

EPR IDENTIFICATION OF HYDROGEN MOLECULES IN BULK SILICON

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ABSTRACT

Silicon samples implanted with hydrogen have been studied by electron paramagnetic resonance (EPR). In heavily implanted (10^{17} cm^{-2}), 1 mm thick silicon, a new EPR spectrum could be detected after a short (20 minutes) low-temperature (250 °C) heat treatment. This spectrum could be identified as originating from a paramagnetic state of an interstitial hydrogen molecule. The defect was found to exhibit axial symmetry along the $\langle 111 \rangle$ crystallographic directions. Such a result is in line with recent theoretical calculations predicting hydrogen to freeze out in the form of interstitial molecules. In addition, evidence is obtained indicating that more elaborate hydrogen clusters exist.

INTRODUCTION

Recently hydrogen in silicon enjoys a growing amount of interest among theoretical and experimental physicists. This is motivated by the dramatic effect of hydrogen on the electronic properties of silicon. Hydrogen can very easily satisfy dangling bonds or attach itself to donors or acceptors and thus terminate their electrical activity by compensating the charge carrier, i.e., capturing or supplying an electron [1]. Especially shallow acceptors (B, Al, Ga, In and Tl) are easily neutralized [2].

Another amazing feature of hydrogen is its diffusion in the silicon lattice. It is a very fast diffuser, moving several orders of magnitude faster than any other impurity known (10^{-4} - $10^{-3} \text{ cm}^2 \text{ s}^{-1}$ at 1000 °C). For the diffusion several models are proposed [1], including one in which the (positively charged) proton hops between orthorhombic (C_{2v}) and bond-centered (BC) sites. In another model the negatively charged hydrogen atom travels from one cubic interstitial site to another, passing through hexagonal sites. Diffusion through diatomic, molecular hydrogen is not likely, since, although it is more stable than monatomic hydrogen, its activation energy (the threshold for diffusion) is too high; about 2.7 eV, as compared to the small energy barrier of 0.3 eV for atomic hydrogen. Even if we take into account the H-H dissociation energy of 1.6 eV, it is still energetically favorable to diffuse through a monatomic species [3].

When the silicon crystal is at sufficiently low temperature and hence the hydrogen atom is frozen in the lattice, this atom can occupy various positions with different symmetries, including bond-centered (BC) and antibonding (AB) sites. Both have trigonal symmetry, because in both cases the hydrogen atom is situated on a $\langle 111 \rangle$ crystal axis. Other possibilities are interstitial cubic (T_d), orthorhombic (C_{2v} , on a $\langle 100 \rangle$ axis), monoclinic (C_{1h} , on a mirror plane) and hexagonal symmetries. For negatively charged hydrogen the cubic interstitial position is predicted as the lowest energy state, H^0 can be either on this T_d site [1] or on the BC site [4],

whereas positively charged hydrogen is believed to relax to the BC site [1, 5]. Therefore, one expects BC hydrogen in p-type silicon and T_d hydrogen in n-type silicon.

