

EPR spectroscopy of platinum-hydrogen complexes in silicon

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Two similar defects in silicon, resulting from doping with platinum in an atmosphere containing water vapor, were studied by means of electron paramagnetic resonance. Both spectra have effective electron spin $S = \frac{1}{2}$, and exhibit platinum- and hydrogen-related hyperfine structure and remarkable behavior under band-gap illumination. One of the centers has been identified with the recently reported Pt-H₂ complex. Ligand hyperfine interaction and values of electron localization on two silicon neighbors and two protons have been measured and found to support the model of the Pt-H₂ center. The second spectrum, labeled Si-NL53, is also reported here. This spectrum has trigonal symmetry and displays hyperfine interactions with three equivalent platinum nuclei. Spin-Hamiltonian parameters of the spectrum were determined and the microscopic model of the defect is proposed. It has been concluded that annealing at high temperature in water-vapor atmosphere provides a high concentration of hydrogen in the bulk silicon and that it can be trapped there forming stable complexes with platinum.

I. INTRODUCTION

Transition metal (TM) impurities continue to attract considerable attention in view of their ability to create deep electrical levels in silicon. In particular, the role of platinum as a dopant in silicon has been extensively investigated and a variety of platinum-related defects, including isolated substitutional platinum,¹ platinum pairs,^{2,3} and even a six-platinum cluster,⁴ have been detected by means of electron paramagnetic resonance (EPR). At the same time, hydrogen, intentionally incorporated into material by hydrogen plasma exposure or by implantation, can passivate the electrical activity of such deep defect centers.⁵ It has been concluded that the Pt acceptor can be passivated by hydrogen injection.⁶ Since unintentional contamination by hydrogen often occurs during chemical etching⁷ or due to boiling in water, the process of hydrogen passivation is not always fully under control. However, in spite of its high diffusivity even at low temperatures, incorporation of hydrogen into the bulk silicon is restricted by formation of immobile complexes with other defects. Nevertheless, as it has recently been demonstrated, hydrogen-acceptor complexes can be formed in the bulk silicon as a result of annealing of a sample at about 1300°C in hydrogen-gas atmosphere followed by rapid quench to room temperature.^{8,9}

Recently an EPR spectrum of the platinum-hydrogen complex has been reported.¹⁰ It occurs as a result of annealing of samples containing platinum at a temperature of 1250°C in the atmosphere of hydrogen gas.

The objective of the present study was to examine

further the mechanisms of TM-hydrogen complex formation at high temperature. We intended to investigate water-vapor atmosphere as a possible source of hydrogenation. In the course of the study another EPR spectrum has been discovered. It was attributed to a platinum-hydrogen complex, different from the already reported Pt-H₂ defect. We present a detailed spectroscopic investigation of both centers.

II. EXPERIMENT

The material for this study was prepared from *n*-type float-zoned or crucible-grown silicon, typically containing $3 \times 10^{16} \text{ cm}^{-3}$ phosphorus. The samples of $3 \times 3 \times 8 \text{ mm}^3$ dimensions were covered with a layer of metallic platinum sufficiently thick to supply the saturation concentration of the dopant at the diffusion temperature of 1200–1300°C. During the diffusion process the samples were kept at the diffusion temperature in a quartz ampule with its cold end outside the furnace; some drops of aqueous solution of HCl were placed into the evacuated tube. The presence of HCl turned out not to be essential for the production of the defects which are the subject of this paper; simply wet ambience appeared to be sufficient.

The diffusion was typically performed for 72 h at 1200°C. After diffusion samples were either shortly heated to 1300°C and then rapidly quenched to room temperature or subjected to the procedure of retarded quenching. The latter required that the sample was

kept for about half a minute in a temperature range 800–900°C and subsequently quenched in water. After quenching, the surface layer of the sample was removed by etching. Alternatively, in a controlling experiment, layers of $\sim 65\ \mu\text{m}$ were removed mechanically without etching.

The EPR experiments were carried out at a temperature of about 7 K in an X-band superheterodyne spectrometer, equipped with a TE₀₁₁ cylindrical cavity and field modulation at 12.3 Hz, tuned to detect the dispersion part of a signal. The samples could be *in situ* illuminated via a quartz rod.

