Hydrogen interaction with impurities in silicon
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“There’s nothing remarkable about it. All one has to do is hit the right keys at the right time and the instrument plays itself.”

- Johann Sebastian Bach -

Chapter 5

EPR SPECTROSCOPY OF Pt–H₃ AND Pt–Fe₃ COMPLEXES IN HYDROGENATED SILICON

ABSTRACT

We report on the observation of two paramagnetic centers identified as platinum-related complexes in n-type platinum-doped hydrogenated silicon. The first center, labeled Si-NL65, is characterized by a resolved hyperfine structure of 1:3:3:1 – 4:12:12:4 – 1:3:3:1 revealing the presence of one platinum atom and three equivalent hydrogen atoms in the complex. The center, with an overall trigonal symmetry, discloses a large anisotropy of platinum- and a slight anisotropy of hydrogen-hyperfine interactions. An analysis using a linear-combination-of-atomic-orbitals (LCAO) approximation provides adequate materials for an atomic model, in which the platinum occupies the substitutional site and three interstitial hydrogen atoms anti-bonding sites to three silicon nearest-neighbor atoms. The second center, labeled Si-NL66, is observed in the platinum-diffused sample co-doped with iron, enriched to 95.1% in the $^{57}$Fe isotope, presenting hyperfine structure of 1:4:1 related to platinum, with each group containing eight spectral lines as due to additional hyperfine interactions with three atoms with $I = 1/2$ and 100% abundance. In this case, as no isotope effect was observed in the samples doped with either hydrogen or deuterium, the direct incorporation of hydrogen in the center was excluded. Having the low symmetry of monoclinic-I, the Si-NL66 spectrum was described as a complex of substitutional platinum and three nonequivalent interstitial iron atoms in silicon.
5.1 Introduction

In the last few years the subject of interaction of hydrogen with transition metal impurities in semiconductors has become of great interest [5.1-5.3]. Especially for silicon, several theoretical and experimental papers have been published concerning new electronic levels related to transition-metal-hydrogen complexes in the band gap [5.4-5.11]. Among these, the experimental studies using capacitance transient spectroscopic measurements such as DLTS and theoretical calculations using first-principle local-density formalism cluster theory have shown great success in identifying the electronic levels of transition-metal–hydrogen complexes in silicon [5.6, 5.9]. Results obtained from these techniques are closely similar and support each other, for the first time, creating quite a good correlation between theoretical calculation and experiment. However, in several cases the chemical combination and the structure of the defects are not directly, fully, identified. One problem is that electron paramagnetic resonance (EPR), an outstanding and powerful technique for defect characterization, has shown a drawback in determining the transition-metal–hydrogen complexes due to its lower sensitivity compared to that of the DLTS method and due to the low concentration of transition-metal–hydrogen complexes [5.12].

From the experimental point of view the DLTS technique has the advantage of high sensitivity and the ability to measure a very low concentration in a thin surface layer of the samples. Hydrogen introduction can easily be accomplished by wet chemical etching, i.e., the hydrogen is injected into a surface layer while etching the transition-metal doped samples in CP4 or CP6, different mixtures of HNO₃:HF:CH₃COOH solution. The measurements were done following heat treatments at certain temperatures from 100 to 350 °C depending on transition metal. In most cases, the assignment to transition-metal–hydrogen related complexes was based on the appearance of electronic levels and the hydrogen depth distribution. In contrast to this, samples used for EPR or IR absorption measurements usually are bulk samples which require a more difficult and less controlled hydrogenation process to produce uniform defect concentrations of $\sim 10^{14} - 10^{15} \text{ cm}^{-3}$ throughout the investigated samples. The hydrogenation process, therefore, usually is done by heating the sample in H₂ gas or wet environment of water vapor at high temperatures between 1200 and 1300 °C followed by rapid quenching to room temperature. This method of hydrogen introduction has so far been successfully applied for observation of platinum–hydrogen and gold–hydrogen complexes in silicon [5.3, 5.13, 5.14]. In this study an
extensive investigation of interaction of hydrogen and the transition metal platinum, with and without co-doped enriched $^{57}\text{Fe}$, has been carried out by electron paramagnetic resonance. A large number of samples has been prepared with different initial concentrations of platinum. Different conditions for the formation of transition-metal-hydrogen related centers are established by adjusting the cooling rate of the sample after hydrogen diffusion, and the gas pressure inside the ampoules during diffusion at high temperature. The observation of the Si-NL65 spectrum of the Pt-H$_3$ center with very low creation probability and its characterizing hyperfine interaction with one platinum and three hydrogen atoms provides solid experimental evidence confirming the existence of this center in silicon, as was already concluded from DLTS measurements. The observation of the Si-NL66 spectrum identified as a complex of a platinum and three nonequivalent iron atoms, only after hydrogenation, once again is practical evidence that supports the important issue of hydrogen enhancing the aggregation of impurities into complexes in silicon.

