

EPR STUDY OF PLATINUM - HYDROGEN COMPLEXES IN SILICON

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ABSTRACT

This contribution reports on the observation of the electron paramagnetic resonance (EPR) spectra of two new defects in silicon, resulting from doping with platinum in an atmosphere containing water vapour. The spectra of both defects, labelled 2H-1Pt and Si-NL53 respectively, have effective spin $S=1/2$. They display hyperfine interactions with platinum and hydrogen and a characteristic behaviour under bandgap illumination. The spectrum of the 2H-1Pt defect has orthorhombic symmetry. It was identified as a substitutional platinum atom with two protons, saturating one of the reconstructed bonds between two silicon neighbours. The spectrum of the Si-NL53 defect has trigonal symmetry. It is identified as three substitutional platinum atoms with hydrogen atoms passivating dangling bonds of the nearest silicon neighbours.

1 INTRODUCTION

Transition metal (TM) impurities continue to attract considerable attention in view of their ability to create deep electric levels in silicon. 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 centres [1]. Since unintentional contamination by hydrogen often occurs during chemical etching [2] or due to boiling in water, the process of hydrogen passivation is not always fully under control.

The objective of the present study was to examine further the details of the passivation process in a particular case of platinum dopant and the mechanisms of platinum-hydrogen complex formation at high temperature. We report on the EPR observation of two of such complexes with resolved hydrogen hyperfine structure.

2 EXPERIMENTAL

The material for this study was prepared from n-type float-zoned or crucible-grown silicon, typically containing $3 \cdot 10^{16} \text{cm}^{-3}$ phosphorus. The samples were covered with a layer of metallic platinum and placed into quartz ampoules together with some drops of natural or heavy water. The diffusion was typically performed for 72 hours at 1200°C. After diffusion samples were either shortly heated to 1300°C and then rapidly quenched to room temperature or were kept

for about one minute at 800 – 900°C and subsequently quenched in water (retarded quenching). After quenching the samples were etched or, alternatively, layers of $\approx 150 \mu\text{m}$ were removed mechanically without etching in order to avoid possible contamination by hydrogen [3].

The EPR experiments were carried out at a temperature of about 7 K in a X-band superheterodyne spectrometer, equipped with TE_{011} cylindrical cavity and field modulation at 12.3 Hz, tuned to detect the dispersion part of the signal. The samples could be illuminated via a quartz rod.

3 RESULTS

The EPR measurements revealed the presence of four different spectra. One of them was identified with the well-known Pt^- [4], the second one with a Pt-Pt pair [5]. The other two spectra, labelled 2H-1Pt and Si-NL53, respectively, are the subject of the present paper. In spite of the difference in symmetry both spectra display many similarities. The most striking one is the presence of two different pronounced hyperfine interactions, one about an order of magnitude larger than the other. Both spectra are extremely light sensitive and display a considerable bistability effect. For the fresh samples the spectra can be observed after the sample is cooled to liquid-helium temperature in the dark. Bandgap-light illumination quenches the signals and they can be restored only by warming the sample up to room temperature.

The general view of the spectrum, observed in a fast-quenched sample and labelled for further reference 2H-1Pt, is given in Figure 1. For every orientation the spectrum consists of 3 groups of lines with the integrated intensity ratio corresponding to the natural isotope composition of platinum. A clear difference of the hyperfine structure within the group for a sample produced in natural-water- and heavy-water-vapour atmosphere identifies hydrogen as being responsible for the observed structure. This structure for the hydrogen-containing sample can be accounted for assuming interaction with two equivalent protons. The nuclear spin of

