Electron paramagnetic resonance study of hydrogen-vacancy defects in crystalline silicon

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Electron paramagnetic resonance measurements on float-zone silicon implanted with protons at \(~50\) K followed by heating to room temperature have revealed two signals \(S_1\) and \(S_2\) belonging to the \(S\) group of signals. \(S_1\) and \(S_2\) both originate from defects with spin \(S=\frac{1}{2}\) and monoclinic-\(I\) symmetry. The near-trigonal \(g\) tensors and several sets of \(29\)Si hyperfine splittings all closely resemble those observed previously for \(V^0\), the neutral charge state of the monovacancy binding a single hydrogen atom. Analysis of a tiny proton hyperfine splitting of \(S_1\) provides strong evidence that this signal originates from \(V_2\), the neutral charge state of the divacancy binding one hydrogen atom. Parallel studies of the thermal decays of the \(V^0\), \(S_1\), and \(S_2\) signals and of infrared-absorption lines associated with Si-H stretch modes indicate that \(V^0\) possesses a stretch mode at \(2038.5 \text{ cm}^{-1}\), whereas modes at \(2068.1\) and \(2073.2 \text{ cm}^{-1}\) originate from the \(S_1\) and \(S_2\) defects. On the basis of theoretical results, we argue that the \(2068.1\)-cm\(^{-1}\) mode arises from \(V^0_2\) (the \(S_1\) defect) whereas the \(2073.2\)-cm\(^{-1}\) mode probably belongs to \(V_n^0\), \(n=3\) and \(4\) (the \(S_1\) defect).

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I. INTRODUCTION

The properties of hydrogen impurities in crystalline silicon have been studied intensively in the past.\(^1,2\) As a result of this effort, the structures of a number of hydrogen-related defects have been identified primarily by Fourier transform infrared (FTIR) spectroscopy,\(^3-6\) Raman spectroscopy,\(^7,8\) and ion channeling.\(^9,10\) These techniques have given valuable information about local vibrational modes associated with hydrogen, and the numbers of hydrogen atoms as well as their positions within the defects have been determined. However, little direct information has in general been obtained about the electronic properties of hydrogen-related defects. Apart from the complexes formed when hydrogen combines with a group-III acceptor\(^3,9,10\) or a group-V donor,\(^3,11\) the isolated hydrogen atom at the bond-center site was until recently the only case in which both the structure of a hydrogen defect, i.e., the arrangement of atoms, and its electronic properties were convincingly established.\(^12-14\)

In molecular compounds such as silane, hydrogen and silicon atoms form strong covalent bonds with a typical dissociation energy of \(~3.3\) eV, whereas only \(~2.0\) eV is required to break a Si-Si bond in crystalline silicon.\(^15\) Therefore, we may expect that hydrogen atoms embedded in a silicon matrix will form Si-H bonds even when this implies the breaking of Si-Si bonds. In particular, the binding of hydrogen to vacancies is a strongly exothermic process because these defects possess weak, elongated Si-Si bonds as well as dangling bonds (silicon orbitals occupied by a single electron). Accordingly, vacancies should efficiently trap hydrogen atoms. This expectation was directly confirmed by a FTIR study\(^5\) of proton-implanted silicon in which monovacancies binding two, three, and four hydrogen atoms were identified.

The neutral charge state of the monovacancy containing a single hydrogen atom \(V^0\) was recently identified by electron paramagnetic resonance (EPR).\(^16\) The EPR spectra revealed that \(V^0\) has monoclinic-\(I\) symmetry (point-group \(C_{1h}\)), and that its electron-spin distribution corresponds to a single dangling bond attached to a silicon atom. In accordance with the expected strength of the Si-H bond, the electron spin density at the proton is negligible. The observed weak proton hyperfine interaction is fully accounted for in terms of the magnetic dipole-dipole interaction between the spins of the electron and the proton, considered as classical point dipoles \(~2.7\) \(\text{Å}\) apart.

In addition to becoming captured by monovacancies, hydrogen atoms may also become trapped at small vacancy clusters like the divacancy\(^17\) \(V_2\), the trivacancy\(^18\) \(V_3\), and the planar tetrvacancy\(^19\) \(V_4\), all of which abound in silicon after implantation of protons. In the present work we discuss the neutral charge state of such clusters binding a single hydrogen atom each, which we denote collectively by \(V_n^0\). Each member of this family of defects has an odd number of electrons and is therefore amenable to EPR study. It seems reasonable to assume that the electronic structures of \(V_n^0\) resemble that of \(V^0\). Hence, we may expect that the EPR signals from \(V_n^0\) (like that from \(V^0\)) display the characteristics of a dangling bond in a vacancy-type defect. A major EPR signal, denoted \(S_1\), which answers this description, has previously been observed in proton-implanted silicon.\(^12,19-22\) This signal so closely resembles the signal from \(V^0\) that some care was required in our previous study to separate out the latter. \(S_1\) was in the past claimed to display either trigonal\(^19-21\) or near-trigonal, monoclinic-\(I\) symmetry.\(^22\) More recently, Gorelkinskii and Nevinnyi reported that \(S_1\) in fact consists of two signals in float-zone silicon displaying trigonal and monoclinic-\(I\) symmetries.\(^12\) No microscopic models have been proposed for the defects giving rise to \(S_1\).
In the present investigation of proton- and deuteron-implanted float-zone silicon, we have identified two members of the $S1$ group of signals, which we label $S1_a$ and $S1_b$. Both signals originate from defects with monoclinic-I symmetry. The involvement of a single hydrogen atom in the underlying defects is demonstrated directly for $S1_a$, whereas it is inferred for $S1_b$. We argue that $S1_a$ originates from $V_2H^0$ and that $S1_b$ most likely originates from $V_3H^0$ and possibly also from $V_4H^1$. Parallel EPR and FTIR measurements on identical samples show that $VH^0$ possesses a Si-H stretch mode at 2038.5 cm$^{-1}$, and that two other Si-H stretch modes at 2068.1 and 2073.2 cm$^{-1}$ are correlated with the $S1_a$ and $S1_b$ defects.