5.2 Sample preparation and EPR spectrometer

With the main purpose being the investigation of platinum and platinum-hydrogen complexes in hydrogenated silicon, in this experiment platinum and hydrogen were diffused into silicon by thermal diffusion at high temperatures from 1200 to 1300 °C for a moderate time from a few to 72 hours. As a routine, the diffusion procedure is divided into two steps. In the first step only the transition metal is diffused. After that all samples are measured carefully before subjecting them to further heat treatment to diffuse with hydrogen. Up to 40 samples have been prepared from starting material Czochralski-grown n-type phosphorus-doped silicon single crystal which has a room temperature resistivity of 0.75 to 1.25 Ωcm to the final bar-shaped samples with typical dimensions of 1.5 × 1.5 × 15 mm$^3$, and the longest side parallel to the [011] crystallographic direction. The concentration of platinum was controlled by changing the diffusion time and the amount of platinum rubbed onto one or otherwise four surfaces of the samples. The diffusion pressure was adjusted usually from 100 to 300 mbar by changing the initial argon gas filled in the ampoules. The cooling rate was varied by dropping the ampoules immediately into water at room temperature or by keeping the ampoules in air for a certain amount of time before dropping into water.
Magnetic resonance experiments were carried out using a superheterodyne spectrometer operated in the K-band with the frequency near 23 GHz. Signals were observed with the spectrometer tuned to dispersion under conditions of adiabatic fast passage. The magnetic field was modulated with an amplitude of approximately 0.1 mT and a frequency of 477 Hz. The spectrometer has an option of operation under full computer control. For a more complete description of the equipment and the experimental techniques, see, e.g., Ref. [5.15].

5.3 Experimental results

After platinum diffusion, depending on the quenching speed, the spectra of platinum and several platinum-related complexes are observed in the samples. In the fast-cooling samples the dominant centers are the substitutional platinum Pt(I) and the platinum–iron pair Pt(II) [5.16]. In the samples with a slower cooling rate (kept in air about 5 to 10 seconds before dropping into water at room temperature) the Pt(III) and Pt(VI) pairs are observed simultaneously with the Pt(I) and Pt(II) centers [5.17, 5.18].

![Figure 5.1. Typical EPR spectrum of the Pt–Fe spectrum presenting the hyperfine interaction with one $^{57}$Fe atom for the magnetic field $\mathbf{B} \parallel [011]$ crystallographic direction, the microwave frequency $f = 22.99676$ GHz, temperature $T = 4.2$ K.](image-url)
The identification of the Pt(II) center as Pt–Fe pair was unambiguously confirmed by the spectra observed in the samples co-doped with the $^{57}$Fe enriched iron, which showed the twofold splitting as due to hyperfine interaction with one $^{57}$Fe atom ($I = 1/2, 95.1\%$), in agreement with the previously published result [5.19]. A typical EPR spectrum is shown in figure 5.1 for the magnetic field $\mathbf{B} \parallel [011]$, at temperature $T = 4.2\ K$, and with microwave frequency $f = 22.99676\ GHz$. It is clear that the $^{57}$Fe hyperfine interaction is anisotropic as the splitting is only observed in one of the two group of lines in this direction.

![EPR spectra](image)

**Figure 5.2.** EPR spectra of the Si-NL65 center associated with the trigonal Pt–H$_3$ center observed in the platinum-doped hydrogenated sample (a) for the magnetic field $\mathbf{B} \parallel [011]$ direction; (b) for the magnetic field $\mathbf{B} \parallel [111]$ direction. The spectra are observed under visible-light illumination revealing hyperfine structure of 1:3:3:1 – 4:12:12:4 – 1:3:3:1 as due to hyperfine interaction with one platinum atom and three equivalent hydrogen atoms. The spectrum of the well-known Pt–H$_2$ center is also observed and indicated. The microwave frequency $f = 22.71369\ GHz$ and temperature $T = 4.2\ K$.

