Electronic structure of the neutral silicon vacancy in 4*H* and 6*H* SiC

Mt. Wagner, B. Magnusson, W. M. Chen, and E. Janzén
Department of Physics and Measurement Technology, Linköping University, S-581 83 Linköping, Sweden

E. Sörman and C. Hallin
ABB Corporate Research, S-721 78 Västerås, Sweden

J. L. Lindström
Department of Solid State Physics, University of Lund, S-221 00 Lund, Sweden

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Detailed information about the electronic structure of the lowest-lying excited states and the ground state of the neutral silicon vacancy in 4*H* and 6*H* SiC has been obtained by high-resolution photoluminescence (PL), PL excitation (PLE), and Zeeman spectroscopy of both PL and PLE. The excited states and the ground states involved in the characteristic luminescence of the defect with no-phonon (NP) lines at 1.438 and 1.352 eV in 4*H* SiC and 1.433, 1.398, and 1.368 eV in 6*H* SiC are shown to be singlets. The orbital degeneracy of the excited states is lifted by the crystal field for the highest-lying NP lines corresponding to one of the inequivalent lattice sites in both polytypes, leading to the appearance of hot lines at slightly higher energies. Polarization studies of the NP lines show a different behavior for the inequivalent sites. A comparison of this behavior in the two polytypes together with parameters from spin resonance studies provides useful hints for the assignment of the no-phonon lines to the inequivalent sites. In strained samples an additional fine structure of the NP lines can be resolved. This splitting may be due to strain variations in the samples.

I. INTRODUCTION

Interest in SiC research has increased dramatically within the last decade due to improvements in crystal growth techniques like chemical vapor deposition (CVD), which open up possibilities for devices based on SiC. Even though blue-light-emitting diodes made of SiC have been realized, possible applications are mainly within the field of high-power and high-frequency devices. The most promising polytypes for applications to date seem to be 4*H* and 6*H* SiC.

In contrast to silicon, in SiC many intrinsic defects like monovacancies are stable at room temperature and even above.[1] Detailed knowledge about these defects is, therefore, extremely important for device performance, since intrinsic defects can be introduced during growth and also in device-processing steps like ion implantation.

Electron irradiation has been used extensively for defect characterization in many semiconductors. In silicon it has contributed a lot to understanding of the properties of intrinsic defects, in particular the vacancy.[2] In SiC also many important defects have been characterized using this method, e.g., the negatively charged silicon vacancy in 3*C* SiC, which was shown to have high-spin configuration.[1,3] No electron paramagnetic resonance signals of the silicon vacancy in its neutral charge state have been reported to date.

In this study we focus on the properties of a defect in 4*H* and 6*H* SiC that has been previously assigned from optically detected magnetic resonance (ODMR) data to be the neutral silicon vacancy.[4] It is created in high-quality epitaxial layers by electron irradiation. Characteristic for this defect is a photoluminescence (PL) band with no-phonon (NP) lines at 1.438 and 1.352 eV in 4*H* SiC and 1.433, 1.398, and 1.368 eV in 6*H* SiC. The number of NP lines corresponds to the number of inequivalent lattice sites in the two polytypes. Some properties of these lines in 6*H* SiC were already studied in the 1970s,[5,6] but only recently have the magnetic resonance data essential for the identification of the defect become available.[4] ODMR signals typical for a spin-triplet configuration were observed in Ref. 4 upon resonant excitation of the NP lines. It was not shown, however, whether these triplets are the exact excited states involved in the radiative recombination monitored. From Zeeman experiments presented here we can conclude that this is not the case. All NP lines are shown to occur between singlet excited states and the singlet ground state. Thus the presumably nonradiative spin triplet must be detected indirectly via the singlet-to-singlet emission. This calls for a close reexamination of theoretical results, which in many cases predict a spin-triplet ground state of the neutral silicon vacancy.[7,8]

In addition, fine structure of the PL lines is resolved in this study. This structure is due to the action of the crystal field on the defect, leading to a splitting of the energetically highest-lying NP line even in unstrained samples and an additional shoulder on the high-energy side of all NP lines in strained samples. The polarization of the lines due to the inequivalent lattice sites varies within one polytype. Similarities in the polarization and magnetic properties of the lines in the two polytypes give a hint toward the assignment of the lines to the hexagonal and quasicubic sites existing in the crystals.

