Hydrogen interaction with impurities in silicon
Huy, P.T.

Citation for published version (APA):

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"When we seek to discover the best in others, we somehow bring out the best in ourselves."

- William Arthur Ward -

Chapter 2

CHARACTERIZATION OF HYDROGEN AND HYDROGEN-RELATED CENTERS IN CRYSTALLINE SILICON BY MAGNETIC–RESONANCE SPECTROSCOPY

ABSTRACT

In recent years research by magnetic resonance has contributed substantially to the understanding of hydrogen and hydrogen-related centers in silicon. As usual for magnetic resonance, which was applied in its varieties of electron paramagnetic resonance (EPR) and electron-nuclear double resonance (ENDOR), in several cases profound insight into the microscopic structure of centers has been the result of the studies. This includes atomic structure by identifying the chemical nature of impurity atoms and the symmetry of their geometrical arrangement within the defect, as well as electronic structure by mapping of the defect-electron wave function. In this chapter research will be reviewed on centers which after hydrogenation are in a paramagnetic state. Hydrogen in its pure configuration of an isolated neutral atom on a bond-centered position in trigonal symmetry as the prototype of hydrogen centers, is described first. Hydrogen binding on dangling bonds in mono- or multi-vacancies has resulted in the observation and understanding of several fundamental defect structures, and is considered next. Double donors, such as the substitutional chalcogen atom sulfur, have been found to bind one hydrogen atom on several distinct positions remaining electrically active. Hydrogen interaction with impurities with deep electronic levels has also been observed. We describe, as illustrative example, the observation of the well known one-platinum–two-hydrogen (Pt–H₂) center.
2.1 Introduction

After the first observations of hydrogen passivation of defect levels in silicon, reported in the nineteen-eighties, hydrogen as a multi-purpose impurity in silicon, with either beneficial or detrimental effects, has attracted enormous research interest. Due to its small size and the open lattice of the diamond structure, the hydrogen atom or ion can easily penetrate the bulk of the material. The activation energy for migration is only 0.48 eV, which is among the lowest for impurities in silicon [2.1, 2.2]. Hydrogen can easily intentionally be introduced by diffusion [2.1, 2.3, 2.4], implantation [2.5-2.7], hydrogen plasma treatment [2.8], wet chemical etching [2.9, 2.10] or by boiling in water [2.11, 2.12]. Inadvertently, hydrogen is present, often unknown, as an impurity introduced during process steps in device manufacturing. Due to its half-filled 1s electronic shell the hydrogen atom has a high reactivity. A second electron can be accommodated in this shell with low energy. As a result hydrogen reacts strongly with defects with broken bonds or other centers which offer single valence electrons. For most centers, intrinsic lattice defects or chemical impurities with shallow or deep electronic levels, this condition holds. For this reason hydrogen is involved in a rich variety of defect interactions. As these interactions may change the electronic and optical properties of the material, this behavior of hydrogen is of utmost relevance for material applications. The passivation of shallow acceptors [2.13-2.15] and shallow donors [2.16] is one of the more spectacular effects of hydrogen presence. Another most important application is the passivation of dangling bonds with the elimination of their associated electron traps or recombination centers in amorphous material, for the objective of improving the electrical and optical properties of material used in solar cell production. Strongly motivated by the relevance for materials science, the more fundamental studies of the atomic and electronic structures of hydrogen and hydrogen-related centers have seen intensive activity since around 1985. As important as the passivation process may be for the material properties, the direct observation of passivation products is by definition difficult. Passivated defects do not have electronic levels in the semiconductor band gap and are diamagnetic. The stable hydrogen molecule maybe is the most striking form of hydrogen presence to easily escape detection. For this reason several of the powerful experimental techniques for defect study fail. An outstanding technique for defect characterization as electron paramagnetic resonance, requiring centers with non-zero spin, suffers from the handicap that passivation products
are not detectable. Nevertheless, in several cases the passivation by hydrogen bonding is not complete. For instance, this will happen for larger defects, such as multi-vacancies and interstitial complexes. In the category of double donors and acceptors the binding of one hydrogen atom may lead to partial passivation, with the possible consequence of the conversion of a double dopant into a single dopant. For transition elements with in many cases a high value of electron spin, the binding of a hydrogen atom will not render them diamagnetic. Even, as an opposite effect, the binding of hydrogen can activate a center, such as the iso-electronic impurity carbon [2.9]. Altogether, a vast field for fruitful studies is still left open. As a result, continued efforts with magnetic resonance over the last 15 years have seen a number of successful investigations. In this chapter a brief review of the main results obtained is given confined to four main subjects, which are the isolated hydrogen center, hydrogen–vacancy complexes, passivation of chalcogen double donors by hydrogen, and the interaction of hydrogen with transition-metal impurities in silicon.

2.2 Isolated hydrogen

The most prominent magnetic resonance spectrum related to hydrogen in silicon, no doubt, is spectrum Si-AA9 [2.17, 2.18]. The spectrum is produced both in float-zoned and Czochralski-grown silicon following high-energy hydrogen implantation in the range of 7 to 30 MeV and at the temperature of 80 K. After hydrogen implantation samples received a thermal anneal at 195 K for 40 minutes. The spectrum is observable only under band-gap light illumination and best for high-purity zone-refined silicon. It has been identified as arising from a single neutral hydrogen atom on the bond-centered position between two silicon atoms. A most important feature in the spectrum is the splitting of the main line in two components of equal intensity. The structure is due to the hyperfine interaction with one nucleus of spin $I = 1/2$ and abundance of 100%, which must be identified as hydrogen. This constitutes the first direct evidence in an EPR spectrum of hydrogen presence. Replacing the hydrogen atom by deuterium the number of hyperfine structure lines increases to three, but the splitting almost collapses [2.7]. This is consistent with the nuclear spin $I = 1$ of the deuteron and its smaller nuclear g factor, i.e., $g_d/g_p = 0.15$, providing confirmation of the hydrogen involvement. In the spectrum also hyperfine interaction with $^{29}\text{Si}$ nuclei of the host crystal is discernible. The positions of these resonances are indicated in figure 2.1. Their intensity is near 5% of the main line, which,
given the 4.7% abundance of the $^{29}$Si isotope, implies that two silicon atoms are present in the center on symmetry-equivalent sites. Measuring the angular variation of the resonance fields, patterns revealing the trigonal symmetry for the EPR center are obtained, for the fine structure of the electronic Zeeman effect as well as for the hyperfine interactions with hydrogen and silicon. This leads to the defect model as one hydrogen atom on a bond-centered position, midway between two nearest-neighbor silicon atoms. In the model the hydrogen atom occupies a site with inversion symmetry. The crystallographic pointgroup symmetry is thus established as $\bar{3}m$.