On the basis of these observations the samples were all subjected to the hydrogen diffusion process. The experimental results that show after hydrogenation the Pt(I) center has disappeared, in its place the well-known Pt–H$_2$ center is observed in all samples investigated. Depending on the cooling rate, other centers can be either very dominant or
very weak in intensity. The formation of the Pt–H$_3$ center is in strong competition with the formation of the Pt–Fe pair, as well as other Pt–Pt pairs [5.17, 5.18]. As a result of this competition, the spectrum has a very low formation probability explaining the absence of detection of this center by magnetic resonance in the past. In our experiments by changing the cooling rate over 40 samples with different concentrations of platinum and diffused hydrogen, we observed the Si-NL65 spectrum weakly in only two samples, while the Pt–H$_2$, Fe$_n$, and Pt–Fe centers are intensively observed in all others.

![Diagram](image)

**Figure 5.3.** Angular dependence pattern of the Si-NL65 spectrum as measured for rotation of the magnetic field in the (0 1 1) plane from [100] to [011]. The experimental data recorded for temperature $T = 4.2K$ and microwave frequency $f = 22.71369$ GHz are presented as solid circles. Solid lines are from a computer fit using the spin Hamiltonian described in equation (5.1).

The typical EPR spectra of the Si-NL65 center are depicted in figure 5.2(a) for the magnetic field $B // [011]$ and in figure 5.2(b) for $B // [111]$ crystal direction of the sample at 4.2 K under visible-light illumination and for the microwave frequency $f = 22.71369$ GHz. The spectrum is characterized by the relative intensity of spectral lines of nearly
1:3:3:1 – 4:12:12:4 – 1:3:3:1 obviously revealing the hyperfine interaction with one platinum atom ($I = 1/2$ and 33.8%) and three atoms with $I = 1/2$ and 100% abundance. Consistent with this hyperfine structure, the Si-NL65 spectrum is attributed to a Pt–H$_3$ center. Also seen in figure 5.2 is the spectrum of the Pt–H$_2$ center with well-known hyperfine structure of 1:2:1 – 4:8:4 – 1:2:1 of spectral lines, as indicated. The Fe$_i$ center has completely disappeared and the Pt–Fe center is still weakly detected.

Measuring the full angular dependence of the spectrum, i.e., the position of all spectral lines versus angle of applied magnetic field, the symmetry of the center is determined to be trigonal with the principal $g$ values $g_{||} = 1.96728$ and $g_{\perp} = 2.15699$. In figure 5.3 the angular dependence pattern of the Si-NL65 spectrum as measured for rotation of the magnetic field in the (0 1 1) plane from [100] to [011] is presented. The solid lines are simulations using spin-Hamiltonian parameters as listed in table 5.1; the points are experimental data.

![Graph](Image)

**Figure 5.4.** EPR spectrum of the Si-NL66 center for magnetic field $B$ // [011], microwave frequency $f = 22.61104$ GHz, temperature $T = 4.2$ K. The spectrum indicated by the stick diagrams is characterized by hyperfine structure of 1:4:1 as due to hyperfine interaction with one platinum atom. Further splitting into eightfold structure of each spectral line is also resolvable. The spectra of the Fe$^0$, the Pt–Fe, and the P$^0_s$ centers are observed with much higher intensity.
The second spectrum, the Si-NL66, is observed only in the hydrogenated samples co-doped with iron, in an enrichment to 95.1% of the $^{57}$Fe isotope. A typical spectrum is plotted in figure 5.4 for the magnetic field $\mathbf{B} \parallel [011]$, microwave frequency $f = 22.61104$ GHz, and at 4.2 K. The spectrum is characterized by more complicated hyperfine structures, which are angular dependent and unresolved in most directions of applied magnetic field. This hyperfine structure, as shown in more detail in figure 5.5, reveals hyperfine interaction with at least one platinum atom and three other atoms with nuclear spin $I = 1/2$ and abundance close to 100%, creating a platinum hyperfine structure of 1:4:1, with each group containing up to eight lines.

![Graph](image)

**Figure 5.5.** Part of the EPR spectrum of the Si-NL66 center observed in the deuterated samples reveals the hyperfine interaction with one platinum and three non-equivalent iron atoms with $I = 1/2$. The spectrum is recorded for the magnetic field $\mathbf{B}$ about 1° away from the [011] crystallographic direction, microwave frequency $f = 22.91678$ GHz and temperature $T = 4.2$ K.