II. EXPERIMENTAL DETAILS

The samples used were CVD-grown epitaxial layers ($\sim$70 μm thick) with low *n*-type doping (mid 10^{14} cm^{-3}). After growth the substrate was removed, resulting in free-standing

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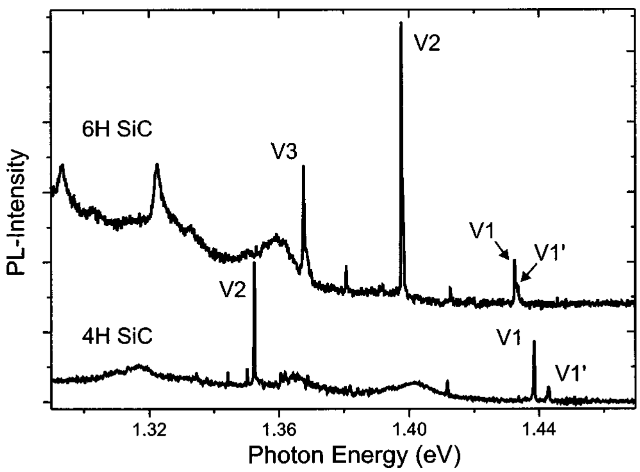

FIG. 1. PL spectra of electron-irradiated 6*H* SiC (upper curve, $T=10\,\mathrm{K}$) and 4*H* SiC (lower curve, $T=34\,\mathrm{K}$). In 6*H* SiC three no-phonon lines ($V1$, $V2$, and $V3$) are visible. In 4*H* SiC there are only two such lines ($V1$ and $V2$). At elevated temperatures a hot line $V1'$ appears at slightly higher energy than $V1$ in both polytypes. Due to the larger energy separation between $V1$ and $V1'$ in 4*H* SiC than in the 6*H* polytype, a higher measuring temperature was used in order to make $V1'$ visible. The NP lines are followed by a strong phonon-assisted sideband. The luminescence was detected through the edge of the samples; no polarizer was inserted. An excitation density of approximately 1 W/cm^2 was used.

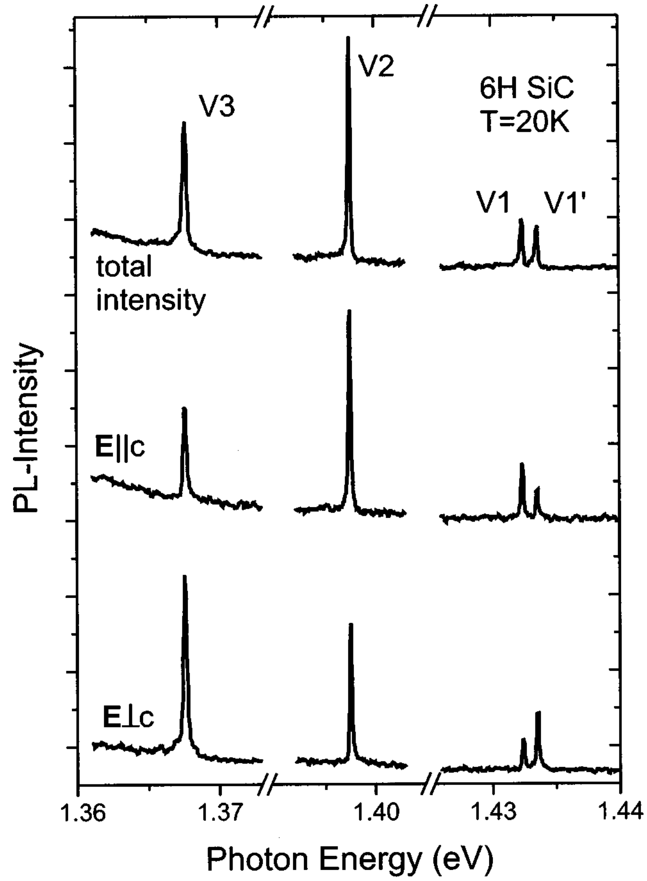

FIG. 2. PL spectra showing the different polarization of the various NP lines in electron-irradiated 6*H* SiC ($T=20\,\mathrm{K}$). $V1'$ and $V3$ have $\mathbf{E}\perp c$ polarization, while $V2$ has strong $\mathbf{E}\parallel c$ polarization and $V1$ weak $\mathbf{E}\parallel c$ polarization.

