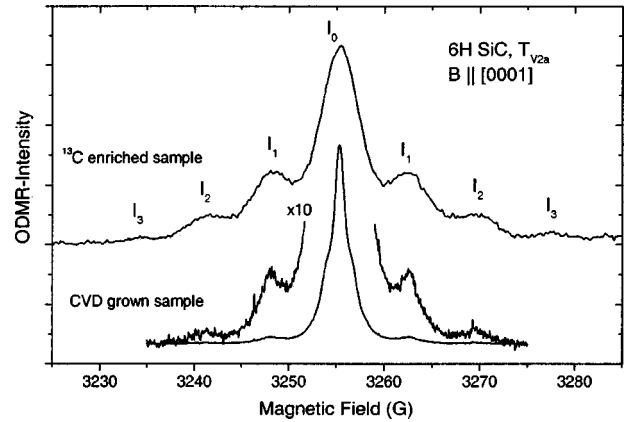


FIG. 1. Optically detected magnetic resonance (ODMR) spectra of a ^{13}C enriched 6*H*-SiC sample (upper curve) and a CVD grown 6*H*-SiC sample (lower curve). The photoluminescence was excited resonantly at V_2 , resulting in ODMR signal T_{V_2a} . Lines I_1 to I_3 originate from ligand hyperfine interaction with ^{13}C atoms in the NN shell (details are explained in the text). The magnetic field was applied parallel to the c axis of the crystals, the measurement temperature was approximately 15 K.

assisted sideband. The number of NP lines reflects the number of inequivalent lattice sites on which the defect can reside. There are two such sites in the 4*H* polytype, resulting in two NP lines V_1 at 1.438 eV and V_2 at 1.352 eV, and three NP lines in 6*H*-SiC: V_1 (1.433 eV), V_2 (1.398 eV), and V_3 (1.368 eV) corresponding to the three inequivalent lattice sites in 6*H*-SiC. Details of this emission can be found in Ref. 7. ODMR signals typical for spin triplet states are found when the luminescence is resonantly excited on each of the NP lines. These triplet lines were named T_{V_1a} and T_{V_2a} in 4*H*-SiC and T_{V_1a} , T_{V_2a} , and T_{V_3a} in 6*H*-SiC.

Figure 1 shows ODMR spectra (triplet line T_{V_2a}) of the ^{13}C enriched 6*H*-SiC sample (upper part) and the CVD grown 6*H*-SiC sample (lower part) when the laser was tuned to NP line V_2 and the magnetic field oriented parallel to the c axis of the crystals. There are two inequivalent sites of the four NN C atoms at this magnetic-field orientation: One site with a C atom along the c axis from the vacancy and the other with three C atoms at an angle of $\sim 71^\circ$ off the c axis (referred to below as the site off the c axis). Ligand hyperfine interaction with the three C atoms off the c axis gives rise to a strong signal I_1 at approximately 7 G from the central line I_0 even in the CVD grown sample. This line occurs when one of these three equivalent sites is occupied by a ^{13}C atom. Line I_2 in the ^{13}C enriched sample is a sum of two components: The nonequivalent NN site along the c axis can be occupied by a ^{13}C -atom, leading to a line approximately 14 G from I_0 . At the same position a signal is expected for the situation when two of the three C atoms off the c axis are ^{13}C . (For the CVD sample the probability of finding two ^{13}C atoms in the NN shell is vanishingly small. Line I_2 therefore only originates from the nonequivalent C atom along the c axis.) In a similar way, I_3 contains contributions from (a) three ^{13}C atoms residing on the sites off the c axis and (b) one ^{13}C atom off the c axis plus one ^{13}C -atom along the c axis. For configurations with even more ^{13}C atoms the inten-