![Image of EPR spectrum](image)

**Figure 2.1.** Electron paramagnetic resonance spectrum of the Si-AA9 center observed in proton/deuteron-implanted silicon. Observation conditions: Sample illumination, temperature 77 K, magnetic field parallel to [100], microwave frequency 37.47 GHz. (a) Hyperfine interactions with $^1$H and $^{29}$Si are indicated by the arrows, (b) hyperfine structure in deuterium-implanted silicon. Adapted from Gorelkinskii and Nevinnyi [2.18].

For the quantitative analysis of the spectroscopic information the spin Hamiltonian

$$H = \mu_B \mathbf{B} \cdot g_e \mathbf{S} + \sum_{ij} [-(\mu_i I_i) \mathbf{B} \cdot \mathbf{I}_j + \mathbf{S} \cdot \mathbf{A}_j \cdot \mathbf{I}_j], \tag{2.1}$$
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is appropriate, with index j indicating the magnetic nucleus (proton p, deuteron d, silicon $^{29}\text{Si}$, or muon $\mu$). Principal values of the tensors, parallel and perpendicular to the threefold rotation axis, are given in table 2.1. Substantial support to the model follows from studies of the anomalous muonium atom, Mu* or $\mu^-e^-$, in silicon, which forms an analogue of the neutral hydrogen on the bond-centered site. On the one hand, the muon can be considered as a light isotope, mass $m_\mu = 207.769 \, m_e$, of hydrogen with $m_p = 1837.15 \, m_e$; on the other hand, as a lepton, it has $g_\mu = 2.0016 = 2$. The muon spin rotation ($\mu$SR) method allows the determination of the hyperfine interactions with muon and silicon nuclei [2.19, 2.20]. Results, included in table 2.1, directly show that the hyperfine interactions with the $^{29}\text{Si}$ neighbors nuclei are almost identical in Mu* and $(\text{H}_8\text{C})^0$. On comparing the hyperfine interaction with the proton in $(\text{H}_8\text{C})^0$ and the muon in Mu* one finds $a_\mu/a_p = 2.93$ and $b_\mu/b_p = 3.01$. This matches quite well with the ratio of the magnetic moments of muon and proton: $\mu_\mu/\mu_p = (g_\mu/m_\mu)/(g_p/m_p) = 3.17$. It may be concluded from these EPR results on the Si-AA9 center and the data for Mu* obtained by $\mu$SR that the structures of the two centers are equivalent. Also included in table 2.1 are theoretical data based on first-principles calculations of the hyperfine interactions [2.21]. The agreement with data from experiment is satisfactory and in particular the signs of the interactions, positive or negative, are given by the theory, allowing adjustment of experimental results. To these hyperfine coupling strengths the usual analysis based on a wave function constructed as a linear combination of atomic orbitals (LCAO) can be applied. With restriction to the hydrogen atom and its two neighboring silicon atoms the wave function is given by

$$\psi = \eta_1(\alpha_1\phi_{1s} + \beta_1\phi_{1p}) + \eta_{Si1}(\alpha_{Si1}\phi_{Si13s} + \beta_{Si1}\phi_{Si13p}) + \eta_{Si2}(\alpha_{Si2}\phi_{Si23s} + \beta_{Si2}\phi_{Si23p}), \quad (2.2)$$

with wave functions on the atoms normalised by $\alpha_j^2 + \beta_j^2 = 1$. The isotropic parts $a$ and anisotropic parts $b$ of the hyperfine interactions are related to the s- and p-type wave functions, respectively, by

$$a_j = (2/3)\mu_0g_\mu g_p\eta_j^2\alpha_j^2|\phi_j(0)|^2 \quad \text{(2.3)}$$

and

$$b_j = (2/5)(\mu_0/4\pi)g_\mu g_p\eta_j^2\beta_j^2<r_{jp}^{-3}>. \quad \text{(2.4)}$$
For the two silicon atoms the analysis is straightforward. With \( a = -94.9 \) MHz and \( b = -22.0 \) MHz, and using the atomic parameters \(|\phi_{\text{Si}3s}(0)|^2 = 31.5 \times 10^{30} \text{ m}^{-3}\) and \(<r_{\text{Si}3p}^{-3}> = 16.1 \times 10^{30} \text{ m}^{-3}\) [2.22], one obtains \( \eta_{\text{Si}}^2 = 0.24 \), \( \alpha_{\text{Si}}^2 = 0.095 \) and \( \beta_{\text{Si}}^2 = 0.905 \). Considerable spin density is thus localised on the two nearest-neighbor silicon atoms in orbitals of strong p-type nature. Analysis of the hyperfine interaction with the hydrogen nucleus is more complex, as is immediately obvious from the negative sign of the isotropic parameter \( a \), opposite to the sign of \( b \), which is at variance with equations (2.3) and (2.4). Appreciable admixture of hydrogen p orbitals, as included in equation (2.2), is highly unlikely as the corresponding states are high in energy. In equation (2.2) one must have \( \beta_{\text{H}} = 0 \). The anisotropy in the hyperfine interaction is induced by remote spin density, in particular that on the silicon neighbor atoms. Accepting a point spin density distribution on these two atoms, the anisotropy parameter \( b \) can be calculated from the equation

\[
\eta_{\text{Si}}^2 = \frac{(\mu_0/4\pi)g_\mu \mu_\text{H} \eta_{\text{Si}}^2}{r^{-3}}.
\]  

(2.5)