layers. The high-purity samples were irradiated with 2.5 MeV electrons at room temperature with a dose of 10^{17} cm^{-2}. No annealing step was performed. The spectra were recorded either via a Spex 0.85 m double-grating monochromator with a liquid-nitrogen-cooled Ge detector (model North Coast) or a cooled GaAs photomultiplier tube attached at the exit slit, or via a Bomem DA8 Fourier transform infrared (FTIR) spectrometer using a Ge detector or a Si-avalanche photodiode. A tunable Ti:sapphire laser was used as excitation source in PL experiments. Excitation energies were 1.49 eV in the Zeeman setup and 1.59 eV in the FTIR setup. At these energies the samples are essentially transparent, leading to a uniform excitation profile in the sample. In PL excitation (PLE) experiments the excitation wavelength of the Ti:sapphire laser was varied, while the detection wavelength was fixed. For the Zeeman experiments an Oxford split-coil superconducting magnet producing fields up to 5 T with optical access from side windows was used. In the polarization studies the luminescence was detected through the edge of the samples and a linear polarizer was inserted into the light beam.

III. RESULTS

A. Photoluminescence

After electron irradiation a new PL band appears in 4*H* and 6*H* SiC in the near-infrared region (Fig. 1), which was not present before. At low temperatures (1.6 K) it consists of two NP lines in 4*H* SiC at 1.438 eV (labeled $V1$) and 1.352 eV ($V2$) and three NP lines in 6*H* SiC at 1.433 eV ($V1$), 1.398 eV ($V2$), and 1.368 eV ($V3$). The number of NP lines corresponds to the number of inequivalent lattice sites in the different polytypes. At elevated temperatures additional lines appear at slightly higher energies than $V1$ in both polytypes. They are labeled $V1'$. The splitting between $V1$ and $V1'$ is much larger in 4*H* SiC than in 6*H* SiC. Because of the thermal redistribution of carriers in PL experiments a higher temperature is needed in 4*H* SiC in order to observe $V1'$. Besides the NP lines a strong phonon-assisted sideband is visible.

The exact position of the NP lines varies with the strain in the samples as shown earlier,[9] but the splitting between $V1$ and $V1'$ and even the width and shape of the lines also depend on the strain. Nevertheless, $V1'$ seems to appear even without external strain on the sample, i.e., with as little glue under the sample as possible. This is consistent with the observation of $V1'$ in the Lely platelets used by Gorban and Slobodyanyuk.[5]

In the same study it was realized that the NP lines corresponding to the inequivalent sites are polarized differently in 6*H* SiC.[5] The observation was that $V1'$ and $V3$ have strong $\mathbf{E}\perp c$ polarization, $V1$ has weak $\mathbf{E}\parallel c$ polarization, and $V2$ has strong $\mathbf{E}\parallel c$ polarization. These results are confirmed in this study (Fig. 2). In addition, we obtained similar spectra for the 4*H* polytype (Fig. 3). Here only $V1'$ has strong $\mathbf{E}\perp c$ polarization, whereas $V1$ and $V2$ have weak $\mathbf{E}\parallel c$ polarization.

$V1$ and $V2$ in 4*H* SiC and $V1$, $V2$, and $V3$ in 6*H* SiC belong to the inequivalent lattice sites of the defect center. This is shown by the fact that it is not possible to excite the