III. RESULTS

In fast-quenched samples a spectrum of the Pt-H₂ defect with appreciably high intensity has been observed. Another spectrum was observed in retarded-quenched samples which were also annealed for 3 h at 540°C. It is labeled Si-NL53 for further reference. In spite of the difference in symmetry both spectra display many similarities. The most striking one is the presence of two pronounced hyperfine splittings, one about an order of magnitude larger than the other. Both spectra are extremely light sensitive and display a considerable bistability effect, depending also on the actual Fermi level position in the material. A similar reaction on light was observed for both defects but has been studied in detail only for the Pt-H₂ spectrum. For the “fresh” sample the spectrum can be observed after the sample is cooled to liquid-helium temperature in the dark. Band gap light illumination quenches the signal, which can be restored only by warming the sample up to room temperature. If the Fermi level is being shifted, due to a series of anneals, the effect reverses: the spectrum, not observable immediately after cooling in the dark, can be created with the band gap light illumination and then remains stable when the light is switched off. Again, only warming the sample up to room temperature and cooling it down in the dark restores the original state.

In what follows the individual features of both spectra are outlined in more detail.

A. Pt-H₂ center

The general form of the spectrum recorded with magnetic field parallel to a $\langle 100 \rangle$ crystal axis is given in Fig. 1. For every orientation the spectrum consists of three groups of lines with the integral intensity ratio corresponding to the natural isotope composition of platinum. Hyperfine structure within the group can be accounted for assuming interaction with two equivalent magnetic nuclei with nuclear spin $I = \frac{1}{2}$ and natural abundance 100%, thus being indicative for hydrogen. In Fig. 2 the hyperfine structure, as observed in the experiment, is shown together with the results of simulations for two and four hydrogen atoms. The EPR spectrum of the sample prepared in heavy-water (D₂O) vapor atmosphere is depicted in Fig. 3. The difference of the

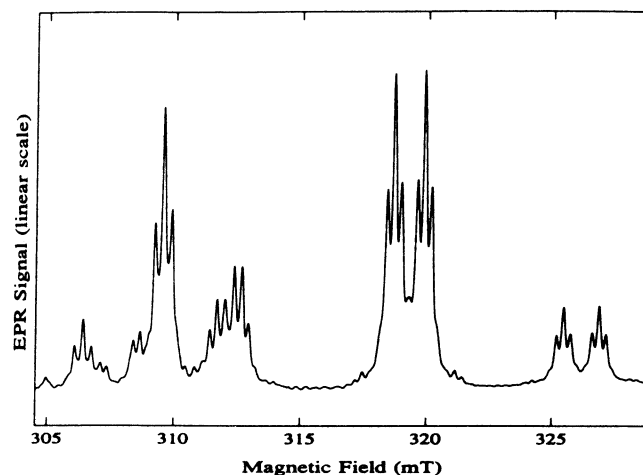


FIG. 1. Pt-H₂ spectrum as recorded with magnetic field $\vec{B}$ along a $\langle 100 \rangle$ direction. Temperature is 7.5 K, microwave frequency $\nu = 9.2208\ \text{GHz}$.

structure is caused by the difference of the nuclear spin and magnetic momentum between proton and deuteron.

Also the hyperfine splitting due to interaction with ²⁹Si nuclei in two shells was observed, as can be concluded from Fig. 1. This isotope has nuclear spin $I = \frac{1}{2}$ with natural abundance of 4.7%. The relative intensity of the outer doublet corresponds then to the presence of two sites in the shell. The inner structure is only partially resolved and is probably associated with a shell of two to

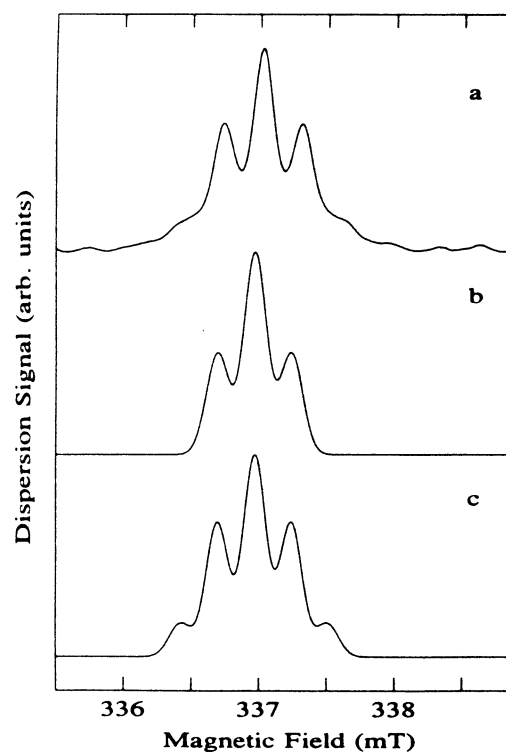


FIG. 2. Hyperfine structure of a Pt-H₂ spectrum line. (a) Experiment, $\vec{B} \parallel \langle 100 \rangle$, microwave frequency $\nu = 9.2208\ \text{GHz}$. Additional hyperfine splitting due to ligand interaction with silicon lattice is observable. (b) Simulation for the interaction with two and (c) with four equivalent hydrogen nuclei.