With the calculated \( \eta_{\text{Si}}^2 = 0.24 \) on each atom and the observed \( b = 8.4 \) MHz the required distance between hydrogen atom and silicon neighbor is found as \( r = 0.165 \) nm. In the rigid lattice the hydrogen inserted on the BC site is at the distance of 0.118 nm from the silicon neighbors. The slightly increased value found for the distance is consistent with the established outward relaxation of the silicon atoms, theoretically calculated as being 0.041 nm [2.23] or 0.045 nm [2.24] and here experimentally determined as 0.047 nm, and the enhanced p-type character of the orbital. In this description the spin density is localised on the silicon atoms without a lobe pointing preferentially inwards towards the hydrogen atom. Such an assumption is consistent with the anti-bonding nature as regards the silicon orbitals. A one-electron LCAO diagram, as given by figures 2.2(a) and 2.2(b), shows the hydrogen atom on the site of the inversion center. The orbital belongs to the \( a_{1u} \) irreducible representation in the pointgroup \( \overline{3}m \). For the hydrogen an isotropic hyperfine interaction with \( a = -23 \) MHz is measured. In the LCAO analysis, using the equations (2.2) and (2.3) and ignoring the problem of the minus sign, this results in \((\eta_{\text{H}})^2 = 0.016 \). Although the calculated localisation is small, it is inconsistent with the \( a_{1u} \) symmetry type of the orbital carrying the unpaired spin requiring a node at the hydrogen site. A solution towards this
problem is provided by considering all three electrons in the system as given in Refs. [2.25, 2.26].

Figure 2.2. Formation of a three-center bond for hydrogen in a bond-center site. (a) Schematic illustration of orbitals in the bond-centered configuration, (b) corresponding energy levels obtained from simple molecular-bonding (or tight binding) arguments for an elemental semiconductor. b and a indicate bonding and antibonding states. The paramagnetic electron occupies the antibonding state, which has a node on the H atom at the bond center. After Van de Walle [2.32].

Several other important features of the single hydrogen center in silicon have been studied by magnetic resonance. This includes defect alignment induced by uniaxial stress and thermal relaxation [2.27], isochronal thermal annealing in dark conditions of (H\textsubscript{BC})\textsuperscript{+} in the temperature range 190–220 K, and of the Si-AA9 spectrum of (H\textsubscript{BC})\textsuperscript{0} under illumination between 110 and 130 K [2.18, 2.28-2.30], the stable position of H\textsuperscript{+} and H\textsuperscript{0} on the bond-center site versus the position of H\textsuperscript{-} on the tetrahedral interstitial site [2.23, 2.31, 2.32], together with the negative-U character of the donor and acceptor levels rendering the neutral charge state unstable [2.24, 2.33, 2.34].
Table 2.1. Hyperfine parameters from EPR and μSR experiments and from spin-density functional theory, for the center Si-AA9 and anomalous muonium, Mu*, together with coefficients η, α', and β' from LCAO analysis.

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<td>2.21</td>
<td>2.18</td>
<td>2.20</td>
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2.3 Hydrogen–vacancy centers

As early as 1967 the S1 EPR spectrum was observed, following 3 MeV proton irradiation at room temperature and absent after neutron irradiation, for which production conditions required the presence of hydrogen [2.5, 2.35, 2.36]. The spectrum corresponds to centers produced along the proton track with increasing density towards the end of the particle range. Spin-Hamiltonian parameters for the <111>-axial defect are $S = 1/2$, $g_\parallel = 2.0010$, $g_\perp = 2.0103$. In a 10-minutes isochronal anneal study the centers annealed out at temperatures in the range 200–300 °C. The production was proportional to implantation dose. In the higher resolution offered by Q-band EPR it was later discovered that the S1 center actually is composed of several components, up to 5 in Czochralski silicon, with either the trigonal or the monoclinic-I symmetry [2.18, 2.37]. Only recently the centers were unambiguously identified as hydrogen related and their structure was unravelled in great detail. In this more recent literature the components of the S1 group of spectra are now labelled as VH°, S1a and S1b [2.6, 2.38]. Another spectrum, Si-B2, is very similar to
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S1. Both spectra belong to $S = 1/2$ centers with the trigonal symmetry, have equal g tensors within error limits, and equal temperatures for loss of spectra by thermal anneal, near 300 °C. It has therefore often be assumed that the two spectra are in fact identical. It is, however, to be noted that in the original paper the spectrum B2 has been observed after N$^+$ and P$^+$ implantation [2.39] and in a later independent dedicated study also as the result of He$^+$, B$^+$, C$^+$ and N$^+$ implantation and neutron irradiation [2.40]. In this latter case any specific evidence for hydrogen presence was absent. This should leave open the possibility that B2 and S1 are different, maybe quite similar, centers with accidentally the same characterization parameters. As another option, in view of the established frequent presence of hydrogen in nominally pure silicon crystals, the possibility that samples were unintentionally contaminated with hydrogen is open as well.

Production conditions and features of the spectra led to their identification as vacancy-type defects with hydrogen saturating a dangling bond [2.18]. In the most recent research the detailed models for the S1 centers were established. Spectrum VH$^0$ is related to a mono-vacancy with one of its four dangling bonds saturated by a hydrogen atom. The center undergoes a Jahn-Teller distortion resulting in monoclinic-I symmetry, pointgroup C$_{1h}$, or m, as observed at low temperatures, below 45 K. In this case the presence of the one hydrogen atom is established by just resolved hyperfine interaction. The deuterium hyperfine splitting, which will be around 6.5 times smaller, remains unobservable as it is smaller than the line width. In agreement with the model a strong hyperfine interaction is present with a unique silicon atom, isotope $^{29}$Si. At higher temperatures a motional effect sets in related to electron switching between bonds, resulting in an apparent trigonal symmetry of the center, as observed when measuring the spectrum above 110 K. The transition in the temperature range is illustrated in figure 2.3 by spectra taken for B $\parallel$ [111]. The low-temperature monoclinic spectrum has the lines labelled A, B, and C. The C line corresponds to centers with their Si–H axis parallel to the magnetic field direction. Their position does not change when the electron hops between the dangling or extended bonds of the other three silicon atoms. Lines A and B correspond to defect orientations which are inequivalent with respect to the magnetic field. With fast bond switching present, the resonance field will move to the weighted average of the original frozen positions. This will be at position AB = (2A + B)/3. The process can be followed in figure 2.3 for the temperatures spanning the relevant range of interest. The activation energy for the electron jump process is determined as $E_a = 0.06$ eV. Such a value is equal to the one
measured for the same process in the phosphorus–vacancy complex (E center) with its EPR spectrum Si-G8 [2.22]. This agrees with expectations, as the atomic and electronic structure models for VH⁰ and VP⁰ have much in common. Spin-Hamiltonian parameters of the VH⁰ center are given in table 2.2.