II. EXPERIMENTAL DETAILS

A. Sample preparation

Samples shaped as rectangular parallelepipeds measuring $15 \times 5 \times 0.5$ mm$^2$ with the large faces normal to the [111] axis and the small faces $(5 \times 0.5$ mm$^2$) normal to the [110] axis were cut from float-zone silicon with a quoted content of carbon and oxygen below $10^{16}$ cm$^{-3}$. The material was uncompensated $n$ type with a resistivity of $\sim 600$ $\Omega$ cm, corresponding to a phosphorus concentration of $\sim 9 \times 10^{12}$ cm$^{-3}$. The samples were polished on both large faces, and were subsequently etched lightly in a mixture of HF and HNO$_3$ to remove surface defects.

During the implantation, the samples were mounted inside a vacuum chamber on a copper block, which was in good thermal contact with the cold finger of a closed-cycle helium cryocooler. The samples were cooled to a temperature of $\sim 10$ K by means of a thermostatted gas flow through a quartz dewar tube inserted into the microwave cavity. The sample was glued to a short brass rod, which was connected to a goniometer head by a stainless-steel capillary tube in order to minimize the thermal leak. The sample temperature was monitored with a copper-constantan thermocouple placed within the stainless-steel tube, in contact with the brass rod approximately 15 mm down stream from the sample.

The microwave frequency $\nu_0$ and the static magnetic field $B_0$ were monitored continuously during scans by means of a Hewlett-Packard 5350B frequency counter and a Bruker ER035M NMR gaussmeter. The NMR probehead was placed between the microwave cavity and one of the pole pieces of the magnet. The $g$ factor measured for polycrystalline DPPH (diphenylpicrylhydrazyl) with this setup was 2.003 55, indicating that systematic errors due to field offset were absent.

The one-axis goniometer allowed rotation of the sample around the normal to the horizontal plane containing $B_0$, and, moreover, the goniometer-cavity assembly could be tilted several degrees in the vertical plane containing $B_0$. With this facility we could make $B_0$ follow the (110) plane of the sample to within $0.3^\circ$ by adjusting the tilt angle to obtain a complete coalescence of corresponding EPR lines from defect sites interrelated through reflection in that plane. The orientation of $B_0$ within the (110) plane, specified by the angle $\varphi$ between $B_0$ and the [001] axis, was determined similarly from the coalescence of symmetry-related lines observed for $B_0$ directed along the three major axes [001], [111], and [110]. The accuracy achieved was $\pm 0.2^\circ$.

The signals $S1_a$ and $S1_b$ discussed here have very similar, near-trigonal $g$ tensors and therefore overlap heavily. Attempts to enhance the separation of the signals by recording the EPR spectra at $Q$ band (35 GHz) rather than at $X$ band were frustrated by a substantial increase of the linewidth: the observed peak-to-peak width of the $S1$ lines was 2–3 times larger at $Q$ band than at $X$ band, suggesting a significant local variation of the $g$ values. Consequently, the small proton hyperfine splitting of the $S1_a$ signal, as well as all but the largest $^{29}$Si hyperfine splittings, could only be resolved at $X$ band. The present results are therefore based on $X$-band spectra in which the desired resolution enhancement was obtained by third-harmonic detection.$^{23,24}$ The magnetic field was modulated at 33 kHz, while the EPR signal was lock-in detected at 100 kHz. The signal obtained in this way resembles closely the third derivative of the absorption curve. The peak-to-peak width is reduced compared with that of the first-derivative curve by 26% for Gaussian line shape and 44% for a Lorentzian line shape, and, furthermore, the “tails” of the curve are strongly suppressed. As the third-derivative signal is inversely proportional to the fourth

FTIR study showed that low-temperature implantation reduces the number of different defect structures.

B. EPR measurements

EPR spectra were recorded with a Bruker ESP300E spectrometer operated in the absorption mode at $\sim 9.2$ GHz ($X$ band), in conjunction with a Varian E-257 variable temperature device, which allowed the sample temperature to be set in the range 90–570 K by means of a thermostatted gas flow through a quartz dewar tube inserted into the microwave cavity. The sample was glued to a short brass rod, which was connected to a goniometer head by a stainless-steel capillary tube in order to minimize the thermal leak. The sample temperature was monitored with a copper-constantan thermocouple placed within the stainless-steel tube, in contact with the brass rod approximately 15 mm down stream from the sample.
power of the linewidth, detection of relatively weak, narrow EPR lines is possible even when they are almost obliterated by intense, broad lines in the first-derivative spectrum. The third derivative of a Gaussian or Lorentzian line shape has a pair of weak "sidebands" on either side of the main peak. These artifacts can be removed by addition of a small-amplitude 100-kHz field modulation to the 33-kHz modulation. In the present experiments no such sidebands were observed, however, so that no 100-kHz modulation was employed. The line shapes of $S_{1,a}$ and $S_{1,b}$ are neither Gaussian nor Lorentzian, which may suggest a superposition of lines with different widths and, hence, account for the absence of sidebands in the resolution-enhanced signals.