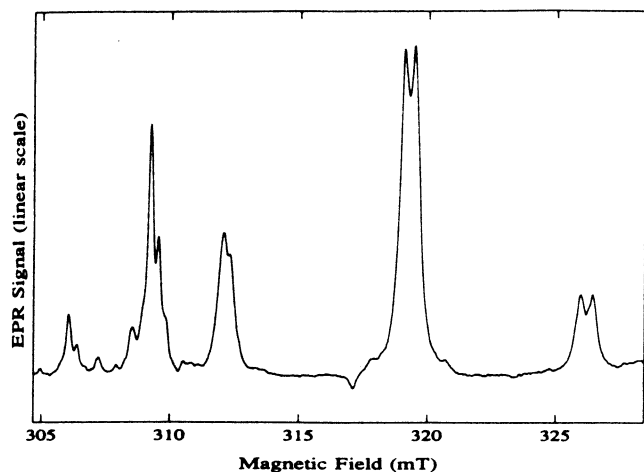


FIG. 3. Pt-H₂ spectrum obtained in sample after diffusion in D₂O-containing atmosphere. Magnetic field is parallel to $\langle 100 \rangle$ crystalline axis. The temperature is 7.5 K and the microwave frequency $\nu = 9.2184$ GHz.

four equivalent lattice sites.

In most of the passivation treatments of silicon reported so far, hydrogen penetrates only a surface layer of roughly 10 μm thickness. In order to check the hydrogen distribution in our case, we removed mechanically the surface layers of a sample from dimensions $3.02 \times 2.85 \times 11.34$ mm³ to $2.86 \times 2.78 \times 11.20$ mm³ without subsequent etching in order to avoid possible introduction of hydrogen at this stage.¹¹ Following that treatment the EPR spectrum was again recorded and no reduction of its intensity has been concluded. This result serves as an essential proof that in the present case hydrogen has been introduced into the bulk of the sample.

A series of anneals at temperatures from 250°C up to 500°C has been performed in order to examine the stability of the defect. It has been found that the signal does not change significantly after anneals at temperatures below 450°C. On the other hand, 3 h of annealing at 500°C destroyed the spectrum completely.

The angular dependence of the spectrum of the Pt-H₂ defect can be fitted with the electron spin $S = \frac{1}{2}$ and the following spin Hamiltonian:

$$\mathcal{H}_{\text{Pt-H}_2} = \mu_B \vec{B} \cdot \vec{g} \cdot \vec{S} + \vec{S} \cdot \vec{A}^{\text{Pt}} \cdot \vec{I}^{\text{Pt}} + \sum_{k=1}^2 \vec{S} \cdot \vec{A}_k^{\text{H}} \cdot \vec{I}_k^{\text{H}}, \quad (1)$$

which contains the Zeeman interaction term and the terms describing the hyperfine interactions with one ¹⁹⁵Pt nucleus $\vec{A}^{\text{Pt}}$ and two hydrogen atoms $\vec{A}_k^{\text{H}}$.

The angular dependence of this spectrum is given in Fig. 4. The points correspond to the experimental data and the solid lines represent the simulation with the spin Hamiltonian of the above given form and parameters as summarized in Table I. For an easy comparison the parameters of the Pt⁻ center are also included in the table. The symmetry of the $\vec{g}$ tensor as well as of the hyperfine tensor $\vec{A}^{\text{Pt}}$ is orthorhombic. Hyperfine interaction with hydrogen is almost isotropic; the experimentally observed