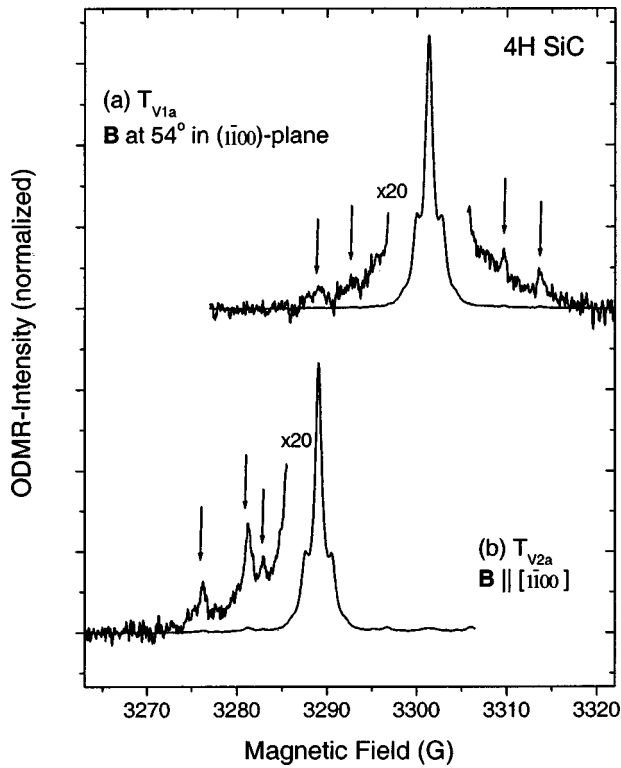


FIG. 2. ODMR spectra of the high-purity 4H-SiC sample grown in CVD. In (a) the photoluminescence was excited resonantly at line V1 and the magnetic field applied 54° off the c axis in the $(\bar{1}100)$ plane and in (b) excitation occurred at line V2 with the magnetic field parallel to $[1\bar{1}00]$. The weak lines due to ligand hyperfine interaction with ^{13}C atoms in the NN shell are magnified and marked with arrows.

sity of the expected lines is too low to be detected. The measured intensity ratio of the four lines observed is 100:38:16:3.5. A best fit to the experimental data gives rise to a ^{13}C concentration of $(19.5 \pm 0.5)\%$, yielding a ratio of 100:38:16:4. This concentration is, within the experimental error, in good agreement with the one deduced from the SIMS measurements $[(21.7 \pm 2)\%]$.

Since the defect has axial symmetry along the c axis, all three carbon sites off the c axis have to be occupied. From a symmetry point of view, the carbon atom along the c axis could be absent. Using the ^{13}C concentration from SIMS, the expected intensity ratio of the ligand hyperfine lines would, in this case, be 100:38:5.2:0.5. Even taking the ^{13}C concentration as a fitting parameter, no satisfactory agreement between simulation and experimental data can be achieved.

Due to the large linewidth, no angular dependence study could be performed in the ^{13}C enriched sample. However, in careful measurements most ligand hyperfine lines are observable even in the CVD grown samples. Examples are shown in Fig. 2 for excitation at the NP lines in 4H-SiC and in Fig. 3 for 6H-SiC for different magnetic-field orientations. Beside the triplet lines T_{V1a} , T_{V2a} , and T_{V3a} , an additional ODMR signal at 3303 G centered between the two components of the triplet is often found (Fig. 3). This signal is not directly connected to the respective triplet, because its rela-

