Electron paramagnetic resonance and theoretical studies of Nb in 4H- and 6H-SiC

Nguyen Son Tien, Xuan Thang Trinh, Andreas Gällström, Stefano Leone, Olle Kordina, Erik Janzén, Krisztian Szasz, Viktor Ivady and Adam Gali

Linköping University Post Print

N.B.: When citing this work, cite the original article.

Original Publication:

Nguyen Son Tien, Xuan Thang Trinh, Andreas Gällström, Stefano Leone, Olle Kordina, Erik Janzén, Krisztian Szasz, Viktor Ivady and Adam Gali, Electron paramagnetic resonance and theoretical studies of Nb in 4H- and 6H-SiC, 2012, Journal of Applied Physics, (112), 8, 083711.

<http://dx.doi.org/10.1063/1.4759362>

Copyright: American Institute of Physics (AIP)

<http://www.aip.org/>

Postprint available at: Linköping University Electronic Press

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-86385>

Electron paramagnetic resonance and theoretical studies of Nb in 4H- and 6H-SiC

Nguyen Tien Son,¹ Xuan Thang Trinh,¹ Andreas Gällström,¹ Stefano Leone,¹ Olof Kordina,¹ Erik Janzén,¹ Krisztián Szász,² Viktor Ivády,^{1,2} and Adam Gali^{2,3}

¹Department of Physics, Chemistry and Biology, Linköping University, SE-581 83 Linköping, Sweden

²Institute for Solid State Physics and Optics, Wigner Research Center for Physics, Hungarian Academy of Sciences, PO Box 49, H-1525 Budapest, Hungary

³Department of Atomic Physics, Budapest University of Technology and Economics, Budafoki út 8, H-1111 Budapest, Hungary

(Received 13 June 2012; accepted 25 September 2012; published online 19 October 2012)

High purity silicon carbide (SiC) materials are of interest from high-power high temperature applications across recent photo-voltaic cells to hosting solid state quantum bits, where the tight control of electrically, optically, and magnetically active point defects is pivotal in these areas. 4H- and 6H-SiC substrates are grown at high temperatures and the incorporation of transition metal impurities is common. In unintentionally Nb-doped 4H- and 6H-SiC substrates grown by high-temperature chemical vapor deposition, an electron paramagnetic resonance (EPR) spectrum with C_{1h} symmetry and a clear hyperfine (hf) structure consisting of ten equal intensity hf lines was observed. The hf structure can be identified as due to the interaction between the electron spin $S = 1/2$ and the nuclear spin of ^{93}Nb . Additional hf structures due to the interaction with three Si neighbors were also detected. In 4H-SiC, a considerable spin density of $\sim 37.4\%$ was found on three Si neighbors, suggesting the defect to be a complex between Nb and a nearby carbon vacancy (V_C). Calculations of the ^{93}Nb and ^{29}Si hf constants of the neutral Nb on Si site, Nb_{Si}^0 , and the Nb-vacancy defect, $\text{Nb}_{\text{Si}}V_C^0$, support previous reported results that Nb preferentially forms an asymmetric split-vacancy (ASV) defect. In both 4H- and 6H-SiC, only one Nb-related EPR spectrum has been observed, supporting the prediction from calculations that the hexagonal-hexagonal defect configuration of the ASV complex is more stable than others. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4759362>]

I. INTRODUCTION

Silicon carbide (SiC) has long been considered as one of the most promising materials for high-power high-temperature electronics.¹ Single crystal SiC is usually grown at high temperatures and unintentional incorporation of transition metals (TMs) during the growth is unavoidable. Intrinsic defects such as vacancies (V_{Si} and V_C)^{2,3} and their associated complexes (e.g., divacancy⁴ and vacancy-antisite pairs⁵) are also known to be commonly present in as-grown materials and are highly thermally stable.⁶ It has been shown that TMs of column IVB, VB, and VIB like Ti, V, Cr (3d elements), Mo (4d), Ta, and W (5d) introduce deep levels in the band gap of 4H- and 6H-SiC.⁷ The development of device applications requires defect control in SiC in order to achieve high-quality semi-insulating substrates for high-frequency electronics, to improve the carrier lifetime of epitaxial layers and carrier mobility in power devices. Recently, the Si vacancy, divacancy, and some unidentified defects in SiC have been found to be promising for realization of solid state quantum bits.^{8–12} Successful applications of SiC in these areas require a tight control of electrically, optically, and magnetically active point defects in the material.