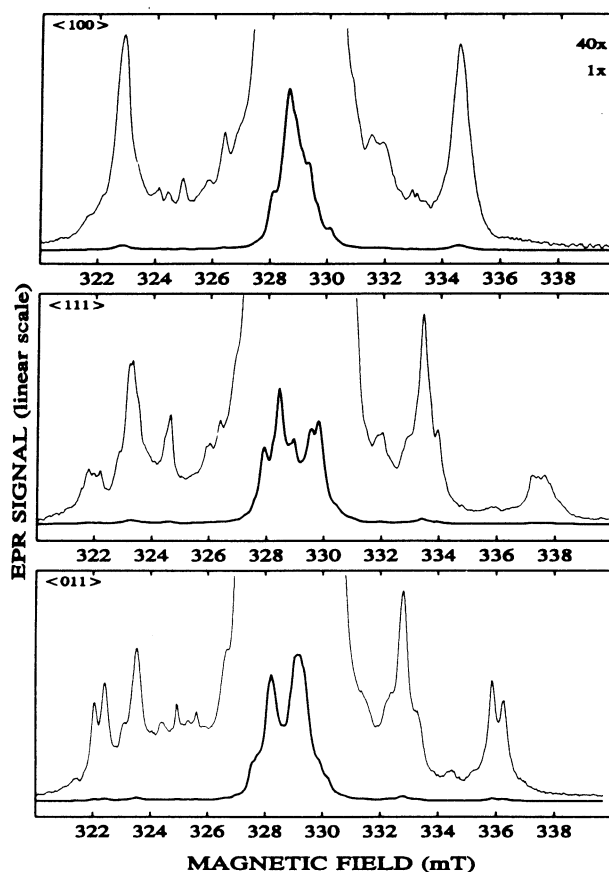


Figure 1: Spectra of Si-NL52, as measured at the X-band (9.225718 GHz) spectrometer, for a magnetic field along the crystallographic directions $\langle 100 \rangle$, $\langle 111 \rangle$ and $\langle 011 \rangle$, respectively. The microwave power (P_μ) was -20 dBm and the sample temperature $T = 7.7$ K. The observed (integrated) intensity ratio of the (single) side and central lines is, at these conditions, 1:53.

Normal muonium (muonium on a T_d site) and anomalous muonium (muonium on bond-centered position) are both observed in μ SR [6]. Because muonium is chemically equivalent to hydrogen and deuterium, only differing in the mass of the nucleus, also EPR spectra of "normal" hydrogen (deuterium) and "anomalous" hydrogen (deuterium) are expected. The only EPR observation of hydrogen so far has been the Si-AA9 spectrum by Gorelkinskii and Nevinnyi [7]. This trigonal spectrum, observed in a hydrogen-implanted high-purity silicon sample, showed a small hydrogen hyperfine interaction doublet splitting, which changed into a triplet when switching to deuterium implantation, thereby giving direct proof for the presence of (a single) hydrogen in the defect. The evidence for the BC position of the hydrogen comes from the small hydrogen hyperfine interaction, which in LCAO analysis (Linear Combination of Atomic Orbitals) means low charge density on the hydrogen nucleus and large ^{29}Si hyperfine interaction. This is expected for neutral hydrogen, where the paramagnetic electron resides in the antibonding state, since the bonding level is filled with the two silicon-silicon bond electrons. In this case there is no charge density on the hydrogen nucleus and therefore no Fermi-contact interaction, resulting in the absence of hyperfine structure.

For higher concentrations, hydrogen is expected to freeze out in diatomic complexes. There

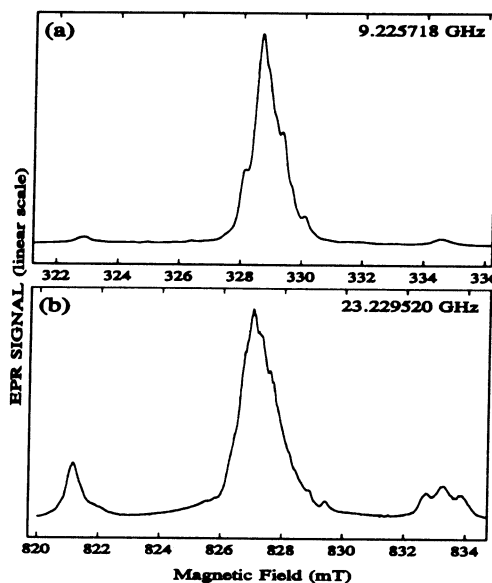


Figure 2: Spectra of Si-NL52, as measured at the X-band (a) and K-band (b) spectrometers, for the magnetic field along the crystallographic direction $\langle 100 \rangle$. This identifies the nature of the splitting as HF interaction and shows that the intensity ratio can change.

are many possibilities for these complexes, but the most likely ones are:

Molecular Hydrogen. This is a normal hydrogen pair, placed interstitially at a T_d site and without much interaction with the silicon lattice. The resulting symmetry is, in principle, trigonal (C_{3v}).

BC². Two hydrogen atoms on BC positions of near Si-Si bonds as described above. This configuration is not very probable, since a hydrogen atom in a Si-Si bond stretches this bond by approximately 30% to 3.2 Å therefore causing strain in the vicinity of the defect, repelling other such structures. The symmetry of this configuration would be monoclinic (C_{1h}). Of the here mentioned structures, this is the only one which is paramagnetic in the neutral charge state.