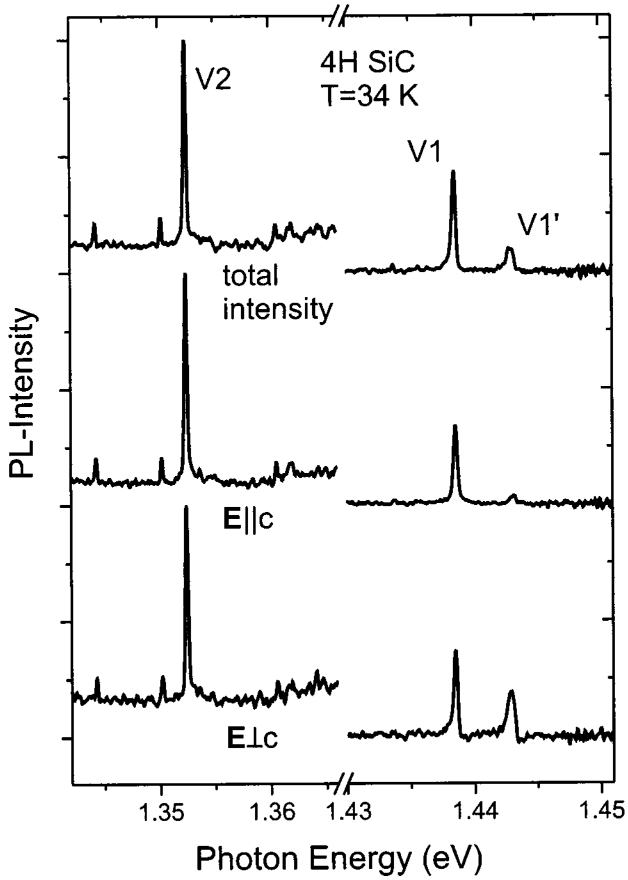

FIG. 3. PL spectra showing the different polarization of the various NP lines in electron-irradiated $4H$ SiC ($T=34$ K). $V1'$ has strong $\mathbf{E}\perp c$ polarization, while $V2$ and $V1$ have weak $\mathbf{E}\|c$ polarization.

energetically lower-lying lines by tuning the laser to the higher-lying lines. Also, there is no thermal redistribution of intensity between the lines at elevated temperatures. The situation is different for the two components $V1$ and $V1'$. These lines are connected, and their relative PL intensities follow a Boltzmann distribution of carriers in the levels. An example of this redistribution in PL is displayed in Fig. 4(a) for $4H$ SiC. In PLE experiments, on the other hand, the relative intensities are independent of temperature [Fig. 4(b), $6H$ SiC]. Identical results are obtained for the other polytype in both experiments. Such behavior is expected if the excited state involved in the transition is split, but not the ground state.

B. Zeeman studies

In earlier work[4] it was shown that signals of various spin-triplet states are observed in ODMR when monitoring the PL emission including the phonon-assisted sideband. From spectral dependence studies it is apparent that two triplet states (denoted T and T', compare Fig. 10 below) can be detected via each NP line. Among these only one (the T triplet) can be selected by resonant excitation of the corresponding NP line with a tunable Ti:sapphire laser. In these experiments the excitation wavelength corresponds to one of the NP lines and the ODMR signal is detected as a change in intensity of the phonon band under the magnetic resonance condition.

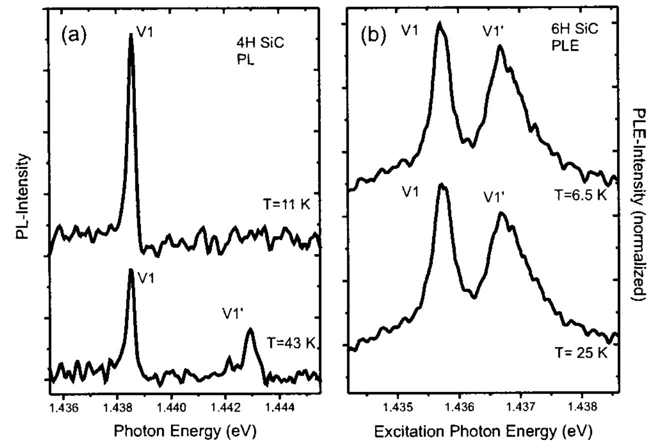

FIG. 4. (a) PL spectra showing the thermal redistribution of intensity between $V1$ and $V1'$ in $4H$ SiC. (b) In PLE, on the other hand, no difference in relative intensity between $V1$ and $V1'$ at various temperatures is visible. The spectrum shows the $6H$ polytype. Thus the two lines are due to a splitting of the excited state involved in the radiative recombination.

One obvious possibility is that the excited state involved in the radiative recombination is the triplet state detected in ODMR. In order to test this possibility Zeeman measurements of the PL were performed at various angles between $\mathbf{B}\|c$ axis and $\mathbf{B}\perp c$ axis. Typical results are shown in Fig. 5 for the $4H$ polytype at $T=45$ K and an angle of 20° between $\mathbf{B}$ and the c axis and in Fig. 6 for the $6H$ polytype at $T=12$ K and an angle of 80° between $\mathbf{B}$ and the c axis. The upper curve is recorded without magnetic field and the lower one at a magnetic field of $B=5$ T. Usually the Faraday configuration $\mathbf{B}\|\mathbf{k}$, where $\mathbf{k}$ is the direction of propagation of the emitted photons, was used, but no difference was observed in Voigt configuration ($\mathbf{B}\perp\mathbf{k}$), except for the change in relative intensity between the NP lines due to the polarization behavior. The excitation density was again approximately 1 W/cm^2 for $6H$ SiC and slightly higher for the $4H$ sample due to the smaller signal intensity.