In 3C-SiC with cubic crystal structure, calculations¹³ found that 3d TMs prefer the Si site to form substitutional impurities. In the 4H and 6H hexagonal polytypes, 3d TMs such as Ti,^{14–16} V,^{17–19} Cr,^{19–21} Sc,²² and Ni²³ are also known to substitute for Si site and the TM centers at different inequivalent-lattice sites

in 4H- and 6H-SiC have been identified. However, there is unclear or no corresponding correlation found for 4d TM impurities such as Mo and Baur and co-workers²⁴ found only one electron paramagnetic resonance (EPR) spectrum related to the donor state Mo^{5+} ($4d^1$) in 6H-SiC. The EPR of the acceptor state of Mo, Mo^{3+} ($4d^3$), has also been observed for a single lattice site in *n*-type 6H- and 15R-SiC.¹⁹ In 6H-SiC, Irmscher and co-workers²⁵ found only one EPR spectrum related to the neutral W^{5+} ($5d^1$) substituting for Si. From the reported data, there is no clear analogy in the electronic structure between the 3d TMs and others in the 4d and 5d series in SiC. It has been suggested that TMs occupy both substitutional and center-bond sites in Ge.²⁶ Assali and co-worker²⁷ also found that Mn is energetically more favorable in a divacancy site as compared to the B site in boron nitride (BN) and forms split-vacancy defects. In SiC, it is not clear if the 4d and 5d TMs with larger ionic radii prefer the Si site to form isolated substitutional defects or a split-vacancy site as in BN.

In high-temperature chemical vapor deposition (HTCVD) or CVD growth of SiC, tantalum carbide (TaC) is commonly used for coating some parts exposed to high temperatures in reactor.²⁸ Recently, niobium carbide (NbC) has been used as an alternative to TaC coated parts. The unintentional incorporation of Ta and Nb impurities in SiC during HTCVD growth is expected. Tantalum has been unambiguously identified by radiotracer deep level transient spectroscopy (DLTS).²⁹ However, DLTS cannot distinguish if the impurity occupies the substitutional or interstitial site, and if it is isolated or associated

with other defects. Recent calculations³⁰ show that Nb preferentially forms an asymmetric split-vacancy (ASV) defect. In this work, we present detailed EPR results of unintentionally Nb-doped 4H- and 6H-SiC grown by HTCVD in a reactor containing NbC parts. The hyperfine (hf) constants of ^{93}Nb and ^{29}Si neighbors of the neutral Nb at Si site, Nb_{Si}^0 , and at split-vacancy sites, $\text{Nb}_{\text{Si}}\text{V}_{\text{C}}^0$, were calculated and compared to the obtained EPR data, supporting the identification of the neutral Nb ASV defect in 4H- and 6H-SiC.

II. EXPERIMENTAL DETAILS

The 4H- and 6H-SiC samples used in this study were grown by HTCVD in a reactor with several parts made of NbC. The Nb-doped material is semi-insulating and the concentration of Nb unintentionally incorporated in the 4H-SiC sample is $\sim 3 \times 10^{16} \text{ cm}^{-3}$ as determined by secondary ion mass spectrometry (SIMS). EPR measurements were performed on X-band ($\sim 9.5 \text{ GHz}$) Bruker E500 and E580 spectrometers using a continuous helium-flow cryostat which allows the regulation of the sample temperature from 4 K to room temperature. For photo-excitation EPR (photo-EPR) experiments, a 250 W halogen lamp, a 0.25 m single grating Jobin-Yvon monochromator, and appropriate optical filters were used.

III. RESULTS AND DISCUSSION

In all unintentionally Nb-doped 4H-SiC samples, in addition to the broad and isotropic SI-1 signal ($g = 2.0026$),³¹ an EPR spectrum consisting of ten lines of equal intensity with the splitting varying from $\sim 2.5 \text{ mT}$ (for the low-field lines) to $\sim 3.1 \text{ mT}$ (for the high-field lines) was observed at temperatures below 100 K. Fig. 1 shows the spectrum observed in darkness at 44 K for the magnetic field $\mathbf{B}$ parallel to the c-axis ($\mathbf{B} \parallel \mathbf{c}$ corresponding to the angle 0°). The signal is not sensitive to illumination. The observed hf structure can be identified due to the hf interaction between the electron spin $S = 1/2$ and a nuclear spin $I = 9/2$ of an element having 100% natural abundance. There are only few elements having the maximum possible nuclear spin $I = 9/2$ and a 100% natural abundance: ^{93}Nb , ^{209}Bi , and two indium isotopes, ^{113}In (4.29%) and ^{115}In (95.71%). Bi and In are not common impurities in SiC while the presence of Nb in the sample has been confirmed by SIMS. Therefore, the observed hf structure can be unambiguously identified to be related to Nb.