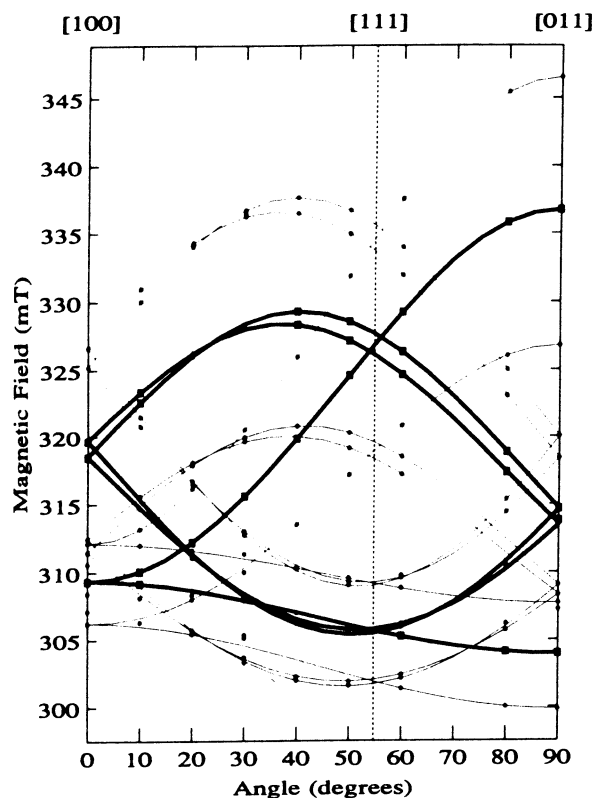


FIG. 4. Angular dependence of the resonance magnetic field for the Pt-H₂ spectrum. Thin and bold lines correspond to the centers with and without the ¹⁹⁵Pt isotope, respectively. Extra splitting is due to misorientation. $T = 7.5$ K and $\nu = 9.2208$ GHz.

anisotropy was not sufficiently pronounced to determine principal axes of the hyperfine tensor. Although the angular dependence of the hyperfine interaction with the pair of silicon neighbors could not be followed, its values were estimated from the scans taken in the main crystallographic directions. Assuming trigonal symmetry of this interaction, we have calculated its principal values to be $A_{\parallel}^{\text{Si}} \approx 124$ MHz and $A_{\perp}^{\text{Si}} \approx 88$ MHz.

On the basis of comparison of our spectroscopic data with those reported in Ref. 10 we conclude that the defect, observed after diffusion of hydrogen gas into a platinum-containing sample and that arising from diffusion of platinum in wet atmosphere are identical. The apparent discrepancy in the value of one of the parameters of platinum hyperfine interaction we attribute to an accidental mistake or a misprint.

One should note that the spin-Hamiltonian parameters of the deuterium-containing defect deviate significantly from those of the hydrogen-containing complex. An isotope shift of the g values is rare but has in the past been concluded for the Pt⁻ spectrum and attributed to the presence of ²⁸Si, ²⁹Si, and ³⁰Si nuclei.¹² A similar effect is reported here for the Pt-H₂ complex for which the influence of the nuclear mass of hydrogen is also observable.

B. Si-NL53

This spectrum has a still more complicated structure than the above-presented Pt-H₂ center. For every ori-

TABLE I. The principal values of the spin-Hamiltonian parameters as reported in Ref. 10 and as fitted for the Pt-H₂ and Pt-D₂ defects. Respective values for the Pt⁻ defect are given for comparison. Eigenvectors of the tensor of the hyperfine interaction with hydrogen were not determined; its values were estimated from the spectra taken with magnetic field along the main crystallographic directions.

Center	Tensor	[100]	[011]	[0 $\bar{1}$ 1]	Unit	Reference
Pt-H ₂	g	2.1298	2.1683	1.9558		10
	A ^{Pt}	171.9	128.9	538.5	MHz	10
	A ^H	9.3	9.3	9.3	MHz	10
Pt-H ₂	g	2.1299	2.1683	1.9563		this work
	A ^{Pt}	175.7	237.3	541.2	MHz	this work
	A ^H	~9.8	~8.2	~7.9	MHz	this work
Pt-D ₂	g	2.1319	2.1688	1.9554		this work
	A ^{Pt}	182.5	239.9	545.8	MHz	this work
Pt ⁻	g	2.0789	1.3865	1.4265		12
	A ^{Pt}	379.3	439.5	550.8	MHz	12

entation it consists of five groups of lines (see Fig. 5), whose integrated intensity ratio, close to 1:4:6:4:1, will be addressed later. In view of the striking similarity with the Pt-H₂ spectrum we assume that also in this case the splitting is due to the hyperfine interaction with platinum while further splitting within a line group is caused by the hyperfine interaction with hydrogen atoms. To describe the structure of the group the involvement of four or six protons ($I = \frac{1}{2}$, abundance 100%) has to be considered. Figure 6 presents the comparison of the simulated line shape, calculated for theoretical intensity ratio (1:4:6:4:1) or (1:6:15:20:15:6:1) of the hyperfine components as expected for four and six protons, respectively, with the experimentally recorded ones. The spin Hamiltonian of this defect can be written in the form

$$\mathcal{H}_{\text{NL53}} = \mu_B \vec{B} \cdot \mathbf{g} \cdot \vec{S} + \sum_{j=1}^N \vec{S} \cdot \mathbf{A}_j^{\text{Pt}} \cdot \vec{I}_j^{\text{Pt}} + \sum_{k=1}^M \vec{S} \cdot \mathbf{A}_k^{\text{H}} \cdot \vec{I}_k^{\text{H}}, \quad (2)$$