Figure 2.3. Spectrum of VH⁰ at different sample temperatures illustrating the transition from the low-temperature monoclinic-I structure at T = 45 K to the motionally averaged trigonal symmetry at T = 145 K. At T = 225 K the S1 resonances S1_a and S1_b dominate the spectrum. Microwave frequency 34.778 GHz, magnetic field B // [1 1 1]. After Bech Nielsen, et al. [2.38].

In the same way as discussed for the Si-AA9 center, an LCAO analysis will yield a mapping of the electron spin distribution. For the single silicon atom, with the observed hyperfine principal values $A_{||} = -435$ MHz and $A_{\perp} = -275$ MHz, corresponding with isotropic value $a = (A_{||} + 2A_{\perp})/3 = -328$ MHz and anisotropic part $b = (A_{||} - A_{\perp})/3 = -53$ MHz, one obtains, using equations (2.3) and (2.4), $\eta^2 = 0.60$, $\alpha^2 = 0.13$ and $\beta^2 = 0.87$. A comparison with the corresponding numbers for the VP⁰ center, $\eta^2 = 0.59$, $\alpha^2 = 0.14$ and $\beta^2 = 0.86$ [2.22], confirms the close similarity of the two defects. From the large s-type
hyperfine interaction on the silicon atom one concludes that the wave function has the $A_g$ symmetry type. The very small isotropic part of the hyperfine interaction with the hydrogen atom, $a = 0.2$ MHz, indicated that no s-type spin density is located on the hydrogen. In contrast to the similar situation for center Si-AA9 one can, however, not conclude that the hydrogen is located on a mirrorplane with a node for the wave function. The low spin density is the result of the strong Si–H bond accommodating two electrons with opposite spin. As before for the Si-AA9 center, the LCAO analysis does not include anisotropic orbitals on the hydrogen site. The anisotropic part of the hyperfine interaction, $b = (-A_1 - A_2 + 2A_3)/6 = 4.15$ MHz has to arise from distant spin density. The unpaired spin on the unique silicon atom can fully account for this interaction for $\eta^2 = 1$ and $r = 0.27$ nm. With a Si–H bond length of 0.148 nm this fits perfectly in an undistorted vacancy model where this distance is 0.28 nm. In a di-vacancy model the distance in the undistorted lattice amounts to 0.47 nm, which is far too big. It confirms the compact model of a mono-vacancy center. Taking $\eta^2 = 0.60$, following the result of the silicon LCAO analysis, the required distance to the silicon atom with the dangling bond becomes 0.22 nm. This shorter distance can correspond to inward distortion of the unique silicon atom.

Two more spectra belonging to the S1 group of spectra were observed following proton implantation at temperatures below 130 K. The two spectra, labelled S1$_a$ and S1$_b$, are single-electron centers with $S = 1/2$, correspond to centers with monoclinic-I, near trigonal, symmetry. The spin-Hamiltonian parameters, as given in table 2.2, are very similar to those of VH$^0$. They are therefore interpreted as multi-vacancy centers in which hydrogen binds to a dangling bond. The main spin density is in another dangling bond of the vacancy structure. Only for S1$_a$ a hydrogen hyperfine structure due to one proton is observable in the spectra; for S1$_b$ such structure is absent. The isotropic part of this hyperfine interaction, $a = 2.3$ MHz, is again very small, indicating low spin density on the hydrogen atom. The anisotropic part, $b = 0.77$ MHz, is explained by remote interaction with spin density on the dangling bond, which, using equation (2.5), should be at a distance $r = 0.47$ nm. This fits perfectly with the geometry of a hydrogen in an undistorted di-vacancy. The S1$_a$ defect is therefore identified as a V$_2$H center in the paramagnetic neutral state. For S1$_b$ the model of a tri-vacancy center with hydrogen, (V$_3$H)$^0$, is proposed, with the tetra-vacancy center (V$_4$H)$^0$ as a possible alternative. In these larger centers, with $r = 0.65$ nm and $r = 0.84$ nm, respectively, the distant hyperfine interaction would be too small to give observable splitting in the S1$_b$ spectrum.
Table 2.2. Spin-Hamiltonian parameters for the VH\textsuperscript{o}, S1\textsubscript{a}, and S1\textsubscript{b} signals. Principal axes are denoted X, Y, and Z, with Y parallel to the [1\overline{1}0] axis, and X and Z in the (1\overline{1}0) plane. θ is the angle between Z and the [110] axis. Principal values of $A_S$ and $A_H$ are given in MHz. \textsuperscript{a}Two equivalent silicon sites, Z is taken along [\overline{1}11] and [\overline{1}1\overline{1}]. \textsuperscript{b}Three nearly equivalent silicon sites, Z is taken along [111]. \textsuperscript{c}Three nearly equivalent silicon sites, Z is taken along [\overline{1}11],[\overline{1}1\overline{1}]. [11\overline{1}].

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<td>Z$^b$</td>
<td>-40</td>
<td>-36.5</td>
<td>-32.5</td>
</tr>
<tr>
<td>$^4A_{Si}$</td>
<td>X, Y</td>
<td>-11</td>
<td>-10.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Z$^b$</td>
<td>-14</td>
<td>-15</td>
<td></td>
</tr>
<tr>
<td>$^5A_{Si}$</td>
<td>X, Y</td>
<td>-6</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Z$^c$</td>
<td>-8</td>
<td></td>
<td></td>
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<tr>
<td>$^6A_{Si}$</td>
<td>X, Y</td>
<td>-10.5</td>
<td>-4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Z$^b$</td>
<td>-13.5</td>
<td>-6</td>
<td></td>
</tr>
</tbody>
</table>
Silicon hyperfine interactions were measured for several shells of the \((\text{VH})^0\), \(\text{S}_1\) and \(\text{S}_1\) centers. They allowed a detailed mapping of the electron spin density in the defect and showed great similarity between the three centers, as reflected in the modelling. Both centers \(\text{S}_1\) and \(\text{S}_1\) anneal out at temperatures around 250 °C. Motional effects, as reported for \((\text{VH})^0\), are not observed for the \(\text{S}_1\) and \(\text{S}_1\) centers.

Table 2.3. Parameters of the Si-HVH and Si-SL1 spectra, ascribed to the orthorhombic-I centers \((\text{VH}_3)^0\) and \(\text{OV}^*\), respectively, observed in an excited spin triplet state with \(S = 1\) [2.44, 2.45]. Hyperfine interactions \(A\) are for the \(^{29}\text{Si}\) isotope of two silicon neighbor atoms.