C. Derivation of hyperfine parameters

The hyperfine tensors describing $^{29}\text{Si}$ splittings and the proton splitting of $S_{1,a}$ were derived by simulation of the entire spectrum: The spin Hamiltonian term in question was first fitted to the spectra measured with $B_0$ along [001], [111], and [110]. Subsequently, the results were checked against several spectra having general orientations of $B_0$ in the (110) plane. Gaussian first-derivative line shapes were used in all simulations. This accounts for some of the residual discrepancies between the simulated and resolution-enhanced experimental spectra. Because the proton hyperfine coupling of $S_{1,a}$ is much smaller than the nuclear Zeeman energy of the proton in the employed field, the proton splitting observed between the principal directions strongly reflects the relative signs of the principal values of the hyperfine tensor. This allowed an unambiguous determination of these signs by means of the simulations.

D. Annealing study

A proton-implanted sample was cut in two pieces, which were used for monitoring EPR signals and Si-H stretch modes (by FTIR) after each step in a sequence of 60-min heat treatments in the temperature range 421–674 K. The temperature increment was ~15 K per step. The sample used for EPR was annealed in the microwave cavity with the device described above, whereas the sample used for FTIR was annealed in a furnace in ambient air. The temperature was monitored with identical thermocouples in the two sets of heat treatments. EPR spectra were recorded at 125 and 312 K, whereas the FTIR spectra were recorded at 12 K. This accounts for some of the residual discrepancies between the simulated and resolution-enhanced experimental spectra. Because the proton hyperfine coupling of $S_{1,a}$ is much smaller than the nuclear Zeeman energy of the proton in the employed field, the proton splitting observed between the principal directions strongly reflects the relative signs of the principal values of the hyperfine tensor. This allowed an unambiguous determination of these signs by means of the simulations.

III. RESULTS

A. Major EPR transitions

Since no hyperfine splittings from implanted deuterons were resolved, the EPR spectra of Si:D are somewhat simpler than those of Si:H. Therefore, we first discuss the $S_{1}$ signals arising from Si:D.

An X-band spectrum of Si:D recorded with conventional first-harmonic detection at 295 K with $B_0$ along the [111] axis is shown in Fig. 1, curve $a$. Two intense lines are observed at 328.6 and 329.9 mT, which agree very well with the positions expected\textsuperscript{19–21} for the lines of $S_{1}$. Hence we assign the lines to this group of signals. When the sample temperature is lowered to 200 K, the broad line at 328.6 mT splits into two partially resolved lines\textsuperscript{25} (curve $b$). The significant enhancement of the spectral resolution obtained with third-harmonic detection in the present study is demonstrated in curve $c$ of the figure.

The $S_{1}$ lines observed at 200 K originate from two distinct, although very similar EPR signals labeled $S_{1,a}$ and $S_{1,b}$ in Fig. 1, curve $c$. When $B_0$ is along [111], $S_{1,a}$ and $S_{1,b}$ both consist of just two resolved lines, which might seem to indicate that $S_{1,a}$ and $S_{1,b}$ originate from trigonal defects with spin $S=\frac{1}{2}$. However, the spectrum recorded with $B_0$ parallel to [110] shows that both signals contain four lines for this orientation (Fig. 2), indicating that the symmetry is monoclinic-$I$ rather than trigonal.

The monoclinic-$I$ symmetry of the $S_{1,a}$ and $S_{1,b}$ defects is confirmed by the variation of the positions of the EPR lines when $B_0$ is rotated in the (110) plane. Figures 3(a) and 3(b) show the line positions measured at 333 and 200 K, respectively. As described below in Sec. III D, $S_{1,b}$ is observed alone at 333 K. The solid lines in Fig. 3(a) are calculated from the spin Hamiltonian,

$$H = \mu_B S \cdot g \cdot B_0,$$

where $\mu_B$ is the Bohr magneton, $S$ the electron-spin operator ($S=\frac{1}{2}$), and $g$ a $g$ tensor with monoclinic-$I$ symmetry fitted to the data points. The dashed lines in Fig. 3(b) represent the fit to the $S_{1,a}$ data obtained with the spin Hamiltonian of Eq. (1), a monoclinic-$I$ $g$ tensor, and spin $S=\frac{1}{2}$. The solid lines
are identical to those in Fig. 3(a). The parameters of the \( g \) tensors for \( S_1^a \) and \( S_1^b \) are given in Table I together with those obtained previously \(^{16} \) for \( \text{VH}^0 \).
TABLE I. Spin Hamiltonian parameters for the VH^0 signal, S1_α, and S1_β. Principal axes are denoted X, Y, and Z, with Y parallel to the [110] axis, and X and Z spanning the (110) plane. Θ is the angle between Z and the [110] axis. Principal values of g and A_H are given in MHz. Limits of error: g, ±0.0001; A_Si, ±1.0 MHz; A_B, ±0.3 MHz.

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Two equivalent silicon sites. Z is taken along [111] and [111].

Three nearly equivalent silicon sites. Z is taken along [111].

Three nearly equivalent silicon sites. Z is taken along [111], [111], and [111].

The 29Si satellite lines have been analyzed with the spin Hamiltonian:

\[ H = \mu_p \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{B}_0 + \mathbf{S} \cdot 1A_{Si} \cdot 1I_{Si} - \mu_S g_S \cdot 1I_{Si} \cdot \mathbf{B}_0, \]

where \(1A_{Si}\) is the 29Si hyperfine-interaction tensor, \(1I_{Si}\) is the nuclear spin operator, and \(g_S\) the nuclear g factor for 29Si. Within the limits of error, the \(1A_{Si}\) tensors obtained for \(S1_\alpha\) and \(S1_\beta\) are axial with their unique principal axis parallel to the (111) direction along which the unique principal axis (Z) of the corresponding g tensor is nearly aligned. The principal values of \(1A_{Si}\) are given in Table I.