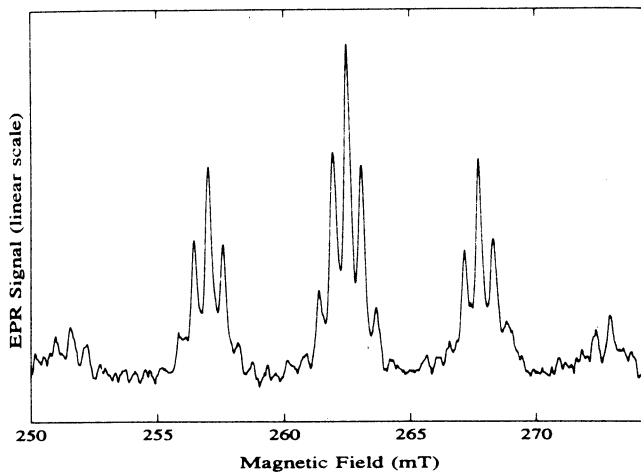


FIG. 5. A part of the Si-NL53 spectrum, recorded with magnetic field parallel to a $\langle 111 \rangle$ crystalline axis. $T = 7.5$ K and $\nu = 9.2164$ GHz.

with $S = \frac{1}{2}$, $I^{\text{Pt}} = \frac{1}{2}$, and $I^{\text{H}} = \frac{1}{2}$, where N is the number of magnetic platinum nuclei incorporated in the defect and index j enumerates these nuclei. Index k enumerates M protons ($M=4$ or 6).

The angular dependence of this spectrum is given in Fig. 7. The angular dependence of the central line can be fitted with a **g** tensor of trigonal symmetry with a $g_{\parallel} = 2.5082$ and $g_{\perp} = 2.0206$. The tensor **A**_{*j*}^{Pt} is not diagonal in this trigonal principal axes system; its principal values are $A_x^{\text{Pt}} = 432.7$ MHz, $A_y^{\text{Pt}} = 327.3$ MHz, and $A_z^{\text{Pt}} =$

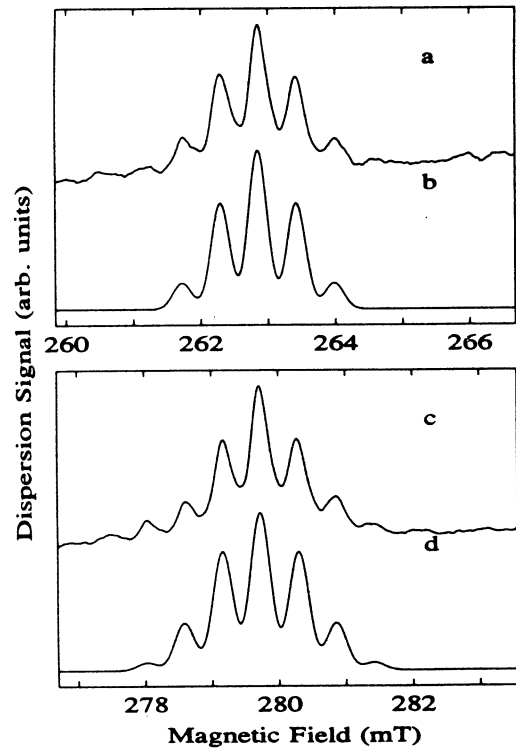


FIG. 6. Hyperfine structure of the Si-NL53 spectrum resonance line, recorded for a magnetic field parallel to (a) $\langle 111 \rangle$ and (c) $\langle 110 \rangle$ crystalline axis and (b) simulated for interaction with four and (d) with six equivalent nuclei with nuclear spin $I = \frac{1}{2}$ and natural abundance 100%.