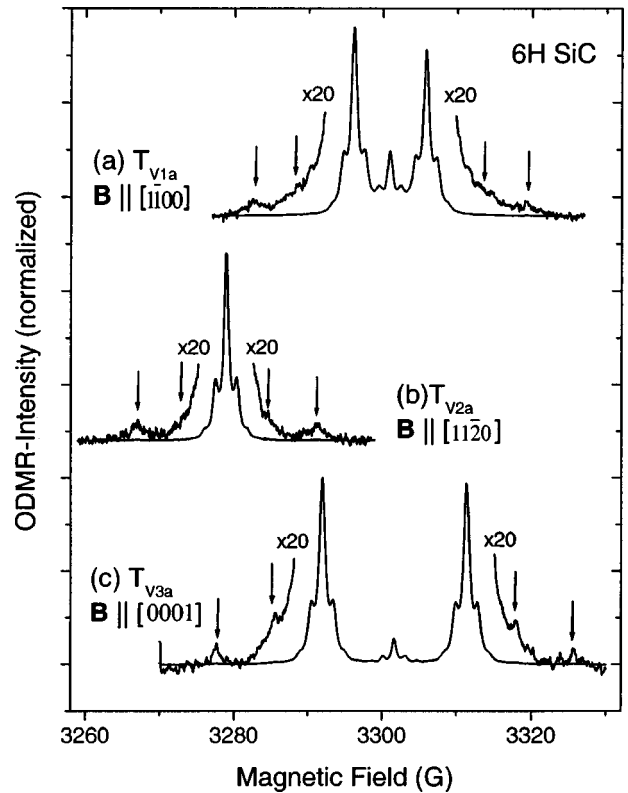


FIG. 3. ODMR spectra of the high-purity 6H-SiC sample grown in CVD. (a) Excitation at line V1, magnetic field parallel to $[1\bar{1}00]$; (b) excitation at line V2, magnetic field parallel to $[11\bar{2}0]$; (c) excitation at line V3, magnetic field parallel to the c axis. The weak lines due to ligand hyperfine interaction with ^{13}C atoms in the NN shell are magnified and marked with arrows.

tive intensity compared to the triplet signals depends on measurement conditions (cf. Fig. 2 in Ref. 7). The origin of these additional lines is currently under investigation and will not be discussed further in this report.

The angular dependence of the ^{13}C ligand hyperfine splitting of the T_{V2a} signal in 6H-SiC is shown in Fig. 4. The difference in magnetic field between the ^{13}C ligand hyperfine lines and the central line I_0 for one of the two triplet signals is displayed versus angle. The magnetic field was rotated both in the $(11\bar{2}0)$ plane and in the $(\bar{1}100)$ plane, the angle is measured from the c axis of the crystal. Thus 0° corresponds to a magnetic-field orientation parallel to the c axis, at 90° the field is oriented along the $[1\bar{1}00]$ or $[11\bar{2}0]$ direction, respectively. The angular dependence is described by the following spin Hamiltonian:

$$\mathcal{H} = \mu_B \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{B} + \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S} + \sum_j \mathbf{S} \cdot \mathbf{A}_j \cdot \mathbf{I}_j. \quad (1)$$

Here μ_B is the Bohr magneton, \mathbf{S} the effective electron spin ($S=1$ for a triplet), \mathbf{g} the g tensor, \mathbf{B} the magnetic field, \mathbf{D} the fine-structure tensor describing the effect of the crystal field, \mathbf{A}_j and \mathbf{I}_j the ligand hyperfine tensor and the nuclear

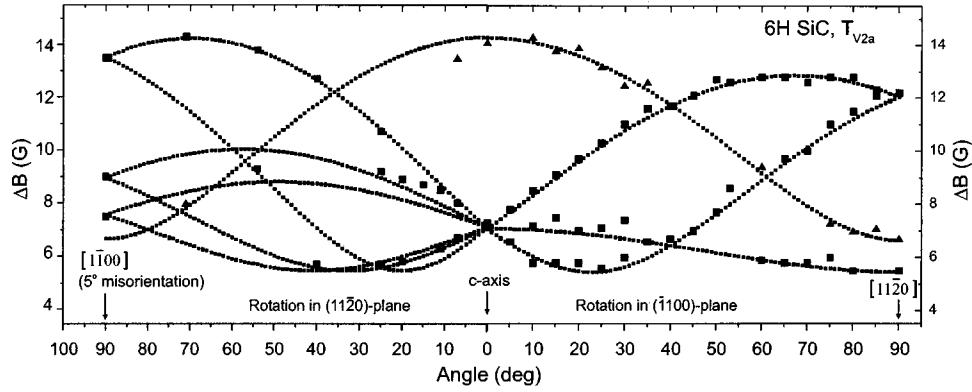


FIG. 4. Angular dependence of the ligand hyperfine splitting due to interaction with ^{13}C atoms in the NN shell for triplet line T_{V2a} in $6H$ -SiC. The difference in magnetic field between the center line and the ligand hyperfine lines for one of the two triplet signals is displayed. The magnetic field was rotated in the $(11\bar{2}0)$ plane from a direction parallel to $[1\bar{1}00]$ (with 5° misorientation) to a direction parallel to the c axis and in the $(\bar{1}100)$ plane from the c axis to $[11\bar{2}0]$. The angle is measured relative to the c axis. Black triangles are experimental datapoints for the C atom along the c axis, black squares represent the C atoms off the c axis. The dashed lines indicate a simulation using the ligand hyperfine interaction parameters given in Table I.