None of the NP lines, including the hot line $V1'$, exhibit any sign of splitting, broadening, or shift at any angle. From the g value of $g\approx 2$ for all of the triplets observed in ODMR

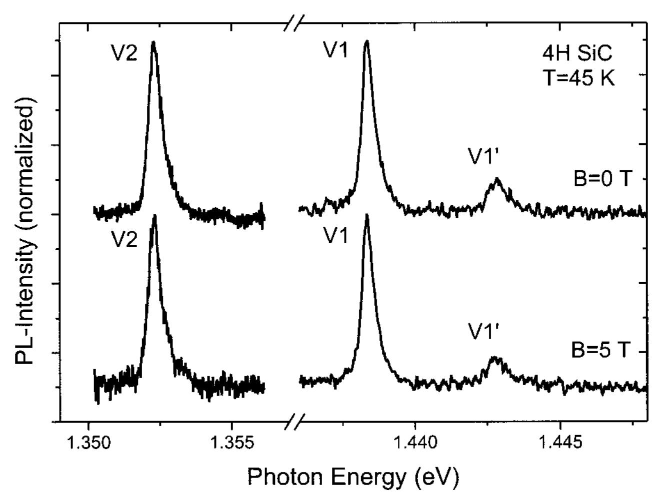

FIG. 5. Zeeman spectra of the PL in electron-irradiated $4H$ SiC at $B=0$ T (upper curve) and 5 T (lower curve). $T=45$ K.

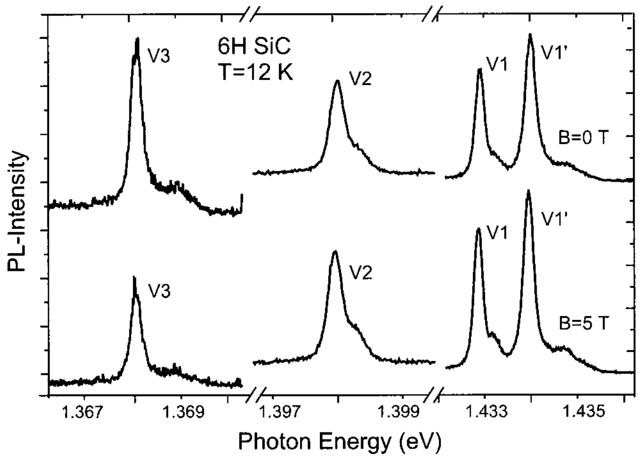

FIG. 6. Zeeman spectra of the PL in electron-irradiated 6H SiC at $B=0$ T (upper curve) and 5 T (lower curve). $T=12$ K.

a splitting between the $M_s=\pm 1$ states of 1.16 meV at $B=5$ T can be expected. This is much larger than the experimental linewidth of typically 0.3 meV, excluding the possibility that the spectral resolution may be insufficient to observe the Zeeman splitting.

If the spin-lattice relaxation time between the magnetic sublevels is extremely short it may happen that the triplet thermalizes completely before recombination. One may then observe only one line at a high field corresponding to the lowest-lying sublevel of the excited state at low temperature. The absence of any shift or additional lines in a magnetic field and at elevated temperatures seems to exclude such a possibility. For additional support, Zeeman studies were also performed on the PLE signals. In this case all magnetic sublevels of the excited state should be visible. But even in these experiments no effect of the magnetic field is observable (Fig. 7 for 4H SiC and Fig. 8 for 6H SiC). This leads to the conclusion that both the excited states and the ground state involved in the radiative transitions are singlets.

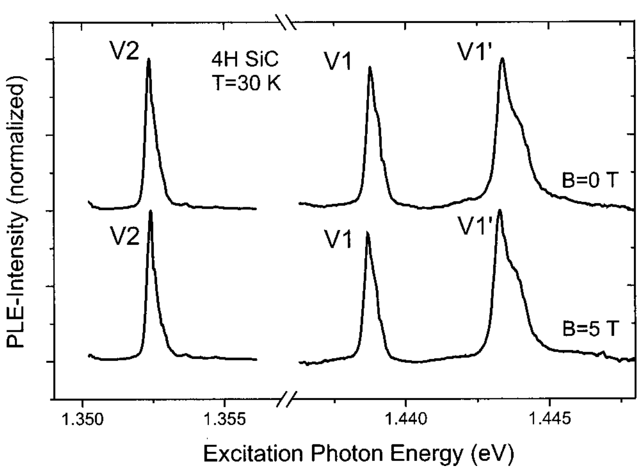

FIG. 7. Zeeman spectra of the PLE in electron-irradiated 4H SiC at $B=0$ T (upper curve) and 5 T (lower curve). $T=30$ K. The detection energy was fixed at 1.203 eV, i.e., deep in the phonon-assisted sideband, and the magnetic field was applied at an angle of 65° off the c axis.