Satisfied Broken Bond. When a broken bond is satisfied with two hydrogen atoms the resulting symmetry is trigonal, but very likely to relax to lower symmetry (up to triclinic C_1) in order to release some of the stress.

Metastable Hydrogen, H₂[•]. This is a pair which consists of a hydrogen atom on both sides of a silicon atom, one on the bond-centered position and one on the antibonding site. This is the only configuration in which the hydrogen atoms are non equivalent. Because both atoms are on the $\langle 111 \rangle$ axis, the symmetry of this complex is trigonal.

Of the above-described complexes, the molecular hydrogen has the lowest calculated energy, even lower than two isolated hydrogen atoms of any type. Therefore these molecules are presumed to be present in undoped material. Neither of these complexes has ever been observed in EPR. In doped silicon the hydrogen atom would be trapped at the donors or acceptors, forming defects of still lower energy.

EXPERIMENTAL

To produce the Si-NL52 spectrum we used as starting material undoped, high-resistivity (6kΩcm) silicon of approximately 1 mm thickness. This material was then exposed to a proton beam from a cyclotron source. The energy of the hydrogen particles, originally circa 30 MeV,

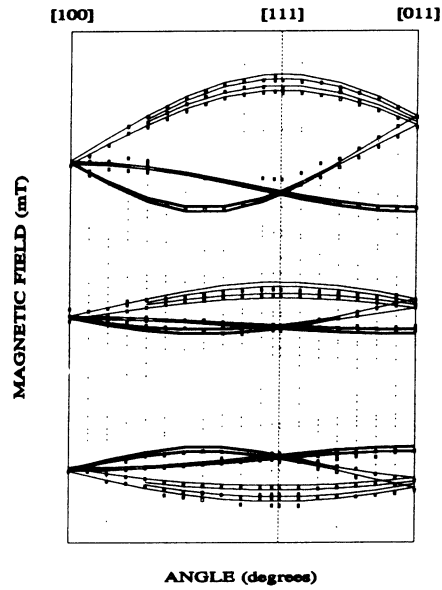


Figure 3: Angular dependence of Si-NL52 for X band. The experimental points of Si-NL52 (\square) as well as unidentified resonances of lower intensity (\cdot) are marked. The solid lines indicate a simulation with the Hamiltonian as described in the text for a microwave frequency of 9.225738 GHz and an intensity threshold of 0.1 (maximum intensity is circa 1).

was moderated and dispersed by placing an aluminum absorber in between the cyclotron source and the target. The ion current of roughly $0.05 \mu\text{Acm}^{-2}$ yielded a dose of circa 10^{17} protons per cm^2 . After this hydrogen implantation the samples received short annealing stages at relatively low temperatures (typically 250°C) in ambient air for approximately 20 minutes, without any form of quenching afterwards. To remove surface defects, the samples were etched in a solution of HF and HNO_3 in a ratio of 1:3. The samples were then placed in our superheterodyne K band and X-band spectrometers operating at 23.3 GHz and 9.2 GHz, respectively. Both had low-frequency field modulation and were tuned for dispersion. The sample was kept at temperatures close to ambient pressure liquid-helium temperature in the center of TE_{011} cylindrical, high Q-factor cavities. Here it was exposed to low-power microwave radiation in the μW range [8]. See table 1 for quantitative details of the used spectrometers.

Table 1: Quantitative specifications of the EPR spectrometers.