From the sample preparation process, there are two intentionally doped elements matching with this requirement, the hydrogen ($I = 1/2$, 100%), and the $^{57}$Fe ($I = 1/2,$
95.1%). However, the direct incorporation of hydrogen into the Si-NL66 center was experimentally excluded following the observation of an identical EPR spectrum in the samples diffused with deuterium. This leaves iron as the most prominent candidate. The angular dependence of the Si-NL66 spectrum as shown in figure 5.6 corresponds to monoclinic-I symmetry with the principal g values as listed in table 5.1.

Figure 5.6. Angular dependence pattern of the Si-NL66 spectrum as measured for rotation of the magnetic field in the (0 1 1) plane from [100] to [011] for microwave frequency $f = 22.61104$. The experimental data, recorded for temperature $T = 4.2$ K, are presented as solid diamonds. Solid lines are from a computer simulation using the spin Hamiltonian described in equation (5.2).

5.4 Discussion

5.4.1 Si-NL65 center

The observation of the Si-NL65 spectrum after hydrogenation with very low formation probability and hyperfine structure of $1:3:3:1 - 4:12:12:4 - 1:3:3:1$ no doubt is strong evidence for the possibility that the center is a complex of one-platinum–three-hydrogen atoms. Indeed, from the experimental data we find that the Si-NL65 spectrum can be very well described with the $S = 1/2$ spin Hamiltonian...
in which the sum is over three equivalent hydrogen atoms. Results of the fit using equation (5.1), as given in table 5.1, disclose a large anisotropic hyperfine interaction of platinum with $A_\perp = 52.2$ MHz and $A_\parallel = 708.8$ MHz, corresponding to an isotropic contact interaction $a = 271.1$ MHz and anisotropic dipole-dipole interaction $b = 218.9$ MHz. For the hydrogen a slightly anisotropic hyperfine interaction is calculated with $A_\perp = 12.7$ MHz and $A_\parallel = 14.5$ MHz, $a = 13.3$ MHz, and $b = 0.6$ MHz. Using the standard analysis based on linear combination of atomic orbitals (LCAO) the spin densities $\eta^2\alpha^2$ in the 6s and $\eta^2\gamma^2$ in the 5d orbital on the site of the platinum atom are determined to be about 2% and 47.6%, respectively. For hydrogen, the hyperfine interaction leads to a localization in a 1s orbital of about 0.95% on each of the three protons.

The slight anisotropy of hydrogen hyperfine interaction of about 0.6 MHz, in a similar interpretation as for the Si-AA9 and Si-NL64 centers, must be due to the electron spin localized on remote orbitals. From this value 0.6 MHz of hyperfine interaction anisotropy, a distance of about 0.5 nm between electron and nucleus is deduced implying the interstitial anti-bonding sites to the silicon nearest-neighbor atoms for the protons.

From these results one recognizes that:

(i) With about 50% of spin density localized on the s and d orbitals of the platinum atom and only about 0.9% spin density localized on each of the three protons, the Pt-H$_3$ center must behave as a platinum-like center in silicon;

(ii) The hyperfine interaction tensor $A^H$ of the Pt-H$_3$ center is resembling closely the values of hydrogen hyperfine interaction tensors reported for the other two transition-metal-hydrogen complexes, the Pt-H$_2$ and Au-H$_2$ centers, i.e., the values of the isotropic and anisotropic parts about 10 MHz and 1 MHz, respectively [5.3, 5.12, 5.13].

This enables us to establish a detailed microscopic model for the Pt-H$_3$ center in which the platinum atom occupies the substitutional site and three interstitial hydrogen atoms are anti-bonding to three silicon nearest-neighbor atoms. In a trigonal symmetry configuration, the three hydrogen atoms are arranged with trigonal symmetry on <111> axes intersecting the substitutional platinum site. The model, as illustrated in figure 5.7, is similar to the microscopic structure proposed for the Pt-H$_3$ center by Jones et al. [5.6] following the theoretical calculation using first-principle local-density formalism cluster theory.
Table 5.1. Spin-Hamiltonian parameters for the Pt–Fe pair, Si-NL65, and Si-NL66 centers, as obtained from computer fits and simulation of the EPR spectra and the EPR angular dependencies. The electron spin $S = 1/2$ for all centers. The iron hyperfine interaction of center Si-NL66 is roughly estimated.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g$</td>
<td></td>
</tr>
<tr>
<td>$A^\text{Pt}$</td>
<td>MHz</td>
</tr>
<tr>
<td>$A^\text{Fe}$</td>
<td>MHz</td>
</tr>
</tbody>
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Si-NL65 – Symmetry trigonal