spin for atom j ($I=1/2$ for both ^{13}C and ^{29}Si), respectively. The \mathbf{g} and \mathbf{D} tensors have been determined in the earlier ODMR study.⁷

The dashed line in Fig. 4 represents a simulation with the following parameter. For the ^{13}C atom along the c axis $A_{\parallel}^{\text{ax}} = 28.6$ G, $A_{\perp}^{\text{ax}} = 13.4$ G, and for the ^{13}C atoms off the c axis $A_{\parallel}^{\text{oa}} = 28.6$ G, $A_{\perp}^{\text{oa}} = 11.0$ G. In a similar way, the ligand hyperfine tensors were deduced for excitation at the other NP lines in $4H$ - and $6H$ -SiC. The results are summarized in

Table I. For a successful fit, it was generally sufficient to assume axial symmetry for the \mathbf{A} tensor along the bonding direction. An exception is line T_{V3a} in $6H$ -SiC. Here, a hyperfine tensor with C_{1h} symmetry with three components in the main axis system has to be introduced for the ^{13}C atoms off the c axis. Therefore, parameters A_{zz}^{oa} , A_{xx}^{oa} , and A_{yy}^{oa} are given. Here A_{zz}^{oa} is defined along the bonding direction and A_{yy}^{oa} in the basal plane parallel to one of the $\langle 11\bar{2}0 \rangle$ directions.

TABLE I. Ligand hyperfine parameters for interaction with ^{13}C -atoms along the c -axis (A^{ax}) and off the c -axis (A^{oa}) in the NN shell and with ^{29}Si -atoms (A^{Si}) in the NNN shell. Interaction with ^{13}C -atoms has axial symmetry along the bonding direction, therefore parameters are given parallel to the bond (A_{\parallel}) and perpendicular to the bond (A_{\perp}). An exception is line T_{V3a} in $6H$ SiC. There a hyperfine tensor with components A_{xx}^{oa} , A_{yy}^{oa} , and A_{zz}^{oa} is defined for the ^{13}C -atoms off the c -axis, where A_{zz}^{oa} corresponds to the tensor component along the bonding direction and A_{yy}^{oa} to the component in the basal plane parallel to one of the $\langle 11\bar{2}0 \rangle$ -directions. Interaction with the ^{29}Si -atoms is isotropic.

Polytype	ODMR/EPR signal	$A_{\parallel}^{\text{ax}}$ (G)	A_{\perp}^{ax} (G)	$A_{\parallel}^{\text{oa}}$ (G)	A_{\perp}^{oa} (G)	A^{Si} (G)
$4H$	T_{V1a}	25.6 ± 3	11 ± 4	28.0 ± 1	11.2 ± 1	2.91 ± 0.02
	T_{V2a}	29.6 ± 3	12.4 ± 1	27.0 ± 1	10.4 ± 1	2.98 ± 0.02
	V_{Si}^{-a}	28.6	12.1	28.6	12.1	2.98
$6H$	T_{V1a}	25.6 ± 1	11.4 ± 1	28.6 ± 1	10.8 ± 1	2.91 ± 0.02
	T_{V2a}	28.6 ± 1	13.4 ± 1	28.6 ± 1	11.0 ± 1	2.80 ± 0.02
	$P3^b$	28.4	11.9^c	28.4	11.9^c	2.99
	T_{V3a}	28.6 ± 1	10.6 ± 1	$A_{zz}^{\text{oa}} = 26.7 \pm 1$	$A_{xx}^{\text{oa}} = 13.4 \pm 1$ $A_{yy}^{\text{oa}} = 9.6 \pm 1$	3.01 ± 0.02
	$P5^b$	28.4	11.9^c	28.4	11.9^c	3.21
	V_{Si}^{-d}	28.7	11.5	28.7	11.5	2.97

^aReference 16.