In addition to the 29Si satellite lines shown in Fig. 5, several pairs of satellite lines with much smaller splittings are observed around the central \(S1_\alpha\) and \(S1_\beta\) lines. This is illustrated in Fig. 6, which depicts the spectrum of Si:D recorded at 200 K with \(B_0\) parallel to the [111] axis. The same satellites are observed in the corresponding spectrum of Si:H. Consequently, we assign them to hyperfine interactions with 29Si nuclei. For both \(S1_\alpha\) and \(S1_\beta\), two sets of satellites with splittings of the order 1 mT could be resolved for most orientations of \(B_0\) in the (110) plane. One of these sets corresponds to two silicon sites that are equivalent by the mirror symmetry of the defect, and the hyperfine tensors associated with these sites are approximately axial. For the orientation of the defect that has the Z axis of the g tensor almost aligned with [111], the unique axes of these hyperfine tensors point along [111] and [111]. The other set involves three nearly equivalent silicon sites; the associated hyperfine tensors are

![Comparison of EPR spectra of Si:D and Si:H recorded with third-harmonic detection. Solid curves: observed spectra; broken curves: simulations based on the g tensors of S1_α and S1_β and the proton hyperfine tensor A_ν for S1_ν listed in Table I. The stick diagrams indicate the splitting of the S1_ν lines due to hyperfine interaction with the nuclear spins of the deuteron and the proton.](image-url)
nearly axial with the unique axes almost parallel to [111]. The available data did not allow a complete determination of the two sets of hyperfine tensors $^{1}A_{Si}$ and $^{3}A_{Si}$, describing the satellites. Therefore, the two tensors $^{2}A_{Si}$, which by symmetry have identical principal values, were taken to be axially symmetric with respect to [111] and [111], whereas three identical axial tensors with axes along [111] were used for the set $^{3}A_{Si}$. A satisfactory representation of the observed splittings was obtained with the principal values of $^{2}A_{Si}$ and $^{3}A_{Si}$ given in Table I.

Apart from the two sets of $^{29}$Si satellites just discussed, $S_{1a}$ has one additional set and $S_{1b}$ has two additional sets that are resolved in the spectrum in Fig. 6. It has not been possible to analyze these three sets in detail. Their intensities indicate that they all involve three near-equivalent silicon sites. If it is assumed that each set may be represented by an axial hyperfine tensor with its unique axis along a [111] direction, the principal values and the specific [111] axes may be estimated from the spectrum shown in Fig. 6. The resulting tensors $^{4}A_{Si}$, $^{5}A_{Si}$, and $^{6}A_{Si}$ are included in Table I. A simulation of the Si:D spectrum in Fig. 6 based on the hyperfine tensors described in this subsection is included in the figure. The agreement between the simulated and observed spectrum indicates that the tensors given in Table I account for all prominent $^{29}$Si satellites.

In EPR spectra recorded at 45 K, the VH$^{0}$ signal displays several sets of $^{29}$Si satellites, which are very similar to those observed for $S_{1a}$ and $S_{1b}$. The hyperfine tensors deduced from the spectra, which were not reported in Ref. 16, are included for comparison in Table I.

The available data did not allow a complete determination of the $S_{1a}$ and $S_{1b}$ components of the left-hand main line are barely distinguishable (see Fig. 1, curve b). Broken curve: simulation obtained with the trigonal hyperfine tensors $^{1}A_{Si}$ listed for $S_{1a}$ and $S_{1b}$ in Table I.

D. Temperature dependence of the $S_{1}$ signals

As noted above, $S_{1a}$ cannot be observed at sample temperatures $T \geq 330$ K. In contrast, $S_{1b}$ remains observable to 450 K. The gradual, reversible decrease of $S_{1a}$ with increasing temperature is illustrated in Fig. 7, which shows the high-field part of the Si:H spectrum recorded with $B_{o}$ along [111] [see also Fig. 4(a)]. The reduction of the height of the $S_{1a}$ line roughly reflects the $T^{-1}$ dependence of the difference between the populations of the spin levels involved in the EPR transition. We ascribe the additional reduction of the height of the $S_{1a}$ lines to a thermally induced increase of the linewidth. Since third harmonic detection was employed to resolve the $S_{1a}$ and $S_{1b}$ lines in Fig. 7, the signal height (for constant line shape) is inversely proportional to the fourth power of the linewidth, implying that only a minute broadening is required to produce a significant decrease in the observed signal height. Even so, an observable broadening of the $S_{1a}$ lines should accompany the decay of the signal. However, owing to the strong overlap with the central $S_{1b}$ line, the broadening of the $S_{1a}$ lines only emerges when the $S_{1a}$ and $S_{1b}$ lines are fitted simultaneously with combinations of Gaussian and Lorentzian line profiles.

E. Thermal decays of EPR signals and Si-H stretch modes

The parallel isochronal annealings of two identical proton-implanted samples, monitored by EPR and FTIR (see Sec. II D), were carried out to search for Si-H stretch modes belonging to VH$^{0}$ and to the $S_{1a}$ and $S_{1b}$ defects. A section of the FTIR spectrum of Si:H recorded before annealing is shown in Fig. 8. Several sharp absorption lines are observed,
among which those labeled H\(^2\)\(^*\), I\(H_2\), and V\(H_2\) were shown previously to represent Si-H stretch modes of these defects.\(^4\)\(^-\)\(^6\) The lines at 2038.5, 2068.1, and 2073.2 cm\(^{-1}\) all shift downwards in frequency by a factor of \(\approx \sqrt{2}\) to 1494.6, 1507.6, and 1511 cm\(^{-1}\), respectively, when hydrogen is replaced by deuterium. Thus these lines also represent local vibrational modes of hydrogen defects and are candidates for Si-H stretch modes associated with V\(H^0\), and the S\(1_a\) and S\(1_b\) defects.