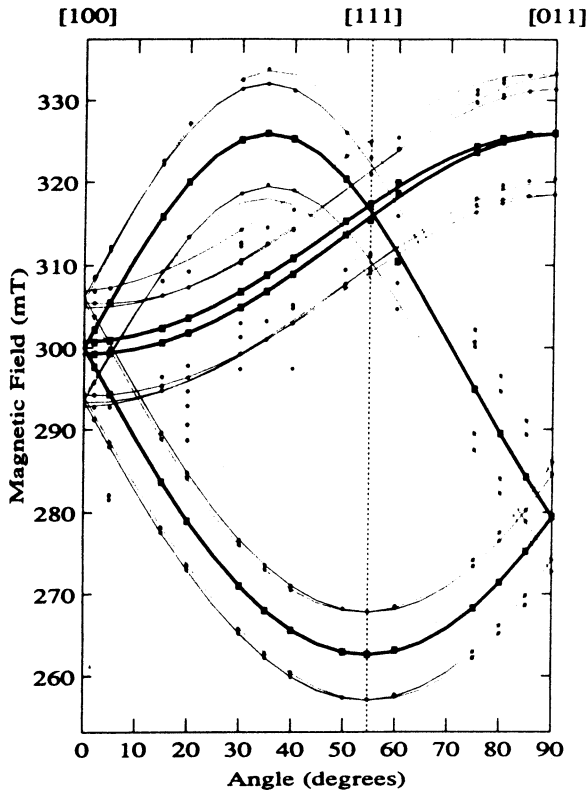


FIG. 7. Angular dependence of the Si-NL53 spectrum. Thin and bold lines correspond to the centers with one and without the ^{195}Pt nucleus, respectively. Extra splitting is due to misorientation. $T = 7.5$ K and $\nu = 9.2164$ GHz.

349.4 MHz. The eigenvector $\vec{n}_y$ is parallel to the $[1\bar{1}0]$ direction and $\vec{n}_z$ lies in the $(1\bar{1}0)$ plane and makes an angle $\theta = 12.4^\circ$ with the $[11\bar{1}]$ direction.

The hyperfine interaction with hydrogen is angular dependent. However, it was not possible to determine principal axes of the hyperfine tensor.

IV. DISCUSSION

Information about the electronic distribution in the defect can be derived from the hyperfine structure of the EPR spectrum. In the conventional one-electron linear combination of atomic orbitals (LCAO) approximation the wave function is written as the superposition of the

atomic wave functions. In this approach the LCAO wave function reads

$$\psi = \eta(\alpha\psi_s + \beta\psi_p + \gamma\psi_d). \quad (3)$$

In the case of a platinum nucleus s and d orbitals are selected; on the site of a silicon nucleus s and p orbitals are appropriate. The s -orbital part of the wave function corresponds to the isotropic part of the hyperfine tensor and the p - or d -orbital parts to the anisotropic part of it. Therefore, the hyperfine tensor $\mathbf{A}$ is usually decomposed as

$$\mathbf{A} = a\mathbf{1} + \mathbf{B}, \quad (4)$$

so that $a = \text{Sp}(\mathbf{A})$ and $\text{Sp}(\mathbf{B}) = 0$. The isotropic part is due to Fermi contact interaction and is given by

$$a = \frac{2}{3} \mu_0 g \mu_B g_N \mu_N \eta^2 \alpha^2 |\Psi_s(0)|^2. \quad (5)$$

If $\mathbf{B}$ is axial and its principal values are $(2b, -b, -b)$, then parameter b is given by

$$b = \pm \frac{2}{5} \frac{1}{4\pi} \mu_0 g \mu_B g_N \mu_N \eta^2 \beta^2 \langle r^{-3} \rangle_p \quad \text{for } p \text{ orbitals}, \quad (6)$$

$$b = \pm \frac{2}{7} \frac{1}{4\pi} \mu_0 g \mu_B g_N \mu_N \eta^2 \gamma^2 \langle r^{-3} \rangle_d \quad \text{for } d \text{ orbitals}.$$

Atomic wave function parameters $|\Psi_s(0)|^2$, $\langle r^{-3} \rangle_p$, and $\langle r^{-3} \rangle_d$ for most atoms are tabulated by Morton and Preston.¹³ Deviation from axuality of the tensor $\mathbf{B}$ is expressed by an extra parameter c such that the principal values of $\mathbf{B}$ are $(2b, -b+c, -b-c)$. For large values of c in comparison with b the LCAO approach is not applicable.

A. Platinum hyperfine interaction

Since for both defects the hyperfine tensors are not exactly axial, the applicability of LCAO analysis is restricted. However, in both cases the hyperfine tensor has a distinguished axis. The results of LCAO decomposition for Pt-H_2 , Si-NL53, and Pt^- centers are given in Table II. One can see that localization of the paramagnetic electron on the platinum nucleus is substantially higher for the Pt-H_2 complex than for the isolated platinum accep-

TABLE II. The results of LCAO analysis of the hyperfine interaction with ^{195}Pt and ^1H nuclei for the Pt-H_2 and Si-NL53 defects. Respective values for the Pt^- defect are calculated on the basis of the data reported in Ref. 12.

Center	Nucleus	a (MHz)	b (MHz)	c (MHz)	α^2 (%)	β^2 (%)	γ^2 (%)	η^2 (%)	Reference
Pt^-	^{195}Pt	456.5	47.1	30.1	11		89	15	12
	^{29}Si	88.9	10.4	1.6	18	82		11	12
Pt-H_2	^{195}Pt	318.1	111.6	30.1	3		97	26	this work
	^1H	~ 8.6	< 1		~ 95	< 5		0.6	this work
	^{29}Si	~ 100	~ 12		17	83		13	this work
Si-NL53	^{195}Pt	369.8	31.5	11.0	13		87	8	this work

tor. This, together with the notion that $\mathbf{g}$ -tensor principal values are different from those of the Pt^- center, evidences the essential role of hydrogen in the structure of the Pt-H_2 defect.