In addition to this hf structure, each ^{93}Nb hf line is accompanied by two pairs of weak hf lines (Fig. 1). These weak hf structures are clearly shown in the inset of Fig. 1. The pair with a larger splitting ($\sim 4.4 \text{ mT}$) has the intensity ratio with the main line of $\sim 9\%$ – 10% while the corresponding value for the two inner hf lines (splitting $\sim 0.86 \text{ mT}$) is $\sim 4\%$ – 5% . These intensity ratios are approximately the natural abundance of two and one ^{29}Si isotope ($I = 1/2$ and 4.69% natural abundance), respectively. This intensity ratios ($\sim 13\%$ – 14%) are indeed close to that of the hf interaction with one ^{13}C ($I = 1/2$, 1.07% natural abundance) atom occupying one of the 12 equivalent C sites in the second neighbor ($\sim 13.4\%$). However, such a hf interaction would give rise to only two measureable hf lines with splitting expected to be isotropic and small (typically ~ 0.35 – 0.4 mT for defects at

FIG. 1. EPR spectrum in Nb-doped 4H-SiC grown by HTCVD measured at 44 K for $\mathbf{B} \parallel \mathbf{c}$ showing a ^{93}Nb hf structure consisting of ten equal intensity lines. The broad line at $\sim 339.26 \text{ mT}$ is the isotropic signal of the SI-1 defect.³¹ Each ^{93}Nb hf line is accompanied by two pairs of weak hf lines and their structures are shown in the scaled up part of the spectrum in the inset. The smaller and larger splitting pairs are due to the interaction between the unpaired electron and the nuclear spins of one Si atom and two equivalent Si atoms, respectively.

the C site³²). Thus, the possibility that the observed hf structures are due to the hf interaction with C neighbors can be excluded. We therefore assign the weak outer and inner pairs as due to the hf interaction of the electron spin with the nuclear spins of two equivalent Si atoms and one Si atom, respectively.

When rotating the magnetic field away from the c-axis, each ^{93}Nb hf line splits into four lines. Each Si hf line is also split into two lines. Fig. 2 shows the spectrum measured at 44 K for $\mathbf{B} \perp \mathbf{c}$ (angle 90°). The splitting of the outer and inner Si hf lines of the low-field part of the spectrum is shown in the inset of Fig. 2. The measured angular dependence of the positions of ^{93}Nb hf lines with the magnetic field rotating in the $(11\bar{2}0)$ plane is shown in Fig. 3. As can be seen in the figure, the angular dependence shows a typical C_{3h} symmetry. With increasing the angle of the magnetic field, the ^{93}Nb hf splitting increases from ~ 2.5 – 3.1 mT to ~ 6.8 – 7.2 mT (at $\mathbf{B} \perp \mathbf{c}$) for the strong lines and decreases from ~ 2.5 – 3.1 mT to ~ 1.5 – 2.3 mT for the weaker lines (Fig. 2).

The angular dependence of the ^{93}Nb hf lines in Fig. 3 for the spectrum in 4H-SiC can be described by the following spin-Hamiltonian:

FIG. 2. EPR spectrum in Nb-doped 4H-SiC measured at 44 K for $\mathbf{B} \perp \mathbf{c}$ showing the hf structures of ^{93}Nb corresponding to different defect sites of a C_{1h} center. At this direction of the magnetic field, each Si hf lines shown in Fig. 1 is split into two lines as shown in the scaled up part of the spectrum in the inset.

FIG. 3. Angular dependence of the Nb-related spectrum (open circles) measured at 77 K with the magnetic field rotating in the (1120) plane. The solid curves represent the simulated angular dependence using Eq. (1) and parameters in Table I. The angles 0° and 90° correspond to the directions $\mathbf{B} \parallel \mathbf{c}$ and $\mathbf{B} \perp \mathbf{c}$, respectively.