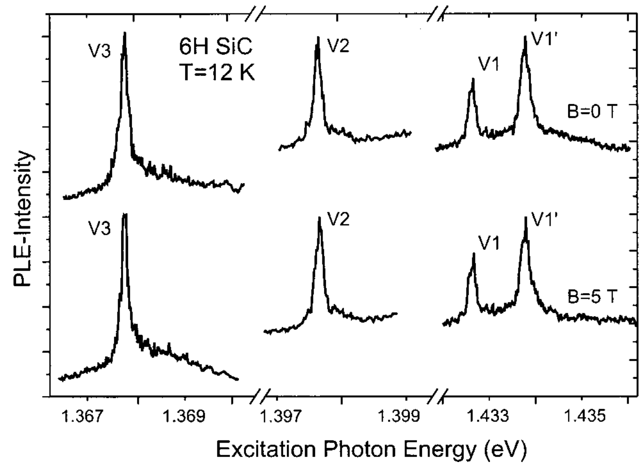

FIG. 8. Zeeman spectra of the PLE in electron-irradiated 6H SiC at $B=0$ T (upper curve) and 5 T (lower curve). $T=30$ K. The detection energy was fixed at 1.215 eV, i.e., deep in the phonon-assisted sideband, and the magnetic field was applied at an angle of 65° off the c axis.

C. Additional fine structure

A closer look at the high-resolution PL and PLE spectra reveals an additional shoulder at the high-energy side of all NP lines. The strength, shape, and splitting from the main line strongly depend on the strain in the samples introduced by varying amounts of glue used for mounting them on the sample holder. When present, the relative intensity of the shoulders compared to the main line is independent of temperature in both PL and PLE experiments. Examples of this are shown in Fig. 9 [PLE of line $V2$ in 4H SiC (a), and PL of line $V2$ in 6H SiC (b); the results are identical in both polytypes].

IV. DISCUSSION

A. Indirect detection of the spin triplets in ODMR

The results of the Zeeman experiments (Sec. III B) proved that the excited states and the ground state of the defect

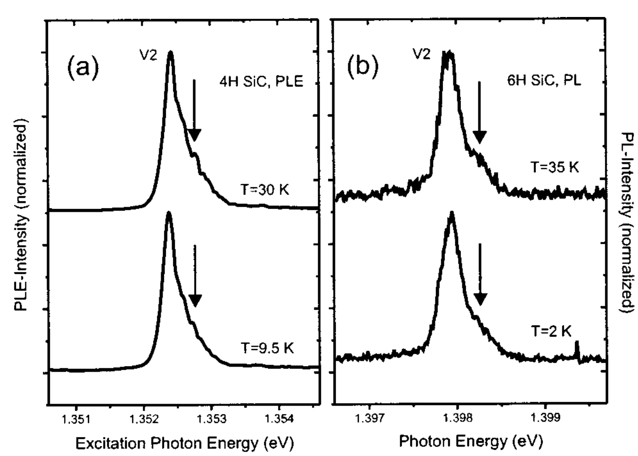

FIG. 9. Examples of the thermal behavior of the additional shoulders on the high-energy side of the NP lines. (a) PLE spectra of line $V2$ in 4H SiC at 9.5 and 30 K; (b) PL spectra of $V2$ in 6H SiC at 2 and 35 K. No thermalization between the main line and the shoulder occurs either in PL or in PLE experiments.