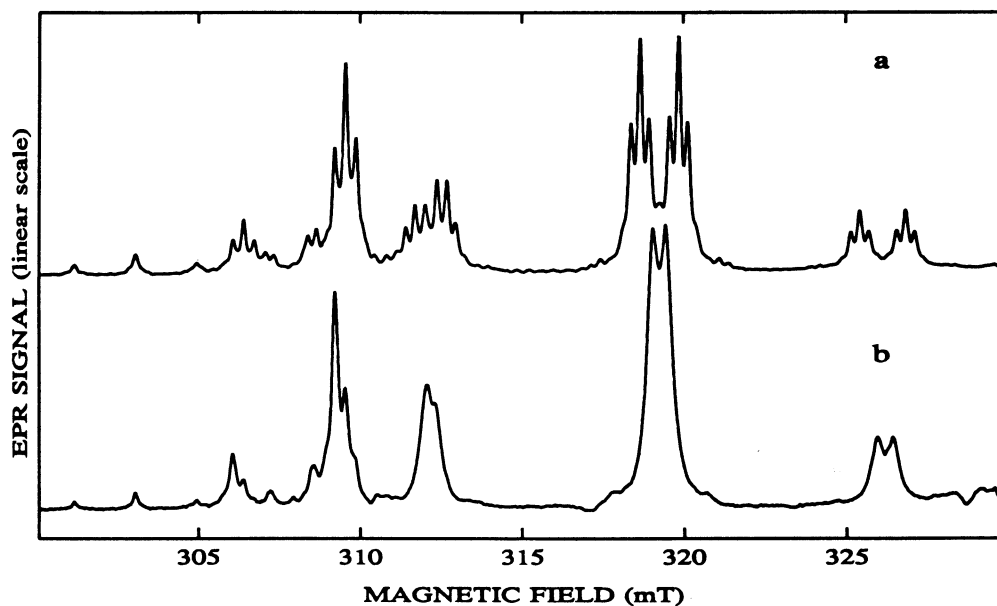


Figure 1: The general view of the 2H-1Pt spectrum, recorded in a $\langle 100 \rangle$ direction after diffusion in water vapour atmosphere (a) and in heavy-water vapour atmosphere (b). Temperature is 7.5 K, $\nu = 9.2208 \text{ GHz}$.

a proton is $I = 1/2$, with magnetic moment of $\mu_H = 2.793\mu_B$; the parameters for a deuteron are $I = 1$, $\mu_D = 0.857\mu_B$. If two deuterons are incorporated in the defect and the width of individual lines is the same, the hyperfine substructure becomes unresolved.

Also the hyperfine splitting due to interaction with ^{29}Si nuclei in two shells was observed, as can be concluded from Figure 1. 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 four equivalent lattice sites.

No reduction of the EPR signal intensity has been concluded after the surface layer of the sample has been removed, thus giving an essential proof that in our 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. It has been found that the signal does not change significantly after anneals at temperatures below 450°C. On the other hand, 3 hours of annealing at 500°C destroyed the spectrum completely.

Another spectrum, labelled Si-NL53, occurs in retarded quenched samples and has a still more complicated structure than the above-discussed 2H-1Pt centre. Its general view is presented in Figure 2. For every orientation it consists of five groups of lines, whose integrated intensity ratio, close to 1:4:7:4:1, suggests that this splitting arises from interactions with three equivalent platinum atoms. In view of the striking similarity with the 2H-1Pt spectrum we assume that the hyperfine splitting within a line group is caused by interaction with hydrogen atoms. To describe the structure of the group the involvement of six protons ($I = 1/2$, abundance 100%) has to be considered.

The angular dependence of the spectrum of the 2H-1Pt defect is given in Figure 3. It can be fitted with effective spin $S=1/2$ and the following spin Hamiltonian:

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

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

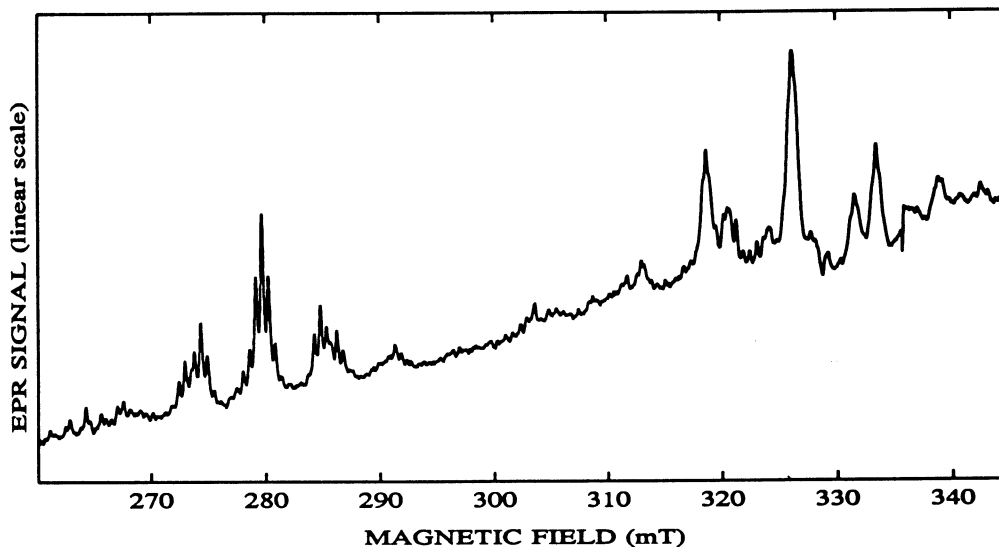


Figure 2: A general view of the Si-NL53 spectrum, recorded with magnetic field parallel to a $\langle 110 \rangle$ crystalline axis. $T=7.5$ K, $\nu=9.2164$ GHz.

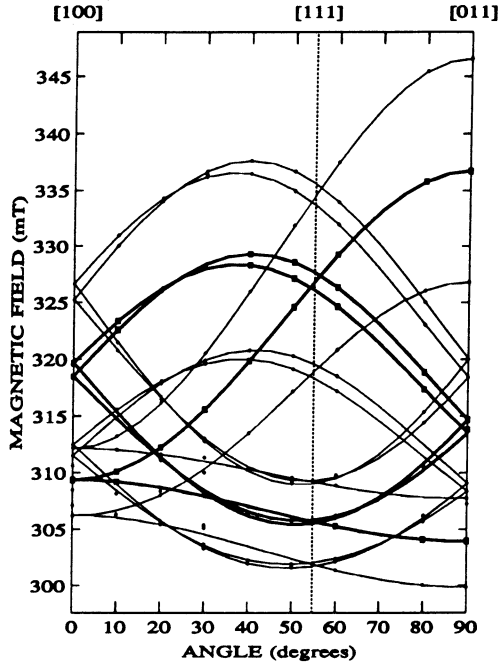


Figure 3: Angular dependence of the resonance magnetic field for the 2H-1Pt spectrum. Thin and bold lines correspond to the centres with and without ^{195}Pt isotope, respectively. Extra splitting is due to misorientation. $T=7.5\text{ K}$, $\nu=9.2208\text{ GHz}$.

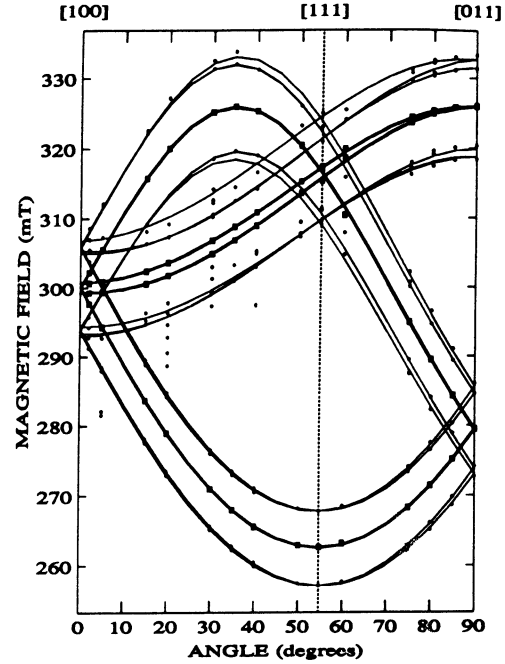


Figure 4: Angular dependence of the resonance magnetic field for the Si-NL53 spectrum. Thin and bold lines correspond to the centres with one and without ^{195}Pt nucleus, respectively. Extra splitting is due to misorientation. $T=7.5\text{ K}$, $\nu=9.2164\text{ GHz}$.

The principal values of the spin-Hamiltonian parameters, obtained from the computer fit, are: $g_x = 2.1682$, $g_y = 1.9558$, and $g_z = 2.1297$; $A_x^{Pt} = 237.3\text{ MHz}$, $A_y^{Pt} = 541.2\text{ MHz}$, and $A_z^{Pt} = 175.7\text{ MHz}$, where the principal axes of the defect are $\mathbf{n}_x \parallel [011]$, $\mathbf{n}_y \parallel [0\bar{1}1]$, and $\mathbf{n}_z \parallel [100]$. Hyperfine interaction with hydrogen is almost isotropic and was estimated to be $\approx 8.5\text{ MHz}$. The spin-Hamiltonian parameters for the deuterium-containing defect are slightly different: $g_x = 2.1688$, $g_y = 1.9554$, and $g_z = 2.1319$; $A_x^{Pt} = 239.9\text{ MHz}$, $A_y^{Pt} = 545.8\text{ MHz}$, and $A_z^{Pt} = 182.5\text{ MHz}$. An isotope shift of the g values due to the presence of ^{28}Si , ^{29}Si , and ^{30}Si nuclei has been observed for the Pt^- spectrum [6]. For the 2H-1Pt complex the influence of the nuclear mass of hydrogen appears to be even more pronounced.