The spectra recorded during the annealings show that the EPR signal from V\(H^0\) and the mode at 2038.5 cm\(^{-1}\) both disappear at about 480 K, whereas S\(1_a\) and S\(1_b\), and the Si-H modes at 2068.1 and 2073.2 cm\(^{-1}\) all decay at about 530 K.

The thermal decays of V\(H^0\) and of the 2038.5-cm\(^{-1}\) mode coincide within the limits of experimental error, as illustrated in Fig. 9. Figure 10 indicates that the same applies to the decays of S\(1_a\) and S\(1_b\), and of the Si-H modes at 2068.1 and 2073.2 cm\(^{-1}\).\(^26\)

We note that the weak FTIR line at 1942.3 cm\(^{-1}\) also decays at about 480 K, and, hence, might seem to be associated with V\(H^0\). However, the initial intensity of this line displays a variation from sample to sample that is unrelated to the variation of the intensity of the V\(H^0\) signal, indicating that the 1942.3-cm\(^{-1}\) line originates from a different defect.

IV. DISCUSSION

A. Assignments of S\(1_a\) and S\(1_b\)

The \(g\) tensors of S\(1_a\) and S\(1_b\), and the hyperfine tensors \(^1A_{\text{Si}}\) describing the large hyperfine interaction with a \(^{29}\)Si
nucleus at a unique site closely resemble the corresponding tensors determined earlier\(^\text{16}\) for VH\(^0\) (Table I). Since VH\(^0\) is a typical vacancy defect in which the unpaired electron resides primarily in a dangling-bond orbital,\(^\text{27}\) we therefore assign S\(_1\)\(_a\) and S\(_1\)\(_b\) to vacancy-type defects with a single dangling bond.

The monoclinic-I symmetry of the g tensors indicates that both defects have a (110) mirror plane. Combined with the presence of a hydrogen atom, established by the hyperfine splitting described by the pair of equivalent silicon sites with unique hyperfine axes along (111) directions and having length 1.48 Å, we find that the vacancy clusters V\(_n\) identified earlier by EPR (Refs. 17, 18, and 27–29) have spin Hamiltonians consistent with that of S\(_1\)\(_b\), we assign S\(_1\)\(_b\) to V\(_3\)H\(^0\). However, we note that the experimental findings do not rule out that larger complexes like V\(_4\)H\(^0\) also contribute to S\(_1\)\(_b\). This assignment is consistent with the lack of resolved proton hyperfine splittings of S\(_1\)\(_b\). With the proton-electron separations 6.5 and 8.4 Å estimated from the unrelaxed models of V\(_2\)H\(^0\) and V\(_4\)H\(^0\) in Fig. 11, the dipolar hyperfine splitting would not be resolved in the EPR spectra. Additional support for the presence of a hydrogen atom in the S\(_1\)\(_b\) defect as well as in the S\(_1\)\(_a\) defect is provided by the observation of Si-H modes with the same annealing behaviors as S\(_1\)\(_a\) and S\(_1\)\(_b\).

**B. Interpretation of the small 29Si hyperfine splittings**

In addition to the obvious assignment of the large 29Si hyperfine tensor \(3A_{Si}\) to the site denoted (1) in Fig. 11, the hyperfine interactions described by the pair of equivalent tensors \(3A_{Si}\) can be associated with the pair of silicon sites labeled (2,2') in the figure, and with the corresponding sites in VH\(^0\). In the case of VH\(^0\), this follows from the observation of 29Si hyperfine satellites at temperatures where the dangling bond jumps swiftly among the sites 1, 2, and 2'. Under those conditions the satellites correspond to three equivalent silicon sites with unique hyperfine axes along [111], [111], and [111]. Hence these satellites represent the hyperfine interaction averaged over the three equivalent positions of the dangling bond in VH\(^0\). The measured (common) principal values of the hyperfine tensors equal those calculated from the algebraic mean

\[
\frac{1}{3} [3A_{Si}(1) + 3A_{Si}(2) + 3A_{Si}(2')] 
\]

which follows: The isotropic component \(a = \frac{1}{3}(A_x + A_y + A_z)\) of the \(A_H\) tensor is 2.3 MHz, which, when compared with the value 1.420 MHz characteristic of atomic hydrogen, indicates a near-vanishing electron-spin density at the proton. Therefore, the anisotropic part of \(A_H\) represents a dipolar coupling between the proton and the electron spin, which resides predominantly in a "distant" dangling-bond orbital. The dipolar hyperfine parameter \(b = \frac{\hbar}{2} (2A_x - A_y - A_z)\) has the value 0.77 MHz. Within the point-dipole approximation, the distance \(\mathbf{R}\) from the proton to the silicon atom carrying the dangling bond may be estimated by the formula

\[
b = g_e \mu_B e_H |\mathbf{R}|^{-3},
\]

where \(g_e\) is the g factor of the electron. The result is \(|\mathbf{R}| = 4.7\) Å. Neglecting relaxations around the defect and assuming that the Si-H bond is aligned with a (111) direction and has the length 1.48 Å, we find that the distance from the proton to the silicon atom carrying the dangling bond is 4.6 Å in V\(_2\)H\(^0\), 6.5 Å in V\(_3\)H\(^0\), and 8.4 Å in V\(_4\)H\(^0\). Consequently, we identify the S\(_1\)\(_a\) defect with V\(_3\)H\(^0\). This identification is consistent also with the observed direction of the unique axis Z of \(A_H\) which deviates by only 4.5° from the [110] axis: Again neglecting relaxations, we find from the model that the vector connecting the proton and the silicon atom carrying the dangling bond lies 6.3° from the [110] direction.

