TRAPPING OF MOLECULAR HYDROGEN IN POROUS SILICON AND AT Si/SiO$_2$ INTERFACES AND A POSSIBLE REINTERPRETATION OF THE P$_b$ CENTER

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ABSTRACT

Many recent studies of the highlighted problem of visible-range photoluminescence of porous silicon (po-Si) indicate the presence of hydrogen in this material. However, its actual role is not clear with the discussed possibilities ranging from passivation of the surface defects to some form of active participation in the photoluminescence (PL) mechanism itself. At the same time, in several magnetic resonance studies of po-Si the so-called P$_b$ center, originally identified with the <111>-directed silicon broken bond stabilized at Si/SiO$_2$ interfaces, has been reported.

Very recently the paramagnetic state of molecular hydrogen in bulk silicon has been identified. The spin-Hamiltonian parameters of the related Si-NL52 EPR spectrum appear to be identical to those of the P$_b$ center. This observation casts severe doubts on the original interpretation of the P$_b$ center while, on the other hand, offering new evidence of a prominent presence of hydrogen molecules both in po-Si and at the Si/SiO$_2$ interface. In this paper the similarities of Si-NL52 and P$_b$ centers are examined in detail, and it is argued that the centers are the same. It is concluded that many features of the P$_b$ center which could not be explained within the broken-bond model can be understood with the interstitial hydrogen molecule model.

INTRODUCTION

With the constantly decreasing dimensions of semiconductor devices, two-dimensional structures like surfaces and interfaces become increasingly important. The active centers in such structures will have relatively more influence on the quality of the device. Therefore, it is important to be able to establish a microscopic picture of these centers.
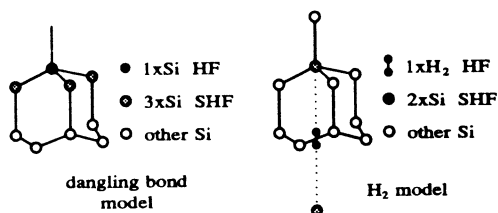

Figure 1 *Microscopic models used for P$_b$ (left) and Si-NL52 (right). The shells of HF and SHF interaction are indicated.*

One of the most familiar defects in Si/SiO$_2$ interfaces is the P$_b$ center, as named by Nishi [1], who first observed it. Later, its identification to a silicon dangling bond stabilized at <111> Si/SiO$_2$ interfaces was done by Poindexter [2]. The proposed structure is depicted

in Figure 1; a single (therefore paramagnetic) electron, localized mainly in a broken bond. The largest term in the spin Hamiltonian is then the Zeeman interaction $\mathcal{H} = \mu_B B \cdot \mathbf{g} \cdot S$, with μ_B the Bohr magneton, B the magnetic field, $\mathbf{g}$ the $\mathbf{g}$ tensor, and S the electron spin $(S=1/2)$. The wave function of the electron spin has also density outside this p-electron state of the dangling bond. Everywhere, where there is a nuclear spin the local density of the wavefunction is probed by the nucleus, because the hyperfine interaction is linearly proportional to the density at the atomic site. For the P_b model of Poindexter the largest interaction is expected with the (nearest) silicon atom to which the dangling bond is connected. In this way the observed hyperfine interaction $(A_\parallel = 438$ MHz, $A_\perp = 255)$ corresponds to 6.9% of an electron in an s-state around the silicon nucleus and 53.4% in p-state [3]. Relative to the defect, the silicon atom is at a trigonal (C_{3v}) site and this symmetry is reflected in the hyperfine interaction. A simulation of the angular dependence of the P_b spectrum is shown in Figure 2. This reveals that the center is indeed axially symmetric around <111>.
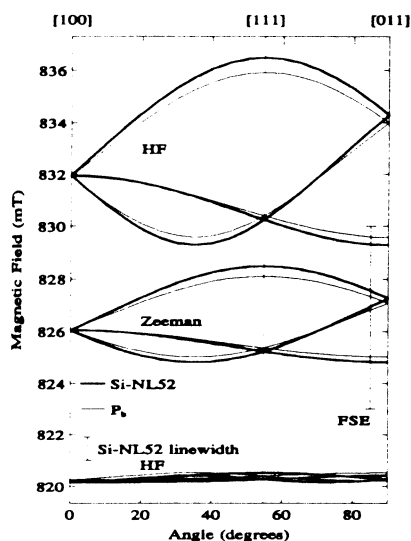

Figure 2 *Simulations of the Si-NL52 (thick trace) and P_b spectra (thin trace) for a microwave frequency of 23.2 GHz. The place of the FSE scan of Figure 6 is indicated with a dashed line.*

The relative intensity of the hyperfine lines, as compared to the Zeeman line, should confirm that a single silicon atom is involved in the interaction. This should be possible, because the abundances of the various isotopes of the involved atom are reflected in the fingerprint spectrum. In a crystal made of natural silicon 95.3% of the P_b centers will have a first-neighbor silicon atom without nuclear spin, resulting in a singlet spectrum, i.e., a Zeeman line. On the other hand, 4.7% of them will have a ^{29}Si atom $(I=1/2)$ in the first interaction shell, producing a doublet spectrum, henceforth called the hyperfine (HF) lines. Therefore the fingerprint spectrum allows for a direct identification of the surroundings of the defect. In the case of the P_b center, the model predicts a (single) HF line intensity of 2.47%, i.e., a ratio of 1:40.5. The reported ratios do sometimes come close to this value, e.g.