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

Here, μ_B is the Bohr magneton, $S = 1/2$, $I = 9/2$, and both the g-tensor and the hf A-tensor of the Nb center have C_{1h} symmetry. The principal values of the g- and A-tensors obtained from the best fit to the data using Eq. (1) are given in Table I. The simulated angular dependence using the obtained spin-Hamiltonian parameters is plotted as solid curves in Fig. 3.

The hf interactions with two equivalent Si_{1-2} atoms and with one Si_3 atom also have C_{1h} symmetry. Due to overlapping with the main lines, the angular dependences of the hf lines of two equivalent Si_{1-2} neighbors and the third Si_3 atom could be observed only at some angles close to $\mathbf{B} \parallel \mathbf{c}$ and $\mathbf{B} \perp \mathbf{c}$. At $\mathbf{B} \parallel \mathbf{c}$, the splitting of ^{29}Si hf lines of each Nb line is in the range 4.33–4.38 mT for the two equivalent Si_{1-2} atoms and ~ 0.85 – 0.91 mT for the third Si_3 atom. At intermediate angles, each ^{29}Si hf lines splits into two lines with the splitting being largest at $\mathbf{B} \perp \mathbf{c}$: ~ 4.34 – 4.48 mT and ~ 5.81 – 5.88 mT for the two equivalent Si_{1-2} atoms and ~ 1.03 – 1.05 mT and ~ 1.78 – 1.85 mT for the third Si_3 atom. In this case, the Si hf tensors have C_{1h} symmetry and their principal values can be estimated directly from the splittings at $\mathbf{B} \parallel \mathbf{c}$ and at $\mathbf{B} \perp \mathbf{c}$ (here, we average the hf splittings of the low-field lines and high-field lines which are about 0.1 mT

TABLE I. Spin-Hamiltonian parameters of the Nb-related center in 4H- and 6H-SiC. The principal A-values are given in the unit of 10^{-4} cm^{-1} . θ and φ are the polar and azimuthal angles, respectively, of the principal axes of the g- and A-tensors measured in degree. The error in the determination of the g-values is ~ 0.0005 . The error in the principal A-values is $\sim 0.4 \times 10^{-4} \text{ cm}^{-1}$ for ^{93}Nb . The A values for ^{29}Si atoms are estimated from the hf splitting at some angles close to $\mathbf{B} \parallel \mathbf{c}$ and $\mathbf{B} \perp \mathbf{c}$ and may have larger errors (up to $\sim 2 \times 10^{-4} \text{ cm}^{-1}$). Two set of parameters with interchanging the principal xx and zz values and corresponding Euler angles (θ and φ) give the same angular dependence. The calculated principal values of the hf tensors for Nb and for nearest Si neighbors of the $\text{Nb}_{\text{Si}}\text{V}_{\text{C}}^0$ and Nb_{Si}^0 defects in 4H-SiC are also given for comparison. The sign of the principal values cannot be determined in EPR experiments. The labels of Si-atoms are shown in Fig. 7. In the Nb_{Si}^0 defect, the hf constants on the second neighbor Si-atoms are low as indicated briefly in the table.

Center	Parameter	g_{xx}	g_{yy}	g_{zz}	A_{xx}	A_{yy}	A_{zz}
4H-SiC	Experiment						
	Nb	2.018	2.0272	1.9891	16.0	30.7	73.7
	θ	72.8	17.2	90	118.4	28.4	90
	φ	90	270	0	90	90	0
	Si_{1-2}				42	41	55
	Si_3				17	10	8
6H-SiC	Nb	2.0184	2.0279	1.9885	16.9	30.9	73.0
	θ	71.1	18.9	90	118.8	28.8	90
	φ	90	270	0	90	90	0
4H-SiC	Calculation						
	$\text{Nb}_{\text{Si}}\text{V}_{\text{C}}^0$						
	Nb				6.8	51.1	73.2
	θ						89.3
	φ						-0.6
	Si_{1-2}				20.2	21.1	35.4
Nb_{Si}^0	Si_3				8.8	7.3	7.2
	Nb				38.6	62.0	72.3
	θ						65.7
	φ						-11.1
	Si_{1-12}				<19.0l	<19.0l	<110.0l

different). The estimated principal values of the Si hf tensors for Si_{1-2} and Si_3 atoms are given in Table I.