Apart from the absence of a resolved proton hyperfine interaction, S\(_1\)\(_b\) is very similar to S\(_1\)\(_a\). Moreover, the concentration of S\(_1\)\(_a\) and S\(_1\)\(_b\) defects are equal within a factor of 2, and their annealing behaviors are nearly identical. These findings immediately suggest that the S\(_1\)\(_b\) defect, like the S\(_1\)\(_a\) defect, belong to the V\(_3\)H\(^0\) family. Noting also that none of the vacancy clusters V\(_n\) identified earlier by EPR (Refs. 17, 18, and 27–29) have spin Hamiltonians consistent with that of S\(_1\)\(_b\), we assign S\(_1\)\(_b\) to V\(_3\)H\(^0\). However, we note that the experimental findings do not rule out that larger complexes like V\(_4\)H\(^0\) also contribute to S\(_1\)\(_b\). This assignment is consistent with the lack of resolved proton hyperfine splittings of S\(_1\)\(_b\): With the proton-electron separations 6.5 and 8.4 Å estimated from the unrelaxed models of V\(_2\)H\(^0\) and V\(_4\)H\(^0\) in Fig. 11, the dipolar hyperfine splitting would not be resolved in the EPR spectra. Additional support for the presence of a hydrogen atom in the S\(_1\)\(_b\) defect as well as in the S\(_1\)\(_a\) defect is provided by the observation of Si-H modes with the same annealing behaviors as S\(_1\)\(_a\) and S\(_1\)\(_b\).
strongly indicates that the $^2\text{A}_{\text{Si}}$ hyperfine tensors represent the spin density at the sites $(2)$ and $(2')$ when the dangling bond is attached to the site $(1)$.

From the similarity of the tensors $^2\text{A}_{\text{Si}}$ of $V_2\text{H}^0$ and $V_3\text{H}^0$ with that of $V^H$ (Table I), we infer that $^2\text{A}_{\text{Si}}$ also for $V_2\text{H}^0$ and $V_3\text{H}^0$ belongs to the pair of equivalent sites $(2,2')$. We note that Watkins and Corbett$^{30}$ earlier carried out a similar analysis of $^{29}\text{Si}$ satellite splittings in the $V^P$ signal ($E$ center), which closely resembles the $V^H$ signal. They obtained the isotropic hyperfine coupling constant $|a| = 37.2$ MHz for $^{29}\text{Si}$ located at the pair of sites corresponding to those labeled $(2,2')$ in Fig. 11. This value of $|a|$ is in fair agreement with the isotropic constants calculated from $^2\text{A}_{\text{Si}}$ for all three $V_3\text{H}^0$ defects.

No experimental clue to the origin of the three hyperfine tensors $^3\text{A}_{\text{Si}}$ has been found. It would seem natural to assign them to the three silicon atoms bonded directly to the atom carrying the dangling bond [the sites labeled $(4)$ in Fig. 11]. However, theoretical results for a related defect, the $P_b$ center, indicate that such an assignment is incorrect. The $P_b$ center may be described as a silicon dangling bond at a Si-SiO$_2$ interface pointing into a microvoid in the silica phase. Accordingly, the essential part of the electronic structure of $P_b$ is expected to resemble a dangling bond in a silicon vacancy. Indeed, the $g$ tensor$^3$ $(g_l = 2.0011, g_\perp = 2.0080)$ and the largest $^{29}\text{Si}$ hyperfine interaction$^3$ $(A_l = -423$ MHz, $A_\perp = -239$ MHz) are similar to those reported here for $V_3\text{H}^0$. The $P_b$ signal furthermore exhibits “shoulders,” indicating the presence of additional hyperfine splitting from $^{29}\text{Si}$ described by the hyperfine parameters $A_l = -42.6$ MHz and $A_\perp = -34.9$ MHz, with the unique axis directed within a few degrees along the $[111]$ symmetry axis of the defect. The similarity with $^3\text{A}_{\text{Si}}$ of the $V_3\text{H}^0$ defects is evident. Calculations by Cook and White$^{12}$ on cluster models of the $P_b$ center unequivocally show that this splitting of the $P_b$ signal originates from a significant spin density on the second-nearest neighbors to the atom carrying the dangling bond, corresponding to the sites labeled $(3)$ in Fig. 11. The hyperfine parameters obtained for the relaxed configuration of the model complex $\text{Si}_{22}\text{H}_{27}$ are $A_l = -36.3$ MHz and $A_\perp = -23.3$ MHz, the unique axis deviating $1.6^\circ$ from $[111]$, in good agreement not only with the experimental result for the $P_b$ center, but also with the tensors $^3\text{A}_{\text{Si}}$ determined for $V_3\text{H}^0$. In contrast, a near cancellation of direct and polarization contributions to the spin density at the three nearest neighbors [the sites labeled $(4)$ in Fig. 11] reduces the $^{29}\text{Si}$ splittings calculated for these sites to $\sim 6$ MHz.$^{32}$ On this basis we assign the hyperfine tensors $^3\text{A}_{\text{Si}}$ to the second-nearest neighbor sites $(3)$. Further experiments, e.g., electron nuclear double resonance measurements, are clearly needed before assignments can be made of the weak $^{29}\text{Si}$ hyperfine interactions described by the tensors $^4\text{A}_{\text{Si}},^5\text{A}_{\text{Si}},$ and $^6\text{A}_{\text{Si}}$.

Our assignments imply that only three of the silicon atoms bordering the vacancy chain carry significant electron-spin densities. Moreover, these spin densities are nearly constant through the series $V^H$, $V_2\text{H}^0$, and $V_3\text{H}^0$. Hence, not only the $g$ tensor but also the detailed distribution of the electron spin is a general characteristic of this kind of defects, and therefore convey little information about the size of the vacancy cluster involved.