^bReference 19.

^cReference 19, calculated from the two lines at $\mathbf{B} \parallel c$ -axis from $A^2 = A_{\parallel}^2(\cos \theta)^2 + A_{\perp}^2(\sin \theta)^2$.

^dReference 18.

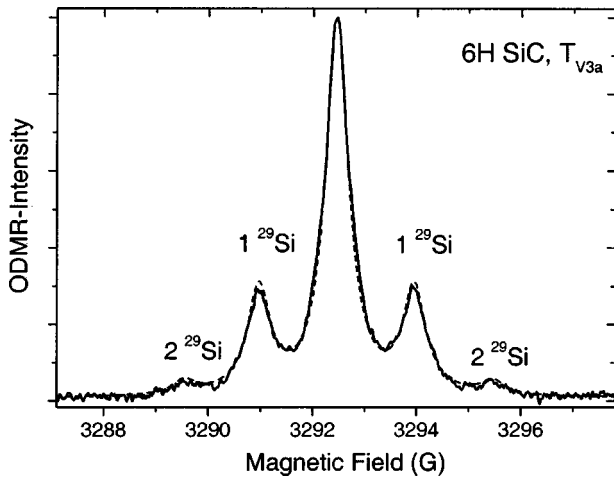


FIG. 5. ODMR spectrum (solid line) recorded at low microwave power (line T_{V3a} in $6H$ -SiC) together with a simulation (dotted line) assuming ligand hyperfine interaction with twelve equivalent silicon atoms. The interaction parameters are given in Table I.

B. Hyperfine interaction with ^{29}Si atoms in the NNN shell

In order to resolve the ligand hyperfine lines due to the ^{13}C atoms in the NN shell, a quite high microwave power had to be used. This leads to a broadening of the lines, therefore, the ligand hyperfine interaction with ^{29}Si atoms in the NNN shell can only be observed in the CVD samples as shoulders on line I_0 (Fig. 1). At lower microwave power, these shoulders can be much better resolved (Fig. 5). The individual lines are as narrow as 0.57 G, so all components are well separated. A simulation assuming interaction with twelve equivalent Si atoms (natural abundance 4.7%) is shown together with an experimental spectrum for line T_{V3a} in $6H$ -SiC. The agreement between experiment and simulation is excellent. Similar results are obtained for excitation at each of the NP lines in the two polytypes.

From a fit to the line positions, the ligand hyperfine parameters for interaction with the ^{29}Si atoms can be obtained with high precision. The parameters for all triplet lines in the two polytypes are isotropic within experimental accuracy, the values are also displayed in Table I.

Even though they are excited via different NP lines, the ODMR signals T_{V1a} and T_{V3a} in $6H$ -SiC could not be distinguished in the earlier ODMR study.⁷ This was due to the fact that their \mathbf{g} and \mathbf{D} values are identical. The same is not true for the ligand hyperfine parameters, therefore, it can be concluded that T_{V1a} and T_{V3a} actually belong to different defect centers.

IV. DISCUSSION

A. Identification

An ODMR or EPR spectrum originating from a point defect consists of several components. If the defect is an impurity, central hyperfine interaction will split the lines in a way characteristic for the impurity element. For a nucleus with nuclear spin I , the line will split into $2I+1$ lines. Most elements consist of more than one stable isotope whose nuclear

spin depends on the number of neutrons in the nucleus. Defect identification is, thus, possible by measuring the relative intensity of the various hyperfine multiplets and comparing with the known relative abundance of possible impurities. This method fails for impurities that consist exclusively or to a very high percentage of only isotopes with nuclear spin $I=0$. There are very few such elements, oxygen being one example.

The amplitude of any hyperfine splitting depends on the probability of finding the electron on the position of the nucleus with which it interacts. Therefore, for a localized defect, the splitting due to the central impurity atom is generally much larger than the ligand hyperfine splitting.

The other components of the ODMR spectrum are due to ligand hyperfine interaction with neighboring atoms. For a localized defect, the amplitude of the electron wave function is generally expected to decrease with increasing distance to the defect site. Therefore, the splitting is also expected to drop for ligand hyperfine interaction with atoms in the NN shell, the NNN shell and atoms even farther away.