	X band	K band
Microwave-frequency	9.2 GHz	23.3 GHz
Field modulation	12.3 Hz	904 Hz
Tuning mode	dispersion	dispersion
Cavity	TE_{011}	TE_{011}
Q factor	43000	5000
Temperature	6 K	4.5 K
Microwave power	-40 - -10 dBm	-40 - +5 dBm
RF power (ENDOR)	—	+36 dBm
RF chopping	—	3.3 Hz

RESULTS

The sample preparations as described above resulted in the generation of the Si-NL52 spectrum, see figure 1, where the spectra are shown for the magnetic field along the principal crystallographic directions $\langle 100 \rangle$, $\langle 111 \rangle$ and $\langle 011 \rangle$, as acquired at the X-band spectrometer. Comparison of the $\langle 100 \rangle$ spectrum to the K band spectrum for the same field direction (see figure 2) shows that the splitting of the outside lines is caused by a field-independent interaction, i.e., a hyperfine term in the Hamiltonian describing the interaction of the electron spin with a (magnetic field of a) nuclear spin. The same analysis also reveals that the splitting of the central line is due to the anisotropy of such a field-dependent term: electronic Zeeman interaction $\mu_B \vec{B} \cdot \vec{g} \cdot \vec{S}$.

Another interesting feature which is revealed by the comparison of the X and K band spectra is the difference in (integrated single line) intensity ratio of the side and middle components. These ratios depend on the operating temperature, microwave frequency and power in an intricate way. Experimental values of 1:3 for high powers and low temperatures at our K band spectrometer to ratios as high as 1:200 have been observed.

The angular dependence of the Si-NL52 spectrum (see figure 3) displays that the symmetry of the originating center must be trigonal (point group C_3 , S_3 , C_{3v} , D_3 or D_{3d}).

In addition to the EPR spectra, a short ENDOR (electron nuclear double resonance) study was started on the defect. This revealed the presence of interacting hydrogen and silicon in the vicinity of the defect, although the interactions are rather small. All lines were in the neighborhood of the nuclear Zeeman frequencies (42.5759 MHz/T for ^1H and 8.458 MHz/T for ^{29}Si [9]). Figure 4 shows a hydrogen ENDOR scan for a magnetic field close to the $\langle 011 \rangle$ direction. Large interactions were not found, neither for hydrogen, nor for silicon.

DISCUSSION

To understand the experimental data the most obvious explanation would be to ascribe the side and central lines to totally different spectra, possibly not even related to the same defect. This would readily account for the fluctuation in intensity ratio. However this model can easily be put aside if one bears in mind that 1) the spectra have identical g-tensors and 2) they show exactly the same electron nuclear double resonance (ENDOR), which can only be explained if we assume that the parts of the spectrum belong to the same defect.

There are still several possibilities for the nuclear spin configuration. The spectrum can be attributed to a combination of two spectra: one without hyperfine interaction because of the absence of nuclear spins in the defect ($I=0$) and one with ligand hyperfine interaction with neighboring ^{29}Si atoms. Although there would be no problem with fitting of the parameters of such a model to the observed line positions, there is a problem with explaining the intensity ratio of the two spectra which is changing from 1:3 to a ratio as high as 1:200, as mentioned before. If one takes into account the fact that ^{29}Si has a natural abundance of 4.70% the expected intensity ratio is 2.46% (1:40.6) if there is one silicon atom in the interaction shell. The experimental data are contradicting this. Apart from this, a drifting intensity of a silicon ligand spectrum has never been observed before, which makes the assignment of the large HF splitting to silicon irrational. For figure 1 the experimental conditions accidentally produce an intensity ratio close to the value expected for ^{29}Si . Figure 2 shows that the intensity ratios can be quite different.

The involvement of a guest atom other than hydrogen in the defect is even more unlikely, since the starting material was undoped. Further, the same arguments can be used against this model as for the case of silicon. This leaves the possibility of hydrogen as the source for the large HF splitting. One hydrogen atom is not enough because this would give rise to a spectrum