In Nb-doped 6H-SiC, an EPR spectrum similar to that in the 4H polytype was observed after illumination of the sample with light of photon energies larger than ~ 1.3 eV. As can be seen in Fig. 4, the spectrum in the 6H-SiC sample measured at 44 K after illumination for $\mathbf{B} \parallel \mathbf{c}$ also shows a hf structure consisting of ten ^{93}Nb hf lines with splitting of ~ 2.54 mT for the low-field lines and ~ 3.3 mT for the high-field lines, which is very similar to that in the 4H-SiC sample. The hf structures due to the interaction with two equivalent Si_{1-2} atoms and with the third Si_3 atom were also detected as shown in the inset of the figure. Their corresponding hf splittings of ~ 4.2 – 4.36 mT and ~ 0.89 mT, respectively, are also very similar to the case of the Nb center in 4H-SiC. Fig. 5 shows the Nb spectrum in 6H-SiC measured at 44 K for $\mathbf{B} \perp \mathbf{c}$. This spectrum is almost coincident with the Nb spectrum measured at the same angle in 4H-SiC. Unfortunately, the ^{29}Si hf structure was not observed for this angle and other intermediate angles due to weaker signals in the 6H-SiC sample. The angular dependence of the spectrum with $\mathbf{B}$ rotating in the (1120) plane is shown as open circles in Fig. 6. The angular dependence is very similar to that of the center in 4H-SiC. The g-tensor and ^{93}Nb hf tensor for the center obtained from the best fit using

FIG. 4. EPR spectrum in Nb-doped 6H-SiC grown by HTCVD measured after illumination with light of photon energy $h\nu \leq 2.8$ eV at 44 K for $\mathbf{B} \parallel \mathbf{c}$ showing a ^{93}Nb hf structure consisting of ten equal intensity lines. The ^{29}Si hf structures due to the interactions with two equivalent Si_{1-2} atoms and the third Si_3 atoms are shown in the inset.

FIG. 5. EPR spectrum in Nb-doped 6H-SiC measured at 44 K for $\mathbf{B} \perp \mathbf{c}$. The hf structures with ten lines related to different defect sites of C_{1h} symmetry center are indicated.

the spin-Hamiltonian Eq. (1) are also given in Table I. Due to lack of data, we could not determine the ^{29}Si hf tensors for the center in 6H-SiC. However, based on the similarity in the hf splitting of two equivalent Si_{1-2} atoms and the third Si_3

FIG. 6. Angular dependence of the Nb-related spectrum (open circles) in 6H-SiC measured at 44 K with the magnetic field rotating in the (1120) plane. The solid curves represent the simulated angular dependence using Eq. (1) and parameters in Table I.

atoms of the Nb center in 4H- and 6H-SiC at the *c*-direction, we expect that the hf tensors of Si₁₋₂ and Si₃ neighbors are also similar.

Using the linear-combination of atomic-orbitals (LCAO) approximation³³ and the atomic hf parameters given by Morton and Preston,³⁴ we estimate the spin localization of $\sim 29.6\%$ on two Si₁₋₂ neighbors and $\sim 7.8\%$ on the third Si₃ neighbor. The observed considerable spin density ($29.6\% + 7.8\% = 37.4\%$) on three nearest Si neighbors suggests that the defect is a complex between Nb and a nearby C vacancy.

Our recent calculations³⁰ show that the isolated substitutional Nb on Si site, Nb_{Si} [Fig. 7(a)], and the asymmetric Nb split-vacancy center [Fig. 7(b)], i.e., Nb at a divacancy but staying more close to the Si vacancy, V_{Si}, than the C vacancy, V_C, have comparable formation energies. The calculations also showed that for Nb_{Si}⁰ the spin is mainly localized on its *d* orbital and very little on neighboring atoms while a considerable spin density is found on two equivalent Si neighbors for the Nb split-vacancy center.³⁰ In this work, we performed the calculations of the full hf tensor of ⁹³Nb and neighboring Si atoms for both the substitutional Nb_{Si} and the Nb split-vacancy defects, Nb_{Si}V_C. We applied the all-electron projector augmentation wave method (PAW)³⁵ together with plane wave (PW) basis set where the defect was modeled in a 576-atom 4H-SiC supercell with Γ -point sampling of the Brillouin-zone. This large supercell ensures the convergent charge and spin densities even for complexes and monitoring the degeneracy of the single particle levels in the fundamental band gap. We found that plane wave cut-off of about 30 Ry provided convergent charge and spin density within PAW framework. Semilocal Perdew-Burke-Ernzerhof