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Model</th>
<th>Principal values coupling tensors</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-HVH</td>
<td>((\text{VH}_2)^0)</td>
<td>(g_{[100]} = 2.002) (g_{[011]} = 2.005) (g_{[0-11]} = 2.002)</td>
<td>MHz</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(D_{[100]} = -348) (D_{[011]} = -302) (D_{[0-11]} = 650)</td>
<td>MHz</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(A_{[{111}]} = 220) (A_{[{111}]} = 114)</td>
<td>MHz</td>
</tr>
<tr>
<td>Si-SL1</td>
<td>(\text{OV}^*)</td>
<td>(g_{[100]} = 2.0076) (g_{[011]} = 2.0102) (g_{[0-11]} = 2.0058)</td>
<td>MHz</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(D_{[100]} = -350) (D_{[011]} = -307) (D_{[0-11]} = 657)</td>
<td>MHz</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(A_{[{111}]} = 216) (A_{[{111}]} = 112)</td>
<td>MHz</td>
</tr>
</tbody>
</table>

Given the strength of the Si–H bond one may expect that vacancy centers with their several dangling bonds, if unreconstructed, can accommodate more than one hydrogen. Such expectations based on simple chemical bonding arguments are corroborated by modern self-consistent theoretical calculations for the mono-vacancy, which predict stability of \(\text{VH}_n\) complexes, with \(n = 1–4\) [2.41]. Experimental evidence for such centers is based on local vibrational mode spectroscopy [2.42, 2.43] and on optical detection of magnetic resonance (ODMR) [2.44]. In the latter study hydrogen/deuterium plasma-treated silicon was electron irradiated. A magnetic resonance spectrum labelled HVH, was observed corresponding to an orthorhombic-I center with electron spin \(S = 1\). This is associated with a \((\text{VH}_2)^0\) center, which due to complete pairing of electron spins is diamagnetic in its ground state. The excited spin triplet state is formed by the illumination inherent in the ODMR method. Hydrogen hyperfine interaction is not resolved but is manifest in the line shape of hydrogenated samples, which is absent in the case of deuteration. Parameters of the spin-Hamiltonian analysis are given in table 2.3. Applying the standard LCAO analysis, the spin density on the hydrogen is found to be a mere 0.9%;
it is low, as usual, reflecting the full occupation of the Si–H bonds. The experimentally observed $S = 1$ triplet state is formed by spins mainly residing on the silicon bond formed by the two non-passivated atoms opposite to the hydrogen atoms in the vacancy; one finds the localisation $\eta^2 = 0.68$ for the two atoms together. Inspection of table 2.3 shows the near coincidence of the parameters for the HVH and SL1 spectra, the latter spectrum corresponding to the oxygen–vacancy complex (A center), which is also observed in an excited $S = 1$ state [2.45]. In both centers two of the vacancy dangling bonds are saturated, by either two hydrogen atoms or one oxygen atom, the spin resides on an extended bond formed between the two remaining silicon atoms of the vacancy. In view of this similarity in the electronic structure of the VH$_2$ and VO centers such a close correspondence of parameters follows reasonable expectations. It build on the similarity as observed for the (VH)$_0$ and (VP)$_0$ centers, as discussed earlier [2.38]. On the proper interpretation of the Si-HVH ODMR spectrum contradicting opinions have been expressed [2.46-2.48].

### 2.4 Hydrogen–chalcogen centers

The interaction of hydrogen with double donors, e.g., the chalcogen elements sulfur, selenium and tellurium, in silicon offers attractive opportunities for impurity-passivation studies. In contrast to passivated single dopants, one expects the complexes formed by partial passivation of dopants with double valency to be observable in magnetic resonance. This might be correlated with the binding of one or more hydrogen atoms to the impurity. Chalcogen impurities represent well-studied substitutional double donors in silicon [2.49]. Early passivation studies using deep-level transient spectroscopy (DLTS) showed that all chalcogen double donors are passivated by binding hydrogen [2.11, 2.50]. Both band-gap levels were removed and no new levels were reported. This means the full passivation of corresponding levels by hydrogen. In contrast, in infrared absorption (IR) five donor states were observed when hydrogen was diffused into sulfur-doped silicon [2.51]. Three of these spectra displayed a hydrogen/deuterium isotope effect.

Magnetic resonance experiments on the hydrogen passivation of sulfur-doped silicon have been carried out as well [2.52]. Following the introduction of hydrogen by diffusion at high temperature in a wet environment of water vapor, the EPR spectra of sulfur and the sulfur pair were replaced by two new spectra, labeled Si-NL54 and Si-NL55, respectively. Figure 2.4(a) illustrates the spectra Si-NL54 and Si-NL55 over the full range of magnetic
field, whereas figure 2.4(b) shows the central part of the spectral region in higher resolution. Following the interpretation of the spectrum as due to S–H complexes, the strong central part, at around 817 mT in figure 2.4(a), corresponds to centers of sulfur isotopes with nuclear spin $I = 0$. The weaker four equal-intensity equidistant lines are due to the hyperfine interaction with the $^{33}\text{S}$ isotope having nuclear spin $I = 3/2$. The relative intensity of the side lines is consistent with the percentage of $^{33}\text{S}$ isotope, in this case enriched to 25.5%. This observation indicates the presence of one sulfur atom in the centers. Identification of the involvement of hydrogen in the Si-NL54 and Si-NL55 centers is more difficult. As the proton has nuclear spin $I = 1/2$ and 100% natural abundance, one would expect to observe the hyperfine structure of twofold splitting in each of the spectral lines. However, in this case, the hyperfine interaction is small and is not resolved in the EPR spectrum. The incorporation of hydrogen was only traced as a slightly different shape of the spectra observed in hydrogen-doped and deuterium-doped samples. To observe and determine the hydrogen effect, the higher resolution of ENDOR is required.