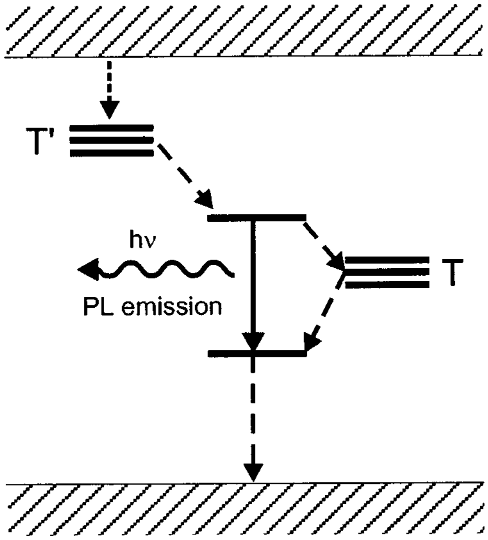

FIG. 10. Schematic picture of the electronic structure of the neutral silicon vacancy in $4H$ and $6H$ SiC and a recombination diagram for the detection of triplets T and T' in ODMR via singlet-to-singlet radiative recombination. A spin-dependent feeding of the excited singlet via T' can be enhanced by microwave-induced transitions within the T' sublevels. Triplet T with its long radiative lifetime acts as a bottleneck for the singlet-to-singlet transition. Emptying of this level under magnetic resonance by transferring carriers from the triplet sublevel with the longest lifetime to another triplet sublevel with shorter lifetime leads to a higher number of defects available for the radiative recombination.

involved in the radiative recombination are singlets. So the triplet level seen in ODMR must be detected indirectly. The fact that the ODMR is excited via the PL NP lines implies that the T triplet must be a level of the same defect, but lying energetically lower (Fig. 10). Since transitions from this triplet level to the singlet ground state are forbidden by the spin selection rule, the radiative lifetime of these levels can be very long. Then nonradiative recombination or excitation transfer to a different defect may be more efficient in emptying the level. Therefore no PL lines can be seen arising from the triplet. Still, the emptying of the triplet may be spin selective. Therefore a magnetic-resonance-induced transition within the triplet may enhance this emptying by transferring carriers from the triplet sublevel with the longest lifetime to another triplet sublevel with a shorter lifetime. This in turn makes the defect available again for radiative recombination, which enhances the luminescence intensity. A similar model was proposed before for a deep-level defect in silicon.[10]

The additional T' triplets seen in ODMR under above-band-gap excitation, on the other hand, are situated higher up in the forbidden band gap.[4] Relaxation from these states to the singlet states involved in the PL emission can be spin selective as well, which explains the observation of these triplets via the singlet-to-singlet transition. Figure 10 shows a schematic of the suggested recombination model.

B. Electronic structure

Vacancies are an important defect system in any semiconductor. Therefore much theoretical effort has been employed to understand the electronic structure of vacancies in their different charge states. No symmetry lowering is predicted by theory for the neutral silicon vacancy.[7,8,11] This is in accordance with the ODMR data, in which the symmetry is determined to be axial along the c axis.[4] On the other hand, theoretical calculations have in many cases predicted a triplet ground state.[7,8] Only recently has a singlet ground state for the neutral silicon vacancy in $3C$ SiC been proposed.[11] At low temperatures only the ground state of the defect can be populated. So transitions detected in PLE must start from this level. In our experiments it is found to be a singlet.

TABLE I. Comparison of the spin-Hamiltonian parameters and the polarization for the NP lines in $4H$ and $6H$ SiC.

NP line	$g_{\parallel}$ [a]	$g_{\perp}$ [a]	D (10^{-8} eV) [a]	Polarization
		$6H$ SiC		
$V1$	2.0035	2.0037	11.4	$\mathbf{E}\parallel c$ (weak)
$V1'$				$\mathbf{E}\perp c$
$V2$	2.0035	2.0038	53.1	$\mathbf{E}\parallel c$
$V3$	2.0037	2.0038	11.4	$\mathbf{E}\perp c$
		$4H$ SiC		
$V1$	2.004	2.004	1.8	$\mathbf{E}\parallel c$ (weak)
$V1'$				$\mathbf{E}\perp c$
$V2$	2.004	2.004	28.8	$\mathbf{E}\parallel c$ (weak)

[a]Reference 4.

Additional information, which may be useful input for theoretical calculations, comes from the polarization experiments. Table I summarizes the polarization results found for the various NP lines together with the spin resonance parameters from Ref. 4. The fact that $V1$ has $\mathbf{E}\parallel c$ polarization and $V1'$ $\mathbf{E}\perp c$ polarization in both polytypes implies (a) that the lines are likely due to the same defect configuration in both polytypes, i.e., the defect is residing on a similar inequivalent lattice site, and (b) that the splitting between $V1$ and $V1'$ is due to a lifting of the degeneracy of different orbital states, which gives rise to the different polarizations. The splitting between $V1$ and $V1'$ is clearly due to a splitting of the excited state involved in the transition, evident from the thermal redistribution of intensity in PL but not in PLE experiments.