The spin Hamiltonian of the Si-NL53 defect can be written in the form

$$\mathcal{H}_{NL53} = \mu_B \vec{B} \cdot \mathbf{g} \cdot \vec{S} + \sum_{j=1}^N \vec{S} \cdot \mathbf{A}_j^{Pt} \cdot \vec{I}_j^{Pt} + \sum_{k=1}^6 \vec{S} \cdot \mathbf{A}_k^H \cdot \vec{I}_k^H \quad (2)$$

with $S = 1/2$, $I^{Pt} = 1/2$, and $I^H = 1/2$, where N is a number of magnetic platinum nuclei incorporated in the defect and index j enumerates these nuclei. N can take the values 0, 1, 2, and 3. Index k enumerates 6 protons.

The angular dependence of this spectrum is given in Figure 4. The angular dependence of the central line can be fitted with a $\mathbf{g}$ tensor of trigonal symmetry with $g_{\parallel} = 2.5082$ and $g_{\perp} = 2.0206$. The tensor $\mathbf{A}^{Pt}$ is not diagonal in this trigonal principal axis system. Its principal values are $A_x^{Pt} = 432.7\text{ MHz}$, $A_y^{Pt} = 327.3\text{ MHz}$, $A_z^{Pt} = 349.4\text{ MHz}$; its eigenvector $\vec{n}_y$ is parallel

to the $[1\bar{1}0]$ direction and $\vec{n}_x$ lies in the $(1\bar{1}0)$ plane and makes an angle $\theta = 12.4^\circ$ with the $[111]$ direction.

4 DISCUSSION

Contrary to all the passivation treatments reported so far, we observe incorporation of hydrogen into the bulk silicon. The results of subsequent annealing treatments evidence that platinum-hydrogen complexes are rather stable and immobile: our attempts to produce the Si-NL53 spectrum by further complexing of smaller 2H-1Pt centres by means of prolonged $250^\circ \div 500^\circ\text{C}$ annealing were not successful. An explanation for these results can be found in the fact that a high concentration of hydrogen in the bulk silicon has been achieved due to exposure to water vapour at high temperature. After quenching all the hydrogen atoms, involved in formation of the stable complexes, are trapped inside the crystal and the rest of hydrogen diffuses out.

On the basis of the above considerations tentative microscopic models of the defects 2H-1Pt and Si-NL53 can be proposed. The structure of the 2H-1Pt defect can be understood as a substitutional platinum ion, occupying a negatively charged lattice vacancy and hydrogen atoms saturating a reconstructed bond between two other silicon neighbours. Hyperfine interaction with two silicon neighbours is consistent with overall orthorhombic symmetry of the defect and supports the assumption of a substitutional position of the platinum ion.

The model for Si-NL53 defect involves three substitutional platinum atoms, while hydrogen atoms saturate reconstructed bonds with six silicon neighbours. This model is in line with the other many-atoms platinum-related defects in silicon [7]. In spite of the overall trigonal symmetry of the complex, the symmetry of the hyperfine interaction with platinum is monoclinic. Indeed, when one of three platinum atoms has a nucleus with magnetic momentum, the three-fold symmetry axis of the defect will be lost, resulting in lowering of the symmetry of the EPR spectrum.

5 CONCLUSIONS

Two new defects in silicon generated by platinum diffusion in a water vapour atmosphere were detected by electron paramagnetic resonance. On the basis of platinum hyperfine structure and clear difference between the spectra detected in hydrogen- and deuterium-doped samples the defects were identified as hydrogen-platinum complexes. Parameters of their spin Hamiltonians were determined. The complexes were found to be rather stable and immobile. It was concluded that hydrogen has been introduced into the bulk material as a result of the above-described treatment.

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