![Figure 2.4](image_url)

**Figure 2.4.** (a) Electron paramagnetic resonance (EPR) and field-scan-ENDOR (FSE) scans of the Si-NL54 and Si-NL55 spectra of S–H complexes over a range of magnetic field also covering the region of sulfur hyperfine splitting; magnetic field $B // [100]$. Sample doped with isotopically enriched sulfur to 25.5% of the $^{33}\text{S}$, nuclear spin $I = 3/2$. (b) Central part of the EPR and FSE spectra of S–H for $B // [011]$. Resonance $F$ shown in figure 2.4(a) is not related to sulfur.
Table 2.4. Spin-Hamiltonian parameters for Si-NL54 and Si-NL55, as obtained from computer fits of the ENDOR and the FSE angular dependencies. Electron spin $S = \frac{1}{2}$. $A^{H,D}, A_{\perp}^{H,D}, Q^{D}$, and $Q_{\perp}^{D}$ are hyperfine and quadrupole tensor principal values for the H and D nuclei. $A^S, A_{\perp}^S, Q^S, Q_{\perp}^S$ are hyperfine and quadrupole tensor principal values for the $^{31}$S nucleus.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Si-NL54</th>
<th>Si-NL55</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g$</td>
<td>1.99886 ± 4 × 10^{-5}</td>
<td>199823 ± 4 × 10^{-5}</td>
<td></td>
</tr>
<tr>
<td>$g_{\perp}$</td>
<td>2.00126 ± 4 × 10^{-5}</td>
<td>1.99974 ± 4 × 10^{-5}</td>
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</tr>
<tr>
<td>$A^S$</td>
<td>143.1 ± 2.7</td>
<td>124.0 ± 2.6</td>
<td>MHz</td>
</tr>
<tr>
<td>$A_{\perp}^S$</td>
<td>137.7 ± 2.7</td>
<td>117.9 ± 2.6</td>
<td>MHz</td>
</tr>
<tr>
<td>$Q^S$</td>
<td>6.6 ± 2.7</td>
<td>5.0 ± 2.6</td>
<td>MHz</td>
</tr>
<tr>
<td>$Q_{\perp}^S$</td>
<td>-3.3 ± 2.7</td>
<td>-2.5 ± 2.6</td>
<td>MHz</td>
</tr>
<tr>
<td>$A^H$</td>
<td>6.281 ± 9 × 10^{-3}</td>
<td>5.801 ± 8 × 10^{-3}</td>
<td>MHz</td>
</tr>
<tr>
<td>$A_{\perp}^H$</td>
<td>3.936 ± 9 × 10^{-3}</td>
<td>5.500 ± 8 × 10^{-3}</td>
<td>MHz</td>
</tr>
<tr>
<td>$A^D$</td>
<td>0.959 ± 3 × 10^{-3}</td>
<td>0.867 ± 2 × 10^{-3}</td>
<td>MHz</td>
</tr>
<tr>
<td>$A_{\perp}^D$</td>
<td>0.591 ± 3 × 10^{-3}</td>
<td>0.823 ± 2 × 10^{-3}</td>
<td>MHz</td>
</tr>
<tr>
<td>$Q^D$</td>
<td>-0.048 ± 3 × 10^{-3}</td>
<td>-0.038 ± 2 × 10^{-3}</td>
<td>MHz</td>
</tr>
<tr>
<td>$Q_{\perp}^D$</td>
<td>0.024 ± 3 × 10^{-3}</td>
<td>0.019 ± 9 × 10^{-3}</td>
<td>MHz</td>
</tr>
</tbody>
</table>

On all spectra extensive ENDOR measurements were made, using both the standard $^1$H hydrogen and the $^2$H deuterium isotopes with 100% enrichment. With all experiments carried out in a K-band spectrometer, with a microwave frequency of 23 GHz, the proton ENDOR is observed near the Larmor frequency 35 MHz and the deuteron spectrum near 5.3 MHz. From the ENDOR data the identification of hydrogen as part of Si-NL54 and Si-NL55 centers under discussion follows in an unambiguous manner. In the identification both the field-shift method and the recording of full angular dependence patterns was applied. For the case of $^2$H with $I = 1$ the nuclear quadrupole interaction was measured. As one single hydrogen trigonal pattern is observed, the incorporation of one hydrogen atom in each center is established. With all spectral components resolved in ENDOR, the
method of field-scanned ENDOR (FSE) utilizing ENDOR tagging of spectral components, can be used for revealing underlying EPR. Results, as are given in figure 2.4(a) and (b), resolve two separated centers Si-NL54 and Si-NL55, which are observed as a superposition in the standard EPR. Under the improved conditions of FSE the angular dependence patterns of the individual components were recorded revealing the overall trigonal symmetry of the centers. From these observations, the quantitative spectroscopic analysis of data was made with an appropriate spin Hamiltonian. Both centers have electron spin $S = \frac{1}{2}$, corresponding to a single unpaired spin. As all observed interactions give a $<111>$-axial pattern, the tensors, i.e., Zeeman splittings $g$, hyperfine interactions $A$ and quadrupole interaction $Q$, have the trigonal form. Parameters of these spectra are collected in table 2.4. Following the experimental observations, it is concluded that the partially hydrogen-passivated sulfur centers have a $<111>$-axial structure. Assuming the S atoms to stay on their regular substitutional site the hydrogen atoms must find a position on a $<111>$ axis through this site. Three different types of site may be distinguished: between the sulfur atom and a nearest-neighbor silicon atom on a bond-centered (BC) site, further away from the sulfur atom on the anti-bonding site of a nearest-neighbor silicon atom (AB-Si), or finally, close to the sulfur atom on an anti-bonding site (AB-S). Which of such positions is actually taken by the hydrogen atom requires more subtle analysis of the hyperfine and quadrupole interaction parameters. Alternatively, the defect modeling is based on state-of-the-art theoretical calculations. An early treatment, predicting full passivation of the sulfur defect by one or two hydrogen atoms in forming complexes of monoclinic or orthorhombic symmetry, is at variance with presented experimental data [2.53]. In more recent research the interstitial BC and AB-Si sites were found to be stable positions for hydrogen, with a small energy difference only [2.54]. In both cases a bond is formed with a nearest-neighbor silicon atom. This allows a plausible interpretation of experimental data by assigning the Si-NL54 spectrum to the S–H complex with hydrogen on the BC site, with Si-NL55 belonging to the complex with H on the AB-Si site.