Lines $V2$ have $\mathbf{E}\parallel c$ polarization in both $4H$ and $6H$ SiC. In addition, the triplets detected in ODMR via these lines have the largest fine structure term D due to the crystal field. This similarity again implies similar chemical surroundings. It has been suggested before that the crystal field may be strongest on the hexagonal site,[12] so the large D value detected via $V2$ may indicate that $V2$ is due to this site.

C. Origin of the additional fine structure

In strained samples additional fine structure appears as shoulders or tails on the high-energy side of all NP lines in both PL and PLE spectra. No thermal redistribution of intensity between these features and the main line occurs. Thus the shoulders are probably due to radiative transitions at a different location of the neutral silicon vacancy under a different degree of strain rather than to another excited state of the same defect center. It was shown before that the PL lines are very sensitive to hydrostatic pressure,[9] which shifts them strongly to higher energies. Because our samples are very thin the glue used for mounting them on the sample holder will induce strain, and this strain will not be uniform. So there will also be a distribution of recombination energies over the sample. It is surprising, though, that this distribution could lead to well-resolved shoulders in some cases instead of an overall broadening of the lines.

V. SUMMARY

The neutral silicon vacancy in $4H$ and $6H$ SiC is shown to have the following electronic structure. The ground state is a singlet. There are excited singlet states approximately 1.4 eV above the ground state, varying in energy at different inequivalent lattice sites. In addition a triplet level must exist between the singlet excited states and the singlet ground state for each inequivalent site. The energy position of this triplet cannot be determined. An additional triplet can be detected in ODMR by above-band-gap excitation. The corresponding level is probably a higher-lying triplet of the same defect, which relaxes spin selectively to the radiative singlets.

In each polytype the highest-lying NP luminescence line splits into components $V1$ and $V1'$, due to a lifting of the orbital degeneracy. $V1'$ has $\mathbf{E}\perp c$ polarization whereas $V1$ has weak $\mathbf{E}\| c$ polarization. For $V2$ $\mathbf{E}\| c$ axis polarization dominates in both polytypes, whereas $V3$ in $6H$ SiC has weak $\mathbf{E}\perp c$ polarization.

In strained samples an additional structure occurs at the high-energy side of all NP lines in both PL and PLE experiments. This structure is tentatively assigned to strain variations in the sample.

A full understanding of the detailed electronic structure and polarization properties calls for in-depth theoretical studies, which have so far yielded predictions that are in many cases in contradiction with the present experimental findings.

[1] H. Itoh, N. Hayakawa, I. Nashiyama, and E. Sakuma, J. Appl. Phys. **66**, 4529 (1989).

[2] G. D. Watkins, in *Deep Centers in Semiconductors*, edited by S. T. Pantelides (Gordon and Breach, Yverdon, Switzerland, 1992), p. 177.

[3] T. Wimbauer, B. K. Meyer, A. Hofstaetter, A. Scharmann, and H. Overhof, Phys. Rev. B **56**, 7384 (1997).

[4] E. Sörman, N. T. Son, W. M. Chen, O. Kordina, C. Hallin, and E. Janzén, Phys. Rev. B **61**, 2613 (2000).

[5] I. S. Gorban and A. V. Slobodyanyuk, Fiz. Tverd. Tela (Leningrad) **15**, 789 (1973) [Sov. Phys. Solid State **15**, 548 (1973)].

[6] S. H. Hagen and A. W. C. van Kemenade, J. Lumin. **9**, 9 (1974).

[7] A. Zywietz, J. Furthmüller, and F. Bechstedt, Phys. Rev. B **59**, 15 166 (1999).

[8] L. Torpo, R. M. Nieminen, K. E. Laasonen, and S. Pöykkö, Appl. Phys. Lett. **74**, 221 (1999).

[9] A. Niilisk, A. Laisaar, and A. V. Slobodyanyuk, Solid State Commun. **94**, 71 (1995).

[10] K. M. Lee, K. P. O'Donnell, J. Weber, B. C. Cavenett, and G. D. Watkins, Phys. Rev. Lett. **48**, 37 (1982).

[11] P. Deák, J. Miró, A. Gali, L. Udvardi, and H. Overhof, Appl. Phys. Lett. **75**, 2103 (1999).

[12] K. M. Lee, Le Si Dang, G. D. Watkins, and W. J. Choyke, Phys. Rev. B **32**, 2273 (1985).