<table>
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<th>Parameter</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g$</td>
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<tr>
<td>$A^\text{Pt}$</td>
<td>MHz</td>
</tr>
<tr>
<td>$A^\text{H}$</td>
<td>MHz</td>
</tr>
</tbody>
</table>

Si-NL66 – Symmetry monoclinic-I

<table>
<thead>
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<tbody>
<tr>
<td>$g$</td>
<td>MHz</td>
</tr>
<tr>
<td>$A^\text{Pt}$</td>
<td>MHz</td>
</tr>
<tr>
<td>$A^\text{Fe1}$</td>
<td>MHz</td>
</tr>
<tr>
<td>$A^\text{Fe2}$</td>
<td>MHz</td>
</tr>
<tr>
<td>$A^\text{Fe3}$</td>
<td>MHz</td>
</tr>
</tbody>
</table>

The similarity of the hydrogen hyperfine interaction tensors of all EPR observed transition-metal–hydrogen complexes in silicon as presented in table 5.2 suggests that though the hydrogen atom lends itself to bind with the transition metal atom to create the complex, its character seems to be very much determined by its own atomic orbital with a spin density localization on the proton about 1%. The hydrogen atom seems to find itself easily stable at the interstitial anti-bonding site to the silicon nearest neighbors.
Figure 5.7. Atomic model for the Si-NL65 center of the Pt–H$_3$ complex in which the platinum occupies the substitutional position on the <111> symmetry axis, and three interstitial hydrogen atoms arrange themselves equivalently in trigonal $C_3v$ configuration anti-bonding to three silicon nearest-neighbor atoms.

Table 5.2. The results of LCAO analysis of the hyperfine interaction with $^{195}$Pt and $^1$H nuclei for the Si-NL65 spectrum of the Pt–H$_3$ center. Values for the Pt–H$_2$ and Au–H$_2$ centers are given for comparison.

<table>
<thead>
<tr>
<th>Center</th>
<th>Nucleus</th>
<th>$a$</th>
<th>$b$</th>
<th>$c$</th>
<th>$\eta_\alpha^2$</th>
<th>$\eta_\gamma^2$</th>
<th>$\eta_Z^2$</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-NL65</td>
<td>$^{195}$Pt</td>
<td>271.1</td>
<td>218.8</td>
<td>-</td>
<td>2</td>
<td>47.6</td>
<td>49.6</td>
<td>this work</td>
</tr>
<tr>
<td>Pt–H$_3$</td>
<td>$^1$H</td>
<td>13.3</td>
<td>0.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Si-NL64</td>
<td>$^{197}$Au</td>
<td>18.5</td>
<td>2.6</td>
<td>-</td>
<td>1.7</td>
<td>6.26</td>
<td>8</td>
<td>[5.3, 5.12]</td>
</tr>
<tr>
<td>Au–H$_2$</td>
<td>$^1$H</td>
<td>9.5</td>
<td>0.95</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.67</td>
<td></td>
</tr>
<tr>
<td>Pt–H$_2$</td>
<td>$^{195}$Pt</td>
<td>318.1</td>
<td>111.6</td>
<td>30.1</td>
<td>2.3</td>
<td>24.27</td>
<td>26.6</td>
<td>[5.13, 5.14]</td>
</tr>
<tr>
<td></td>
<td>$^1$H</td>
<td>8.6</td>
<td>&lt;1</td>
<td>-</td>
<td>-</td>
<td>0.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Now we will consider the charge state of the Pt–H$_3$ center. As predicted from theoretical calculation, the Pt–H$_3$ complex is paramagnetic in its neutral charge state with the e-manifold containing three electrons, being able to trap a single electron. This complex produces a single acceptor level ($-$/$0$) lying exceptionally deep at 1.35 eV below
the conduction band. The Pt–H$_3$ center does not possess any donor levels. The experimental measurement using the DLTS technique by Weber et al. seems to support this calculated result with the observation of a deep acceptor level, the so called H(150), at $E_C - 0.9$ eV, that from the deep-level depth profiling was assigned to the Pt–H$_3$ complex [5.8, 5.9]. The spectrum Si-NL65 of the Pt–H$_3$ center in our experiment is observed only under visible light. To be in its paramagnetic neutral charge state the center has to behave as an acceptor-like center with the capture cross section for holes larger than that for the electrons. The defect is in negative charge state under normal conditions in n-type material, under the light illumination it captures a hole to become a neutral center.