2.5 Hydrogen–transition metal centers

Transition metals are common fast diffusing impurities in silicon, easily present in the material as an unintentional contaminant, due to, e.g., insufficient control over purity in processing treatments. Nearly all of them introduce deep levels in the band gap of silicon,
in this way having a profound effect on materials properties, in particular related to carrier recombination processes. Hydrogen atoms can be bound in the deep local potentials of the transition metal impurities and affect their properties substantially. Interaction between s states of hydrogen with d states of transition metals will lead to new defects with a possibly basically different electronic structure. It is certainly not obvious that hydrogen binding will lead to electrical passivation of these impurities. As a result of exchange coupling between spins in the d shells of transition elements states of high spin, compounded from orbital and intrinsic spin momenta, are formed (Hund’s rule). It is not to be expected that the high spin will be nullified completely by binding one or more hydrogen atoms. Transition-metal–hydrogen complexes can still be paramagnetic, hence be observable by magnetic resonance, creating a field for fruitful studies of hydrogen-bonding physics.

The most detailed studies were performed on a center identified as \([\text{Pt}_{1-c} \text{H}_2\text{I}]^+\), which is observed in platinum-doped silicon after hydrogenation treatment typically for 24–72 hours at 1000–1250 °C [2.3, 2.55]. The spin resonance is described by electron spin \(S = \frac{1}{2}\) and shows the angular dependence of an orthorhombic-I symmetry center. The atomic structure is derived on the basis of the observed hyperfine interactions. The presence of one platinum atom is indicated by the resolved hyperfine splitting related to the \(^{195}\text{Pt}\) isotope, nuclear spin \(I = \frac{1}{2}\) and natural abundance of 33%, resulting in the characteristic splitting of the resonance in three components with the intensity ratio of 0.25 : 1 : 0.25. Presence of two equivalent hydrogen atoms is revealed by triplet structure with amplitudes scaling as 1 : 2 : 1 of all resonances due to the hyperfine fields created by two hydrogen atoms (spin \(I = \frac{1}{2}, 100\%\)). In case of deuteration (spin \(I = 1\)) the associated hyperfine structure will have five components in the intensity ratio of 1 : 2 : 3 : 2 : 1, but their mutual separation will be reduced by the factor \(2\mu_\text{H}/\mu_\text{D} = 6.5\). Due to the smallness of the splitting this has not been observed in resolved form, only as an appropriate line broadening. The spin-Hamiltonian parameters of the center are given in table 2.5. A small difference of the \(g\) tensors and platinum hyperfine interaction was reported for the Pt–H\(_2\) and Pt–D\(_2\) centers [2.3]. Atomic models consistent with the observed symmetry and atomic constituents are given in figure 2.5 [2.56]. The model of the orthorhombic isolated Pt\(^+\) center has provided an obvious starting point for modelling of Pt–H\(_2\). Positions of the hydrogen atoms follow traditional chemical bonding arguments and are consistent with their hyperfine interactions with the defect electron. The isotropic part of hydrogen hyperfine interaction, \(a = 8.6\) MHz [2.3, 2.4], corresponds to a localisation of around 0.6% on each of the two protons. The
position of the hydrogen atoms on a nodal plane of the defect accounts in a natural manner for this small localisation. The still present non-vanishing component can be discussed in terms of many-electron effects, as in the case of center Si-AA9. Anisotropic hyperfine interaction with hydrogen nuclei must be due to electron spin localised on remote orbitals. From the reported values \( b = 0.6 \text{ MHz} \) \([2.3]\) or \( b = 1.1 \text{ MHz} \) \([2.4]\) and with equation (5) a distance \( r \) of 0.4 to 0.5 nm between electron and nucleus is calculated. Assuming one full electron spin to be present in the core position of the defect, the large distance found favors the hydrogen positions anti-bonding to silicon as sketched in figure 2.5(b). In experiment \([2.3]\) hyperfine interactions with two \(^{29}\text{Si}\) atoms have indicated a 26% localisation on these neighbors. In reality the wave function is therefore spread out over a larger region of the defect and the quantitative aspects of the model calculation should be taken with corresponding care. A most important question is about the electrical activity of the Pt-H\(_2\) center. This has been probed by monitoring the effect of Fermi level on the observability of Pt-H\(_2\) in its paramagnetic state. Fermi level changes were imposed by different platinum and/or donor doping concentration, by electron irradiation creating compensating acceptor centers and by illumination \([2.4, 2.55]\). As a result it was concluded that the paramagnetic state of the complex corresponds to \((\text{Pt-H}_2)^-\), and that a level \((\text{Pt-H}_2)^2-/(\text{Pt-H}_2)^-\) is positioned between \( E_{\text{CB}} - 0.045 \text{ eV} \) and \( E_{\text{CB}} - 0.1 \text{ eV} \) and another level \((\text{Pt-H}_2)^-//(\text{Pt-H}_2)^0\) between \( E_{\text{CB}} - 0.23 \text{ eV} \) and \( E_{\text{VB}} + 0.32 \text{ eV} \). Hence, it must be concluded that hydrogenation of platinum-doped silicon leads to the formation of a double acceptor center. Such conclusions are in remarkable agreement with results of other studies.

From deep-level transient spectroscopy levels related to a Pt-H\(_2\) defect were reported at \( E_{\text{CB}} - 0.18 \text{ eV} \) and \( E_{\text{VB}} + 0.40 \text{ eV} \) \([2.57-2.59]\). Very recently published theoretical results place a first acceptor level at \( E_{\text{CB}} - 0.45 \text{ eV} \), but do not report a \((2-/\-\-)/\) level \([2.60]\). In addition to the acceptor level the theoretical study finds a donor level close to the valence band, thus describing Pt-H\(_2\) as an amphoteric defect. In the recent DLTS studies also electrical levels related to Pt-H\(_1\) and Pt-H\(_3\) are identified. The center Pt-H\(_4\) is considered to be a fully passivated Pt center without electrical activity. In an early report on DLTS of hydrogenated platinum-doped silicon the full passivation of platinum was deduced \([2.13]\).