(PBE) functional³⁶ was applied to calculate the spin density. We checked that Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional³⁷ provided the same all-electron spin density at the place of atoms within 3% as PBE functional in VASP³⁸ code at optimized geometries. Optimized geometries were found by minimizing the total energy of the system as a function of the coordinates of atoms where the maximum force acting on the atoms was reduced below 0.01 eV/Å. The optimized geometry was taken to the CPPAW³⁹ code in order to calculate the full hf tensor of selected atoms. This method has earlier been proven to be very successful in identification of defects in 4H-SiC.^{4,5,40,41}

As shown in recent calculations,³⁰ the total energy difference and spin density of Nb_{Si} defect at cubic (*k*) or hexagonal (*h*) site are the same while Nb_{Si}V_C defect uniquely prefers the *h-h* configuration. Thus, we considered the spin densities and hf tensors of Nb_{Si} in *h*-site and Nb_{Si}V_C defect at *h-h* sites. In the neutral charge state, a singly occupied *e* defect level appears for Nb_{Si}, while three-times occupied *e* defect level appears for Nb_{Si}V_C defect in C_{3v} symmetry.³⁰ Both defects are Jahn-Teller unstable but the distortion is subtle for the latter defect with reducing the symmetry to C_{1h}. The calculated hf constants can be found in Table I.

A neutral Nb atom has five electrons (4d⁴5s) to fill six orbital states: one *s* orbital state and five *d* orbital states. Supplying four electrons to four bonds, the neutral substitutional Nb defect has one unpaired electron in the double degenerate *e* state (in C_{3v} symmetry) or the split off *d''* state (in C_{1h} symmetry according to our calculation), giving rise to the spin *S* = 1/2. Since the unpaired electron is localized on a *d* orbital of Nb, the spin density on the neighboring atoms is expected to be small, especially for the twelve second neighbor Si. (The dipole interaction between the electron spin at Nb and a nuclear spin of ²⁹Si occupying one of the 12 equivalent Si sites in the second neighbor shell is expected to be weak and more isotropic than we observe.) This is indeed observed in our hf calculations for the neutral isolated substitutional Nb which show that the ²⁹Si hf constants of second neighbor Si₁₋₁₂ is less than 10⁻⁴ cm⁻¹ (Table I). These calculated ²⁹Si hf constants are very different from that determined by EPR (Table I) and we can safely exclude the isolated substitutional Nb_{Si}⁰ as the defect model of the Nb-related EPR center.

For the neutral Nb-C vacancy complex, Nb_{Si}V_C⁰, there are 11 electrons (five from Nb and six from the neutral divacancy) to fill the combined Nb and divacancy states. The six orbital states of Nb⁰ are strongly mixed with the six orbital states of the neutral divacancy and hence an individual state of the complex cannot be considered as a pure Nb orbital state or a divacancy state. In this case, the six electrons fill three Nb-C bonds and five electrons are on three bonds to the three Si neighbors of V_C. Thus, there will be two Nb-Si bonds being filled and one Si dangling bond having the unpaired electron. Due to C_{1h} symmetry, the dangling bond does not occur equally to the three Si neighbors, but more favorable to two equivalent Si atoms. This leads to a stronger hf interaction with two equivalent Si atoms and a considerable weaker hf interaction with the third Si neighbor. The hf interaction with these nearest Si neighbors is therefore expected to be more

FIG. 7. Schematic picture about (a) Nb_{Si} and (b) Nb_{Si}V_C defects in 4H-SiC. The Si-atoms are labeled in order to identify them in the corresponding EPR spectrum. In Nb_{Si}V_C defect, Si₁ and Si₂ atoms are symmetrically equivalent. The isosurface of the calculated spin density is shown in red color that clouds Nb impurity.

anisotropic and there should be considerable spin localization on the Si dangling bond. This has been observed in our EPR experiments with the spin localization of $\sim 37.4\%$ on three Si neighbors. The principal values of the ^{93}N and ^{29}Si hf tensors of the Nb-related center determined by EPR are also fairly reproduced by calculations for $\text{Nb}_{\text{Si}}\text{V}_{\text{C}}^0$ defect (Table I), suggesting that the observed Nb-related EPR defect is the neutral Nb-C vacancy complex. The observation of only one Nb-related EPR center with similar g-values and hf parameters in 4H- and 6H-SiC supports the suggestion in previous calculations³⁰ that the *h-h* configuration is more stable than other configurations of the Nb-C vacancy complex.