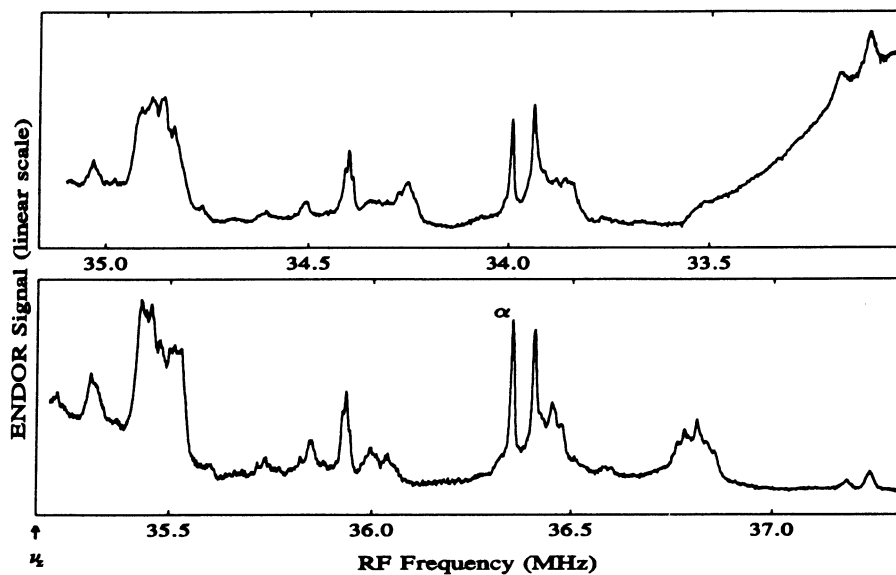


Figure 4: An ENDOR scan for the magnetic field ($B=826.00$ mT) 5° away from $\langle 011 \rangle$. The scan is split at the nuclear Zeeman frequency of hydrogen ($\nu_Z = 35.168$ MHz for this field) and folded back. The symmetric pattern which results indicates that the lines are caused by hydrogen (see also figure 5).

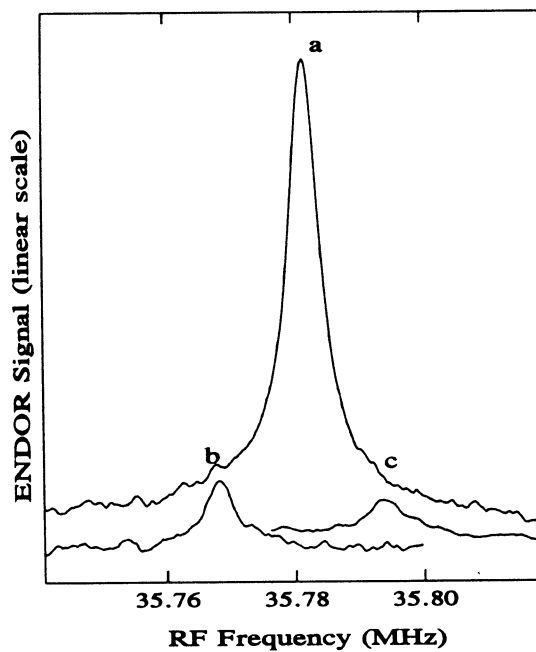


Figure 5: Position of the ENDOR line α of figure 4 for magnetic fields of 824.81 mT (a), 824.50 mT (b) and 825.10 mT (c). This closely follows the dependency expected for hydrogen (42.5759 MHz/T [9]).

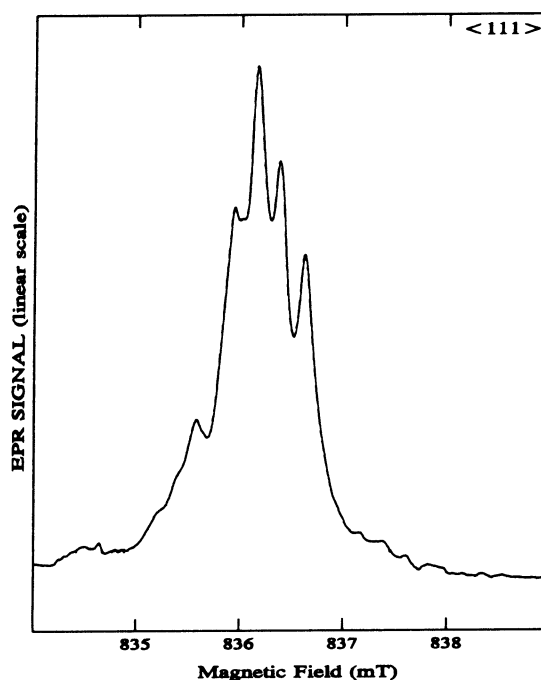


Figure 6: Detail of the Si-NL52 spectrum as acquired at the K band spectrometer. The scan shows the splitting of the HF structure at the $\langle 111 \rangle$ field direction.