No central hyperfine interaction is observed in the measurements presented here. The outermost signals detected are well explained by ligand hyperfine interaction with four C atoms in the NN shell. In a similar way, the lines at distance 1.5 G and 3 G from the central line originate from ligand hyperfine interaction with twelve equivalent Si atoms. From this observation, it is clear that the defect (or one part in a complex defect) must reside on a silicon lattice site.

The absence of central hyperfine interaction requires that the site is either empty (a vacancy) or an impurity, which consists exclusively or to a very high percentage of an isotope with nuclear spin $I=0$. Oxygen fulfills this requirement (^{17}O , the only isotope with nonzero nuclear spin, has a negligible natural abundance of 0.038%), but this assignment can be excluded based on the following arguments: The PL band, via which the ODMR signal is detected, appears precisely under circumstances that favor the formation of vacancies, irradiation with fast particles, growth at high temperatures with high growth rates or thermal quenching. It can be introduced in any starting material via electron irradiation, irrespective of the purity of the sample, as long as it is not strongly p type in the beginning. Actually, the strongest signals are found in the purest samples grown by the CVD technique in which oxygen contamination is expected to be very small. And finally, the ligand hyperfine parameters obtained in this study are extremely similar to the ones that are reported for the silicon vacancy in the negative charge state (see Table I).

Judging from the similarity of all spin Hamiltonian parameters (\mathbf{g} tensor, crystal-field-splitting parameter \mathbf{D} , and ligand hyperfine parameters \mathbf{A}), the ODMR signals discussed here were already reported in EPR of $6H$ -SiC after light illumination (lines $P3$ and $P5$) by Vainer and Il'in in 1981.¹⁹ One major difference in their discussion compared to the one presented here is that they came to the conclusion that the ligand hyperfine interaction with the ^{29}Si atoms occurred only at 6–8 equivalent Si sites. Observation of ligand hyperfine interaction with four silicon atoms surrounding a carbon vacancy was claimed in addition to the ligand hyperfine in-

teraction typical for the silicon vacancy. But this observation is not obvious from the presented spectra. (In fact, the spectra of Vainer and II'in look very similar to the ones reported here, so their calculation may have been erroneous.) From this observation, they concluded that the EPR signals originated from distant silicon vacancy—carbon vacancy pairs. This interpretation is supported by the fact that the small crystal-field-splitting parameter D can be accounted for by assuming magnetic dipole-dipole interaction between carriers residing on the two vacancies.²⁰

However, there are strong arguments against this assignment.

(1) For such distant pairs, the interaction between the two vacancies is supposed to be quite weak. It is, therefore, hard to understand that only the distant vacancy pairs oriented along the c -axis are observed in ODMR (the angular dependence of the triplet lines have been shown to have axial symmetry along the c axis⁷).

(2) From Fig. 5, it is clear that ligand hyperfine interaction actually occurs with *twelve* equivalent Si atoms, not with the six to eight that were reported in Ref. 19.

(3) Only ligand hyperfine interaction typical for the silicon vacancy is observed in the experiments presented here, not the one for the carbon vacancy. This means that basically the entire spin density of the unpaired electrons is localized on the silicon vacancy. But in this case, the assumption of dipole-dipole interaction between the two vacancies does not hold.

Similar arguments against the assignment of the defect to a distant vacancy pair have already been discussed in Ref. 7.

A closer vacancy pair or a complex defect involving the silicon vacancy can also be excluded. Ligand hyperfine interaction is observed with all atoms in the NN shell and the NNN shell, leaving no space for another point defect residing on one of these sites. Such a defect (silicon vacancy plus another defect in the NN shell, presumably the carbon vacancy or the silicon antisite) has been found in electron irradiated n -type $6H$ -SiC by ODMR.²¹ However, this defect was shown to exist with the additional defect residing on either of the carbon sites in the NN shell. The defect discussed here has axial symmetry along the c axis, so the second defect in the complex would have to exclusively sit along the c axis from the silicon vacancy.