### C. Motional effects

As noted above, the $V^H$ defect reorients$^{16}$ when the temperature is raised above $\sim 60$ K by bond switching among the three silicon neighbors that do not bind to the hydrogen atom. Unlike $V^H$, neither $V_2\text{H}^0$ nor $V_3\text{H}^0$ can reorient into an equivalent configuration solely by a similar rearrangement of the Si-Si bonding. Such a rearrangement would yield a defect with triclinic symmetry, which we suspect will have higher energy than the monoclinic-$I$ configuration. This accounts for the absence of motional effects in the temperature range $(60-150$ K) where the $V^H$ signal transforms into a trigonal signal.$^{16}$

Above $200$ K, the trigonal $V^H$ signal broadens and disappears, possibly due to a rapid motion of the hydrogen atom inside the vacancy. If the hydrogen atom in $V_3\text{H}^0$ similarly jumps among the silicon neighbors above $200$ K, a simultaneous reorientation of the dangling bond and the Si-H bond could occur in $V_2\text{H}^0$, implying a rotation of the mirror plane around the $(111)$ axis connecting the two vacancies. A corresponding rotation would not occur in $V_3\text{H}^0$ since this defect is effectively locked to the plane defined by the three vacancies. Therefore, the observation that the $S_{1a}$ lines broaden and disappear at about $310$ K, while the $S_{1b}$ lines persist to higher temperatures may simply reflect the different geometries of $V_2\text{H}^0$ and $V_3\text{H}^0$.

### D. Correlation with Si-H stretch modes

As described in Sec. III E, the $V^H$ signal displays the same annealing behavior as the Si-H stretch mode at $2038.5$ cm$^{-1}$, which is one of the most intense modes observed in our samples (see Fig. 8). Furthermore, in situ type FTIR studies, which we plan to report in a subsequent publication, have shown that the $2038.5$-cm$^{-1}$ mode appears when vacancies become mobile. We conclude that the $2038.5$-cm$^{-1}$ mode originates from $V^H$.

This assignment is consistent with theory. The Si-H stretching frequencies calculated by several groups$^{33-35}$ using different methods are listed in Table II. The frequencies calculated for $V^H$ substantially exceed the observed $2038.5$ cm$^{-1}$. This is expected, however, from comparison of the calculated and observed$^{36}$ frequencies for $V_2\text{H}$ and $\text{H}_2$. If the ratio between the calculated and observed frequencies is assumed to be roughly the same for different hydrogen defects, the “true” frequency of $V^H$ may be estimated from those calculated. The results, included as scaled frequencies in Table II, range from 2039 to $2119$ cm$^{-1}$. Hence they all deviate by less than $4\%$ from the observed frequency.

As shown in Fig. 10, the thermal decays of $S_{1a}$ ($V_2\text{H}^0$) and $S_{1b}$ ($V_3\text{H}^0$) coincide with those of the so far unidentified Si-H stretch modes at $2068.1$ and $2073.2$ cm$^{-1}$. Both modes were earlier found to arise from defects containing a single hydrogen atom.$^{34}$ In addition, uniaxial stress measurements revealed the Si-H stretch mode at $2068.1$ cm$^{-1}$ has monoclinic-$I$ symmetry, whereas the symmetry of the $2073.2$-cm$^{-1}$ defect could not be determined because of overlapping absorption lines.$^{26,34}$ On this basis, we ascribe one of these modes to $V_2\text{H}^0$ and the other to $V_3\text{H}^0$. Interpreting the $\sim 30$-cm$^{-1}$ increase of the Si-H stretch frequency observed when going from $V^H$ to
$V_2^0$ (or $V_3^0$) as reflecting primarily the reduced interaction between the Si-H group and the dangling bond, we may expect a further, small upwards frequency shift from $V_2^0$ to $V_3^0$. Hence, we assign the 2068.1-cm$^{-1}$ mode to $V_2^0$ and the 2073.2-cm$^{-1}$ mode to $V_3^0$. We note that with this assignment, the Si-H stretch frequency of $V_n^0$ increases with $n$ and seems to approach the frequency 2086.3-cm$^{-1}$ observed for a Si-H bond on an ideal monohydride (111) surface.\(^{36}\)

It may be added that Deák \textit{et al.}\(^{33}\) found that the Si-H stretch frequency of $V_2^0$ is 1.1% higher than that of $V_1^0$. If this shift is assumed to apply to $V_3^0$ and $V_4^0$ as well, the frequency of $V_3^0$ estimated from that of $V_4^0$ is 2061 cm$^{-1}$—very close to the observed frequency of the mode assigned to $V_3^0$.

\textbf{E. Comparison with earlier work}

As mentioned in Sec. I several studies of the $S_1$ group of signals have appeared. In the early work,\(^{19–21}\) these signals were assigned to a single defect with trigonal symmetry. Górelkenskii and Nevinniyi\(^{12}\) later found that in proton-implanted float-zone material the $S_1$ group consists of two signals which merge to a single signal of trigonal symmetry at high proton doses. No spin Hamiltonian parameters were given for the two signals in Ref. 12, but it is reasonable to assume that these signals are identical to $S_{1a}$ and $S_{1b}$.

Dvurechenskii and Karanovich\(^{22}\) found that the $S_1$ defect has monoclinic-I symmetry, and reported $g$ and $^{1}A_{N_{L}}$ tensors that are consistent with those of $S_{1a}$, but they did not observe a second component corresponding to $S_{1b}$. However, they observed a new signal, labeled $H_{10}$, in phosphorus-rich material irradiated with neutrons. The spin-Hamiltonian parameters of $H_{10}$ are very similar, not only to those of the $B_{2}$ center\(^{37}\) observed in nitrogen- and phosphorus-implanted material, but also to the parameters of $S_{1b}$. These surprising similarities may be accounted for in the following way: From our identification of the $S_{1a}$ and $S_{1b}$ defects, it may be inferred that the EPR signals from a planar multivacancy with an adjacent substitutional group-V impurity in the mirror plane is virtually indistinguishable from the signal arising from the corresponding defect in which a Si-H unit replaces the group-V impurity. Like the Si-H unit in $V_n^0$, the group-V impurity will be located too far from the dangling bond to produce a resolvable hyperfine splitting. Nor can the impurity influence the $g$ tensor significantly. Indeed we were able to resolve a tiny hyperfine splitting from hydrogen in $V_2^0$ only because the nuclear $g$ factor of the proton is so large. Thus, the main effect of the group-V impurity on the Si-H unit is to dictate an odd number of dangling bonds so that the ground state of the defect has spin $S = \frac{1}{2}$.