In the LCAO description for extended defects a single paramagnetic electron is shared over a few atomic sites. In order to arrive at this situation for the Si-NL53 defect 5d shells of all platinum atoms have to be filled first and then one extra electron has to be shared. The η value for Si-NL53, given in Table II, is to be understood as the localization of the paramagnetic electron on one platinum nucleus. To obtain the total localization on platinum one has to multiply this value by the number of platinum nuclei incorporated in this complex. This number will be discussed in the following section. The LCAO description has not been developed for the platinum pairs, reported in Refs. 3 and 2, due to the fact that in both cases the hyperfine tensors are far from axial and such a description does not seem to be applicable. We note nevertheless that for both the defects the hyperfine splitting and, consequently, the electron localization is lower than that determined here for Si-NL53.

B. Hydrogen hyperfine interaction

Recently the effects of coupling of nuclear magnetic moments of two protons, forming a hydrogen molecule in silicon, were reported.¹⁴ This coupling leads to different intensity ratios of the hyperfine components of the spectrum in view of the formation of ortho- and para-hydrogen molecules with net nuclear spin $I = 0$ and $I = 1$, respectively, and pronounced abundance of the para form at liquid-helium temperature. In all our experiments, both with Pt-H_2 and with Si-NL53, the intensity ratio of the hyperfine components was stable and consistent with that predicted by elementary combinatorics. Therefore, we conclude that in both defects, reported in this paper, hydrogen atoms do not form molecules but interact with the neighboring atoms independently from each other. Further, since the hyperfine interaction with all hydrogen atoms was found to be equal, we conclude that their positions within the defects are equivalent.

The fact that the hyperfine interaction with hydrogen for the Pt-H_2 defect appears to be almost isotropic suggests that Fermi contact interaction in this case is predominant. The parameter $|\Psi(0)|^2$ for a hydrogen 1s orbital can be calculated directly and we obtain a localization of paramagnetic electron $\eta^2 = 0.6\%$ on each of the two protons. The hydrogen hyperfine interaction for the Si-NL53 defect is of the same order of magnitude.

C. Ligand hyperfine interaction

Our estimate of electron localization on a pair of the nearest silicon atoms for the Pt-H_2 defect, though approximate, shows remarkable agreement with that found for the Pt^- center (see Table II). As follows from the theoretical treatment developed for Pt^- (Ref. 15) the elec-

tron localization on the second pair of silicon neighbors is about six times lower than on the nearest neighbor shell. Partially resolved hyperfine substructure, experimentally observed for the Pt-H_2 complex (see Fig. 2), is consistent with such a prediction. The value $\eta^2\alpha^2$ for this second pair has been estimated as 0.3%.¹⁵

V. DEFECT MODELS

The results of our measurements and LCAO analysis fully support the model of Pt-H_2 as proposed in Ref. 10. Hyperfine interaction with two silicon neighbors is consistent with overall orthorhombic symmetry of the defect and supports the assumed substitutional position of the platinum ion. Electron localization on hydrogen atoms is comparable to the one found on the second pair of silicon atoms for the Pt^- defect, which is also consistent with the model proposed in Ref. 10. The combination of tetragonal and orthorhombic static distortions, which for Pt^- was a result of orbital degeneration, could now be explained by presence of hydrogen atoms in one of the reconstructed bonds. This statement could possibly be verified by the defect reorientation under stress. From such a study of the Pt^- defect¹² the authors concluded that this center aligned itself preferentially in those of the six possible orientations which are energetically favored by the applied stress. This reorientation manifests itself in a change of the relative intensities of the resonance lines associated with differently oriented defects and occurs extremely fast even at low temperatures. In the present model of the Pt-H_2 center the distortion takes place during defect formation and its reorientation would imply also hopping of hydrogen atom from one silicon atom to another. Since the temperature required for such hopping can be sufficiently high [for B-H complex it was found to be ~ 60 K (Ref. 16)], the alignment effects are not likely to be observed, especially at low temperatures. Future experiments should clarify this issue.

On the basis of trigonal symmetry of the Si-NL53 spectrum one could expect its formation from a pair of Pt-H_2 defects. However, upon closer inspection of its hyperfine structure, such a possibility has to be rejected. Indeed, for a pair of atoms with isotopic composition of platinum one would expect relative intensities of the hyperfine components to obey the ratio 1:8:17:8:1 instead of the observed 1:4:6:4:1. Moreover, for such a defect, the same symmetry of platinum hyperfine tensor and $\mathbf{g}$ tensor would be expected, either trigonal or monoclinic, thus contradicting the experiment.