IV. SUMMARY

A detailed analysis of the g-values and the ^{93}Nb and ^{29}Si hf structures of the Nb-related EPR spectrum in unintentionally Nb-doped 4H- and 6H-SiC previously assigned to the neutral Nb-C vacancy, $\text{Nb}_{\text{Si}}\text{V}_{\text{C}}^0$, is presented. A strong and anisotropic hf interaction with two equivalent Si atoms and a much weaker hf interaction with the third Si neighbor have been observed, showing considerable spin density on three Si neighbors of the C vacancy ($\sim 37.4\%$ in 4H-SiC). Comparing hf data obtained by EPR and by hf calculations for the neutral isolated substitutional Nb, Nb_{Si}^0 , and the Nb-vacancy complex provides further support for the identification of the defect as $\text{Nb}_{\text{Si}}\text{V}_{\text{C}}^0$. The observation of only one Nb-related EPR spectrum in 4H- and 6H-SiC is in line with the result from previous calculations predicting that the *h-h* configuration of the $\text{Nb}_{\text{Si}}\text{V}_{\text{C}}^0$ defect is more stable than others.

ACKNOWLEDGMENTS

Support from the Swedish Energy Agency, the Swedish Research Council VR/Linné Environment LiLi-NFM, FP7 Grant No. 270197, the NHDP TÁMOP-4.2.1/B-09/1/KMR-2010-0002 program, the Swedish National Infrastructure for Computing, and the Knut and Alice Wallenberg Foundation is acknowledged.

¹M. Bhatnaga and B. J. Baliga, *IEEE Trans. Electron Devices* **40**, 645–655 (1993).

²J. Isoya, T. Umeda, N. Mizuochi, N. T. Son, E. Janzén, and T. Ohshima, *Phys. Status Solidi B* **245**, 1298–1314 (2008).

³E. Janzén, A. Gali, A. Henry, I. G. Ivanov, B. Magnusson, and N. T. Son, *Defects in Microelectronic Materials and Devices*, edited by D. M. Fleetwood, S. T. Pantelides, and R. D. Schrimpf (CRC, Boca Raton, 2008), pp. 615–669.

⁴N. T. Son, P. Carlsson, J. ul Hassan, E. Janzén, T. Umeda, J. Isoya, A. Gali, M. Bockstedte, N. Morishita, T. Ohshima, and H. Itoh, *Phys. Rev. Lett.* **96**, 055501 (2006).

⁵T. Umeda, N. T. Son, J. Isoya, E. Janzén, T. Ohshima, N. Morishita, H. Itoh, A. Gali, and M. Bockstedte, *Phys. Rev. Lett.* **96**, 145501 (2006).

⁶N. T. Son, P. Carlsson, J. ul Hassan, B. Magnusson, and E. Janzén, *Phys. Rev. B* **75**, 155204 (2007).

⁷N. Achtziger and W. Witthuhn, *Silicon Carbide Recent Major Advances*, edited by W. J. Choyke, H. Matsunami, and G. Pensl (Springer-Verlag, Berlin, 2004), p. 537.

⁸A. Gali, A. Gällström, N. T. Son, and E. Janzén, *Mater. Sci. Forum* **645–648**, 395 (2010).

⁹J. R. Weber, W. F. Koehl, J. B. Varley, A. Janotti, B. B. Buckley, C. G. Van de Walle, and D. D. Awschalom, *Proc. Natl. Acad. Sci. U.S.A.* **107**, 8513 (2010).

¹⁰P. G. Baranov, A. P. Bundakova, A. A. Soltamova, S. B. Orlinskii, I. V. Borovykh, R. Zondervan, R. Verberk, and J. Schmidt, *Phys. Rev. B* **83**, 125203 (2011).

¹¹W. F. Koehl, B. B. Buckley, F. J. Heremans, G. Calusine, and D. D. Awschalom, *Nature* **479**, 84 (2011).

¹²A. Gali, *J. Mater. Res.* **27**, 897 (2012).

¹³M. S. Miao and W. R. L. Lambrecht, *Phys. Rev. B* **68**, 125204 (2003).

¹⁴W. J. Choyke and L. Patrick, *Silicon Carbide 1973* (University of South Carolina Press, Columbia, 1974), p. 261.