5.4.2 Si-NL66 center

The suggested interpretation for the chemical composition of the Si-NL66 center is based mostly on the sample preparation conditions and the observed spectrum. In the past, several platinum-related complexes, which contain up to six platinum atoms, have been observed in EPR [5.13, 5.14, 5.20, 5.21]. With the observed multi-line hyperfine structure one may think that the Si-NL66 spectrum is a complex of several platinum atoms. However, from careful inspection of the hyperfine structure of the Si-NL66 spectrum, such a possibility has to be excluded as a defect containing two equivalent platinum atoms will produce a hyperfine structure with relative intensity ratio of 1:8:18:8:1 of the spectral lines and this ratio will be 1:12:51:88:51:12:1 for the complex with three equivalent platinum atoms. In the experiment we had already eliminated the direct involvement of the hydrogen into the Si-NL66 center, leaving $^{57}$Fe iron the only suitable impurity, which may involve in the center. In order to account for the observed hyperfine structure of 1:4:1, in which each of its components contains eight lines with nearly equal intensity, the incorporation of one platinum atom and three iron atoms must be assumed as the most likely option. The complicated hyperfine structure, which is unresolved in most directions of observation, indicates that the three iron atoms are non-equivalent. This non-equivalence of the three iron atoms will result in a lower symmetry of the defect compared to that of Pt–H$_3$ and another similar platinum-related defect, the Pt–Li$_3$ center as reported in Refs. [5.21-5.25]. Indeed, the observed monoclinic-I symmetry of the angular dependence of the Si-NL66 spectrum supports this argument.

Due to the not fully resolved angular dependence of the hyperfine structure and the non-equivalence of hyperfine interaction of the three iron atoms, the exact determination of
the hyperfine interaction tensors of iron atoms is not possible; only estimated values, as listed in table 5.1, can be given. The angular dependence of the Si-NL66 center can be simulated and fitted with electron spin $S = 1/2$ and the following spin Hamiltonian

$$H = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{A}^{\text{Pt}} \cdot \mathbf{I}^{\text{Pt}} + \sum_{i=1,3} \mathbf{S} \cdot \mathbf{A}^{\text{Fe}}_i \cdot \mathbf{I}^{\text{Fe}}_i,$$

(5.2)

with the platinum hyperfine interaction principal values $A_1 = 494$ MHz, $A_2 = 212$ MHz and $A_3 = 281$ MHz. The experimental results as described above are not sufficient to establish a detailed microscopic model for the Si-NL66 center. The tentative model, however, can be sketched with the platinum at the substitutional site bonding to three interstitial irons. The fact that the iron atom has a larger atomic radius compared to that of hydrogen and lithium makes it is more difficult to find three equivalent positions for three iron atoms.

### 5.5 Conclusions

In this study, we have reported two EPR spectra labeled Si-NL65 and Si-NL66 of the Pt–H$_3$ and Pt–Fe$_3$ centers in silicon, respectively. The observation of the Si-NL65 spectrum of the Pt–H$_3$ center with trigonal symmetry is the first observation in EPR of a transition-metal–hydrogen complex containing three hydrogen atoms. A detailed analysis of the experimental data has provided sufficient material for the atomic model of the center in which the platinum occupies a substitutional position and three hydrogen atoms arrange themselves equivalently in trigonal configuration anti-bonding to three silicon nearest atoms on $<111>$ axes passing through the platinum site. This model is in good agreement with the theoretically calculated result obtained by Jones et al. [5.6] Though the energy level of the Pt–H$_3$ center cannot be determined by magnetic resonance, evidence from the EPR observation seems to support the assignment of an acceptor level as measured in DLTS. The Si-NL66 spectrum was attributed to a complex of one substitutional platinum atom and three interstitial iron atoms. Although the direct incorporation of hydrogen/deuterium into the center is not observed, the hydrogen plays an important role in enhancing the formation probability of the Pt–Fe$_3$ center as it only observed in the hydrogenated/deuterated samples. The observation of lower symmetry of the Pt–Fe$_3$ center compared to that of the Pt–H$_3$ and Pt–Li$_3$ centers is a good evidence indicating that if atoms with larger atomic radius are involved to form the complex, it is more difficult to
find equivalent positions for all of the atoms than for the smaller atoms, such as hydrogen or lithium.

References