To match the observed intensity ratio one may try to consider four equivalent hydrogen atoms as being responsible for the large hyperfine splitting. In this case the intensity ratio would be perfectly matched (1:4:6:4:1); however, the symmetry of such a complex could not be trigonal.

One seems to be bound to conclude that the observed hyperfine structure is caused by three equivalent platinum atoms. This would yield the intensity ratio of 0.08:1:4:7:4:1:0.08, in acceptable agreement with the experiment. The resonances arising from the complexes

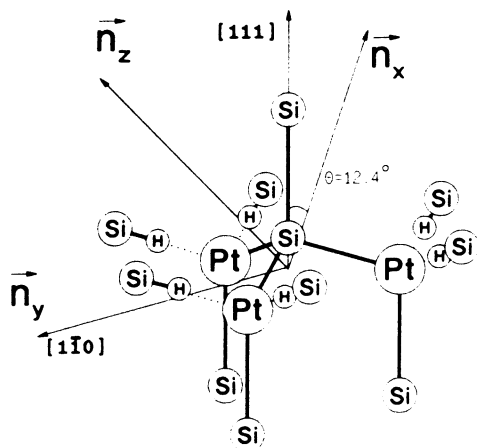


FIG. 8. A possible model of the Si-NL53 complex. $\vec{n}_x$, $\vec{n}_y$, and $\vec{n}_z$ are eigenvectors of the platinum hyperfine tensor.

with three ^{195}Pt nuclei are hidden in noise. Within this model the difference in symmetry between $\mathbf{g}$ tensor and hyperfine tensor can easily be explained: if one of three platinum atoms has a nucleus with magnetic momentum, the hyperfine interaction with this nucleus does not have a threefold symmetry axis. Therefore the hyperfine tensor has the monoclinic symmetry while the symmetry of the $\mathbf{g}$ tensor remains trigonal. In the model hydrogen atoms are placed so as to passivate dangling bonds of neighboring silicon atoms. Platinum atoms are equivalent, i.e., either all substitutional or all interstitial. Although we do not have direct spectroscopic arguments for interstitial or substitutional position, it is tempting to treat the Si-NL53 complex as three Pt-H₂ centers. In this case all platinum atoms are substitutional, while hydrogen atoms saturate reconstructed bonds with six silicon neighbors. One of the possible arrangements is depicted in Fig. 8.

A. Formation of defects

Just as the authors of Ref. 10, we observe incorporation of hydrogen into the bulk silicon. The results of subsequent annealing treatments evidence that the Pt-H₂

complex is rather stable and immobile: our attempts to produce the Si-NL53 spectrum by further complexing of smaller Pt-H₂ centers by means of prolonged 250-500°C annealing were not successful. We conclude therefore that Pt-H₂ complex is being exclusively formed at a high temperature. The fact that Si-NL53 defect was observed after retarded quenching means that the complexes tend to cluster at lower than the diffusion temperature. The role of annealing at 540°C is at this moment not clear. In view of these observations one may argue that hydrogen atoms are incorporated into the crystal simultaneously with the platinum atom and diffuse together with it as a single object. Such notion is, however, in some conflict to Ref. 10 where the Pt-H₂ defect was observed after annealing of a platinum-containing sample in hydrogen atmosphere. We were also able to observe weak EPR signal of Pt-H₂ in the platinum diffused samples annealed subsequently in a wet atmosphere. In both cases hydrogen is introduced in silicon *after* platinum. Our results can only be understood if one assumes that a high concentration of hydrogen in the bulk silicon has been achieved due to exposure to water vapor at high temperature with the hydrogen diffusion being independent of platinum diffusion. Platinum atoms serve as traps for hydrogen; they bind it inside the silicon crystal forming stable immobile complexes. After quenching the remaining hydrogen, which is not involved in formation of such complexes, would diffuse out of the sample.

VI. CONCLUSIONS

Formation of complex defects in silicon resulting from platinum diffusion in a water-vapor atmosphere has been investigated by means of electron paramagnetic resonance technique. One of these complexes has been identified with a Pt-H₂ defect. Our measurements support its model, as recently proposed by Williams *et al.* Another center has been attributed to a cluster of three platinum atoms with six hydrogen atoms passivating dangling bonds of silicon neighbors. Both complexes were found to be stable and immobile at room temperature. It was concluded that hydrogen diffuses into the bulk material from water vapor at high temperature and can be trapped by platinum atoms.

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