¹⁵A. W. C. Van Kemenade and S. H. Hagen, *Solid State Commun.* **14**, 1331 (1974).

¹⁶K. M. Lee, Le Si Dang, G. D. Watkins, and W. J. Choyke, *Phys. Rev. B* **32**, 2273 (1985).

¹⁷J. Schneider, A. Dörnen, S. Leibenzeder, and R. Stein, *Appl. Phys. Lett.* **56**, 1184 (1990).

¹⁸M. Kunzer, H. D. Müller, and U. Kaufmann, *Phys. Rev. B* **48**, 10846 (1993).

¹⁹J. Baur, M. Kunzer, and J. Schneider, *Phys. Status Solidi A* **162**, 153 (1997).

²⁰P. G. Baranov, V. A. Khrantsov, and E. N. Mokhov, *Semicond. Sci. Technol.* **9**, 1340 (1994).

²¹N. T. Son, A. Ellison, B. Magnusson, M. F. MacMillan, W. M. Chen, B. Monemar, and E. Janzén, *J. Appl. Phys.* **86**, 4348 (1999).

²²P. G. Baranov and E. N. Mokhov, *Sov. Phys. Solid State* **38**, 798 (1996).

²³P. G. Baranov, I. V. Ilyn, E. N. Mokhov, and V. A. Khrantsov, *Mater. Sci. Forum* **353–356**, 529 (2001).

²⁴J. Baur, M. Kunzer, K. F. Dombrowski, U. Kaufmann, J. Schneider, P. G. Baranov, and E. N. Mokhov, *Inst. Phys. Conf. Ser.* **155**, 933 (1997).

²⁵K. Irmischer, I. Pintilie, L. Pintilie, and D. Schulz, *Physica B* **308–310**, 730 (2001).

²⁶S. Decoster, S. Cottenier, B. De Vries, H. Emmerich, U. Wahl, J. G. Correia, and A. Vantomme, *Phys. Rev. Lett.* **102**, 065502 (2009).

²⁷L. V. C. Assali, W. V. M. Machado, and J. F. Justo, *Appl. Phys. Lett.* **89**, 072102 (2006).

²⁸M. Syväjärvi, R. Yakimova, R. R. Ciechonski, and E. Janzén, *Diamond Relat. Mater.* **12**, 1936 (2003).

²⁹J. Grillenberger, N. Achtziger, R. Sielemann, and W. Witthuhn, *J. Appl. Phys.* **88**, 3260 (2000).

³⁰V. Ivády, A. Gällström, N. T. Son, E. Janzén, and A. Gali, *Phys. Rev. Lett.* **107**, 195501 (2011).

³¹N. T. Son, B. Magnusson, Z. Zolnai, A. Ellison, and E. Janzén, *Mater. Sci. Forum* **457–460**, 437 (2004).

³²N. T. Son, W. C. Chen, J. L. Lindström, B. Monemar, and E. Janzén, *Phys. Scr.* **T79**, 46 (1999).

³³J. A. Weil and J. R. Bolton, in *Electron Paramagnetic Resonance—Elementary Theory and Practical Applications*, 2nd ed. (John Wiley & Sons, Inc., Hoboken, NJ, 2007), p. 121.

³⁴J. R. Morton and K. F. Preston, *J. Magn. Res.* **30**, 577 (1978).

³⁵P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).

³⁶J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).

³⁷J. Heyd, G. E. Scuseria, and M. Ernzerhof, *J. Chem. Phys.* **118**, 8207 (2003); A. V. Krukau, O. A. Vydrov, A. F. Izmaylov, and G. E. Scuseria, *J. Chem. Phys.* **125**, 224106 (2006).

³⁸G. Kresse and J. Hafner, *Phys. Rev. B* **49**, 14251 (1994); G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).

³⁹P. E. Blöchl, C. J. Först, and J. Schimpl, *Bull. Mater. Sci.* **26**, 33 (2003).

⁴⁰T. Umeda, Y. Ishitsuka, J. Isoya, N. T. Son, E. Janzén, N. Morishita, T. Ohshima, H. Itoh, and A. Gali, *Phys. Rev. B* **71**, 193202 (2005).

⁴¹T. Umeda, J. Isoya, T. Ohshima, N. Morishita, H. Itoh, and A. Gali, *Phys. Rev. B* **75**, 245202 (2007).