of two patterns (hydrogen has a nearly 100% abundant isotope with $I=1/2$). Two atoms are needed to comply with the data. If one assumes a weak coupling between the two hydrogen atoms one would, in principle, expect 4 lines when the field is parallel to the $\langle 100 \rangle$ axis. But when the two atoms are exactly equivalent the middle two lines would coincide. The second-order effect ($\sim A^2$) splitting (0.04 mT) of the central two lines is smaller than the linewidth. The intensity ratio of a side line ($m_{I_1} = m_{I_2}$) as compared to the middle lines ($m_{I_1} = -m_{I_2}$) would be 1:2 and stable. On the other hand, if we assume a strong coupling between the two atoms, as is normal for isolated hydrogen molecules [10], there will be two possible nuclear spin states, namely para-hydrogen with the nuclear spins anti-parallel ($I=0$) and ortho-hydrogen with the spins parallel ($I=1$). The observed spectrum can then be explained by assuming it is a superposition of the triplet and the singlet spectra. Because the para state has lower energy than the ortho state, with a difference of approximately 180 K (for hydrogen in vacuum [10]), it will be (nearly) the only one occupied at low temperatures. The fluctuation of the intensity ratios can now be explained by a conversion from ortho- to para-hydrogen, and vice versa.

Closer inspection of the spectrum reveals an extra splitting of the spectrum, see for instance the detail of the spectrum taken at a magnetic field along the $\langle 111 \rangle$ direction (figure 6). This may be caused by hyperfine interactions with two non-equivalent independent (non molecular) hydrogen atoms. The existence of such elaborate centers falls nicely into the model of hydrogen clustering as predicted by Zhang and Jackson[11], among others. The interaction seems to be $\langle 111 \rangle$ -axial which indicates that the hydrogen atoms are on the extension of the H_2 molecule bond axis.

We can now ascribe the spectrum to a Hamiltonian:

$$\mathcal{H} = \mu_B \vec{B} \cdot \vec{g} \cdot \vec{S} + \vec{S} \cdot \vec{A}_{H_2} \cdot \vec{I}_{H_2} + \vec{S} \cdot \vec{A}_H^1 \cdot \vec{I}_H^1 + \vec{S} \cdot \vec{A}_H^2 \cdot \vec{I}_H^2, \quad (1)$$

with $S=1/2$ and $I_{H_2}=1$ for the triplet spectrum and $I_{H_2}=0$ for the singlet spectrum. In both

Table 2: *Spin-Hamiltonian parameters for Si-NL52. <111>-axial symmetry.*

term	//	⊥	unit
g	2.00069	2.00951	
A_{H_2}	217.8	128.2	MHz
A_H^1	4.8	1.5	MHz
A_H^2	12.1	-5.0	MHz

cases $I_H^1 = I_H^2 = 1/2$. The values of the parameters, obtained by fitting to the experimental data, are given in table 2.

Finally, we want to draw attention to the similarities of Si-NL52 and P_b [12, 13], first observed by Nishi [14]. Comparing the spin-Hamiltonian specifications of Si-NL52 and P_b one notices that they share identical hyperfine parameters - when one corrects for the different nuclear spin value - and (nearly) identical g factors. The P_b spectrum was attributed to a dangling bond, stabilized by oxygen at the Si/SiO₂ interface [15]. This assignment was mainly based on the observation of the alleged ²⁹Si hyperfine lines. Since the starting material used in our study was clean, oxygen-free float-zoned (FZ) silicon the spectrum cannot originate from oxygen-related defects such as described above. Although, at this moment, the possibility that the two spectra originate from different defects cannot be excluded, serious doubts about the interpretation of the P_b center appear justified and a model as depicted in this paper may be considered. The observation of the spectrum at Si/SiO₂ interfaces could be caused by the presence of hydrogen molecules trapped at the interface. How such a model can coexist with the data of passivation of P_b by hydrogen is not clear at present. A full study of the P_b /NL51 controversy is currently underway and will be published in the near future.

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