An interstitial defect would seriously distort the surroundings of the vacancy and affect the distribution of the spin density. The isotropic interaction with the ²⁹Si atoms in the NNN shell can then not be explained. This lowering of the symmetry has been observed for the Si-Frenkel pair (silicon vacancy plus silicon interstitial) in EPR experiments.⁸

In conclusion, the ODMR signals observed originate from an isolated silicon vacancy. The question of which charge state the vacancy is in was discussed extensively in Ref. 7. A charge state with an even number of electrons is necessary in order to explain the triplet and singlet⁹ states found. Recently, EPR signals with identical spin Hamiltonian parameters as the ODMR lines discussed here have been found in $4H$ - and $6H$ -SiC simultaneously with the signals originating

from the negative charge state of the silicon vacancy.¹² Since there is no theoretical or experimental evidence for a negative- U behavior of the silicon vacancy in SiC, the ODMR signals therefore can only be due to the neutral (V_{Si}^0) or doubly negative charge state (V_{Si}^{2-}). Irradiation with high-energy particles generally tends to increase the resistivity of n type starting material, i.e., the Fermi level moves closer to midgap. The luminescence at 1.4 eV, by which the ODMR signals are observed, originates from internal transitions within the vacancy, which places the ground state at least 1.5 eV below the conduction-band edge. The ground-state level of the doubly negative charge state is calculated to be in the upper half of the band gap.²² The existence of excited states 1.5 eV above this level, which are still within the gap is therefore unlikely.

B. Comparison with the negative charge state of the silicon vacancy

In addition to the ligand hyperfine parameters obtained in this work, Table I also shows the corresponding parameters for the negatively charged silicon vacancy previously reported. The values are strikingly similar, except for the fact that no difference was found in the negative charge state for ligand hyperfine interaction with the C atom along the c axis from the silicon vacancy compared to the C atoms off the c axis in the NN shell. This difference is small but detectable in the neutral charge state.

The EPR signal of the negatively charged silicon vacancy has some unexpected properties, which are even more striking in view of the results presented here. Only one basically isotropic line is found in $3C$ -, $4H$ -, and $6H$ -SiC, suggesting a spin $S=1/2$ configuration.² After the original discovery of the lines, electron nuclear double resonance experiments revealed that the true spin state is actually $S=3/2$.¹⁶ In a crystal field, three EPR lines are expected for such a configuration. The absence of the additional lines has been explained by a vanishing crystal-field parameter D for the negatively charged silicon vacancy. No convincing physical mechanism for this has been put forward, and it is difficult to understand why in such a case a nonvanishing (if small) crystal-field splitting is observed for the neutral charge state.

In addition, no site dependence is found for the EPR signal of the negatively charged silicon vacancy. The observation of only one line can be explained by the assumption of identical g values for all inequivalent lattice sites. While very similar g values are actually found in the neutral charge state, the ligand hyperfine interaction parameters, both for the ¹³C atoms in the NN-shell and the ²⁹Si-atoms in the NNN shell, clearly differ. A similar difference should be expected even for the negative charge state, leading to the appearance of more ligand hyperfine lines, which is not observed. It should be pointed out that the ODMR experiments under resonant excitation used here provide an advantage compared to EPR. Signals from each inequivalent lattice site can be obtained without contribution from the other sites. This is not possible in EPR, therefore, signals from one inequivalent lattice site may be hidden underneath the much stronger signal of another site.

V. SUMMARY

Ligand hyperfine interaction with four C atoms in the NN shell and twelve Si atoms in the NNN shell have been observed for the triplet lines T_{V1a} and T_{V2a} in 4H-SiC and T_{V1a} , T_{V2a} , and T_{V3a} in 6H-SiC. The parameters of this interaction are very similar to the ones found for the negatively charged isolated silicon vacancy in the respective polytypes. Arguments are presented against the assumption

of the defects being complexes like distant silicon vacancy—carbon vacancy pairs. It is, therefore, concluded that the observed ODMR lines originate from the isolated silicon vacancy.

ACKNOWLEDGMENT

The authors would like to thank Dr. S. Rosander for his help with the electron irradiation.

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