Within this framework, the similarity of $B_{2}$ and $H_{10}$ with $S_{1a}$ may be taken to suggest that $B_{2}$ and $H_{10}$ both belong to a family of defects in which planar vacancies have a group-V impurity atom as a neighbor in the plane. It has often been assumed that the $S_{1a}$ and $B_{2}$ defects were identical.\(^{12,20,21}\) Now, it appears, however, that although their EPR signals are hard to distinguish, these defects belong to two different but closely related families. To reduce the confusion, it might be helpful to reserve the label $S_1$ for hydrogen-related defects and use the label $B_2$ for the family involving group-V impurities.

Finally, we may comment on the $N_{L}52$ center,\(^{38}\) which has been observed in proton-implanted float-zone silicon. The principal values of the $g$ tensor of $N_{L}52$ are similar to those of $S_{1b}$. Moreover, if the weak hyperfine lines ascribed to $H_2$ in Ref. 38 are instead interpreted as $^{29}$Si hyperfine satellites, the principal values of the $^{1}A_{N_{L}}$ tensor become $A_{Z} = -436$ MHz and $A_{X} = A_{Y} = -256$ MHz, in good agreement with the parameters found for $S_{1a}$ and $S_{1b}$. These observations suggest that the assignment of $N_{L}52$ to $H_2$ should be reconsidered.

V. SUMMARY

Two EPR signals labeled $S_{1a}$ and $S_{1b}$ have been observed in proton-implanted, float-zone silicon. Both signals belong to the $S_1$ group and originate from monoclinic-I defects with $g$ tensors that show only a slight deviation from trigonal symmetry. The involvement of a single hydrogen atom in the $S_{1a}$ defect is proven directly, whereas the evidence of the presence of hydrogen in the $S_{1b}$ defect is circumstantial. The $g$ tensors and the large $^{29}$Si hyperfine splitting associated with a single silicon site correspond to an unpaired electron that occupies a dangling bond in a planar vacancy-type defect binding a hydrogen atom in the plane. From the analysis of the hydrogen hyperfine interaction, the $S_{1a}$ defect is identified with $V_2^0$. The $S_{1b}$ defect is identified with $V_3^0$, although $V_4^0$ cannot be ruled out. In contrast to the $V_4^0$ signal described earlier, $S_{1a}$ and

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TABLE II. Comparison of calculated and observed frequencies $\omega$ of Si-H stretch modes (in cm$^{-1}$). $\omega_B$ and $\omega_A$ denote frequencies of the asymmetric and symmetric stretch modes, respectively. The frequencies in brackets (denoted scaled) are determined from those calculated by multiplication with a common factor that yields the best agreement between the scaled and the observed frequencies for $VH_2$ and $IH_2$. |
S1\textsubscript{a} do not display motional effects that may be associated solely with rearrangements of Si-Si bonds. However, S1\textsubscript{a} broadens and disappears above 310 K whereas S1\textsubscript{b} is little affected. It is suggested that S1\textsubscript{a} broadens because the hydrogen atom jumps among the silicon neighbors to the vacancy. In V\textsubscript{2}H\textsuperscript{0} this may lead to a reorientation of the defect, whereas no reorientation occurs in V\textsubscript{2}H\textsuperscript{0} since the mirror plane is locked by the three ‘‘immobile’’ vacancies.

From parallel annealing studies with EPR and FTIR, it is concluded that V\textsubscript{2}H\textsuperscript{0} possesses a Si-H stretch mode at 2038.5 cm\textsuperscript{-1}. In addition, the stretch modes at 2068.1 and 2073.2 cm\textsuperscript{-1} are assigned to V\textsubscript{2}H\textsuperscript{0} and V\textsubscript{3}H\textsuperscript{0}, respectively.

The EPR spectra of V\textsubscript{3}H\textsuperscript{0} are similar to that of V\textsubscript{2}H\textsuperscript{0}, and thus reveal no direct electronic interaction between the Si-H group at one end of the defect and the dangling bond at the other. Hence the length of the vacancy chain could be inferred only in case of V\textsubscript{2}H\textsuperscript{0} from a tiny dipole-dipole hyperfine interaction with the proton. The number of vacancies separating the Si-H group from the dangling bond is reflected, however, in the observed Si-H stretch frequency which increases with increasing chain length.

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25. At sample temperatures below 65 K, a strong EPR signal originating from V\textsubscript{2}H\textsuperscript{0} in its stationary form is observed (see Ref. 16) in the field range covered by Fig. 1. Above 125 K, a motonally averaged form of the VH\textsuperscript{0} signal appears (see Ref. 16). This rotationally averaged signal is visible only in a rather narrow temperature window, and at 200 K it is broadened significantly.

26. The annealing curve of the 2073.2-cm\textsuperscript{-1} mode is influenced by the overlap with another mode at 2072.4 cm\textsuperscript{-1} that displays a different annealing behavior. Therefore, annealing curves relating to Si-H modes have been determined from the best fit to the absorbance lines obtained with a superposition of Lorentzians with fixed widths.