Obviously in contradiction to the more recent observations, it may have occurred that the level at \( E_{\text{CB}} - 0.1 \text{ eV} \) has been too shallow and the midgap level has been too deep for observation. In a close parallel to the magnetic resonance the platinum–hydrogen complexes were investigated by optical absorption due to the local vibrational modes
(LVM) of hydrogen [2.4]. Absorptions at 1888.2 cm\(^{-1}\) and 1901.6 cm\(^{-1}\) were identified as anti-symmetric and symmetric hydrogen stretching vibrations, respectively, in the paramagnetic state of Pt-H\(_2\). Corresponding pairs of bands for the PtHD and Pt-D\(_2\) centers are at the frequencies 1894.6 cm\(^{-1}\) and 1366.9 cm\(^{-1}\) for PtHD and at 1362.5 cm\(^{-1}\) and 1370.7 cm\(^{-1}\) for Pt-D\(_2\). The isotope shifts confirm the presence of two hydrogen atoms in the centers. Vibrational spectroscopy is not restricted to the paramagnetic state of the complex. There are corresponding pairs of vibrations for the two other charge states. By varying the charge state of the defect, the changes in vibrational frequencies have helped to locate the levels. Probing the thermal stability of the Pt-H\(_2\) center it was found that the EPR spectrum anneals out by exposure to 500 °C for 3 hours [2.3] or to 600 °C [2.55]. The simultaneous loss of LVM spectra indicates that both spectra are associated with the same center [2.55].

**Figure 2.5.** Tentative models for the Pt-H\(_2\) complex in silicon. (a) in the left side of the picture—hydrogen terminating bonds inwards into the vacancy (hydrogen atom inside the cage, close to platinum atom) (b) on the right side—hydrogen atom pointing away from the platinum atom (outside the cage, bonds to silicon atom). Orthorhombic symmetry allows distortions of the center, which leave the (011) mirrorplane symmetry.

Another spectrum of a more complex structure has been interpreted as arising from a trigonal [Pt\(_x\)-(H\(_2\))\(_2\)]\(_3\) center [2.3]. It is formed by hydrogenation of platinum-doped silicon
when a retarded quenching procedure is applied. Centers revealing the tendency of platinum to coalesce into larger complexes with Si–Pt$_3$ groups as building blocks have earlier been identified [2.61, 2.62]. In the common way important atomic structure information is derived from the observed hyperfine interactions. For a center with three equivalent platinum atoms a sevenfold line splitting should occur, each component corresponding to a distinct total $m_i$ in the range $-3/2$ to $+3/2$, in steps of $1/2$. Given the abundance 0.33 of the magnetic isotope $^{195}\text{Pt}$ the expected intensities must reflect the ratios $0.01 : 0.13 : 0.57 : 1 : 0.57 : 0.13 : 0.01$. As shown in figure 2.6 such a structure is actually observed, with the reservation, however, that the two outermost lines are missing; due to their weakness they are below the noise level.

![Figure 2.6](image_url)

**Figure 2.6.** Part of the Si-NL53 spectrum recorded with the magnetic field parallel to a [111] crystal direction, at the microwave frequency of 9.2164 GHz and at temperature $T = 7.5$ K. Hyperfine structure due to three platinum atoms (isotope $^{195}\text{Pt}$, $I = 1/2$, abundance 33%) and six hydrogen atoms (isotope $^1\text{H}$, $I = 1/2$, abundance 100%) is exhibited.

As also shown in figure 2.6, each of the $^{195}\text{Pt}$ components has characteristic identical further structure, which is caused by hydrogen hyperfine effects. As the number of
components in this latter structure is odd, there must be an even number of hydrogen nuclei responsible for it. From comparison with the observed spectra this number of hydrogen atoms is deduced to be 6. Predicted intensities scaling as $1 : 6 : 15 : 20 : 15 : 6 : 1$ are in good agreement with experimental line heights. Besides, six hydrogen atoms can easily be incorporated in a defect model of the required trigonal symmetry. Spin-Hamiltonian parameters of the spectrum, known under label Si-NL53, are given in table 2.5. As for Pt-H$_2$ also for the present center the electron spin localisation on the hydrogen is small, again near 0.6%.

**Table 2.5. Principal values of the spin-Hamiltonian parameters for the hydrogen-platinum complexes Pt-H$_2$, Pt-D$_2$ and Si-NL53.**

| Center  | Tensor | $||[100]||$ | $||[011]||$ | $||[0\bar{1}1]||$ | Unit | Reference |
|---------|--------|------------|------------|----------------|------|-----------|
| Pt-H$_2$ | $g$ | 2.1299 | 2.1683 | 1.9563 | MHz | [2.3] |
|         | $A_H^P$ | 175.7 | 237.3 | 541.2 | MHz | |
|         | $A_G^H$ | $\approx$9.8 | 8.2 | 7.9 | MHz | |
| Pt-D$_2$ | $g$ | 2.1319 | 2.1688 | 1.9554 | MHz | |
|         | $A_H^P$ | 182.5 | 239.9 | 545.8 | MHz | |
| Si-NL53 | $g$ | 2.5082 | 2.0206 | | MHz | [2.3] |
|         | $A_H^P$ | 432.7 | 327.3 | 349.4 | MHz | |
|         | $\perp[100]$ | // [1 $\bar{1}$ 0] | $\perp[1 \bar{1} 0]$ | | |

It should be noted that in the defect model as presented in Ref. [2.3] the hydrogen atoms are not finding their positions on a symmetry plane with a node of electron density. To explain the low spin density the effective pairing-off of spins in the hydrogen bond has to be invoked, as for several others of the hydrogen-related centers. As was found for the Pt-H$_2$ defect, also the Si-NL53 center is observed as a so-called bulk defect in silicon samples with minimum dimensions of more than 1 mm. Mechanically removing a layer of about 10 $\mu$m thickness all over the sample surface did not notably reduce the signal intensity. It follows that centers throughout the volume of the samples become hydrogen bonded using the introduction method of high-temperature diffusion. It is this bulk
passivation that has allowed the powerful but less sensitive tools of optical and magnetic resonance spectroscopy to be employed for defect characterization. This forms an apparent contrast with other common introduction techniques as chemical etching, ion implantation and plasma treatment.

Deep-level transient spectroscopy has made substantial contributions to understanding the reactions between hydrogen and transition elements. Besides gold and platinum, the hydrogen interaction processes were studied for the 4d elements rhodium [2.63], palladium [2.58, 2.64, 2.65] and silver [2.10, 2.58, 2.66] and for the 3d elements titanium [2.58, 2.67], vanadium [2.68, 2.69], chromium [2.69], cobalt [2.58, 2.70, 2.71], nickel [2.58] and copper [2.72]. Reports on magnetic resonance characterization are scarce. They are limited only to iron [2.73] suggesting a fruitful field of future research left uncovered.

References


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(1994).


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