1:67 [4]. But also ratios as high as 1:300 [5] have been observed. This cannot be understood within the broken-bond model of the P_b center.

For P_b also the next (super)hyperfine (SHF) interaction shell was resolved. In this case the intensity of the SHF lines (5% to 7.5%) indicated the presence of two or three Si atoms in the interaction shell, consistent with the model as described above (see also Fig. 1). However, the reported trigonal spectral class of the SHF interaction [4] cannot be explained with the model; the three next-nearest neighbors in the model of Figure 1 are on monoclinic I (C_{1h}) positions.

THE Si-NL52 SPECTRUM

A recent EPR study of high-dose-hydrogen-implanted pure silicon [6] revealed a trigonal spectrum (Si-NL52) with a spin Hamiltonian, comprised of an electronic Zeeman term and an HF interaction, i.e., similar to the Hamiltonian used to describe P_b:

$$\mathcal{H} = \mu_B B \cdot \mathbf{g} \cdot S + S \cdot \mathbf{A} \cdot I \tag{1}$$

The relative intensities of the HF lines of Si-NL52 depend on temperature and microwave power in a strong way. Ratios as high as 1:100 to as low as 1:3 have been observed. A microwave-power dependence of the individual components of the spectrum is depicted in Figure 3. This reveals that the changing of relative intensities cannot be due to saturation of the spectrum, since this occurs only for powers higher than -20 dBm, and the ratio is already varying for much lower powers. Following this observation, several possible causes for the anomalous variation of the ratio have been studied:

Defect-band formation. For high densities of the defect, the wave functions have significant overlap and the formation of a defect-band is expected [7]. The electrons in this band have an isotropic g value, close to the free-electron value of 2.0023. This is not observed for Si-NL52, where every resonance belongs to the same trigonal spectrum.
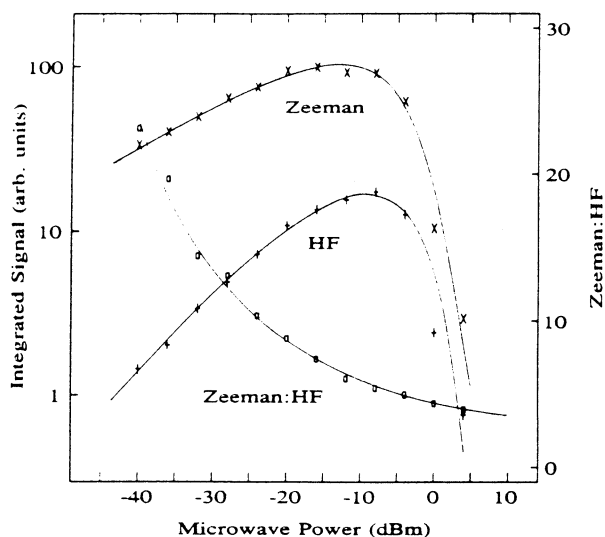

Figure 3 *Microwave power dependence of the Zeeman and HF components of Si-NL52. The ratio is changing even before saturation sets in.*

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Nuclear core polarization (NCP). For S=1/2 and I=1, the level diagram of Eq.1 is drawn in Figure 4. At low temperatures (4 K), the spin systems preferably are in the lowest three levels ($m_S = -1/2$), with a negligible inhomogeneity in the distribution over the different nuclear states. The ratio of the occupancy of the lower levels and the higher levels is determined by the Boltzmann factor $x = e^{g\mu_B B/kT} \approx 1.3$ at T=4.2 K. The most important relaxation for the electron spins is then the cross-relaxation (λ_X) in which simultaneous change of the electron and nuclear spins occurs, while conserving total spin. Apart from this relaxation path also electronic (λ_E) and nuclear (λ_N) relaxations are to be considered, although they are of less importance. The differential equations then have the form:

$$
\begin{aligned}
dN_1/dt &= \lambda_N(N_2\text{-}N_1) &&+ \lambda_E(xN_6\text{-}N_1) &&+ \lambda_X(xN_5\text{-}N_1)\\
dN_2/dt &= \lambda_N(N_3\text{-}N_2) - \lambda_N(N_2\text{-}N_1) &&+ \lambda_E(xN_5\text{-}N_2) &&+ \lambda_X(xN_4\text{-}N_2)\\
dN_3/dt &= -\lambda_N(N_3\text{-}N_2) &&+ \lambda_E(xN_4\text{-}N_3) &&\\
dN_4/dt &= \lambda_N(N_5\text{-}N_4) &&- \lambda_E(xN_4\text{-}N_3) &&- \lambda_X(xN_4\text{-}N_2)\\
dN_5/dt &= \lambda_N(N_6\text{-}N_5) - \lambda_N(N_5\text{-}N_4) &&- \lambda_E(xN_5\text{-}N_2) &&- \lambda_X(xN_5\text{-}N_1)\\
dN_6/dt &= -\lambda_N(N_6\text{-}N_5) &&- \lambda_E(xN_6\text{-}N_1).
\end{aligned}
\tag{2}
$$

(6) $m_s = \frac{1}{2}$, $m_I = +1$

(5) $m_s = \frac{1}{2}$, $m_I = 0$

(4) $m_s = \frac{1}{2}$, $m_I = -1$

(3) $m_s = -\frac{1}{2}$, $m_I = -1$

(2) $m_s = -\frac{1}{2}$, $m_I = 0$

(1) $m_s = -\frac{1}{2}$, $m_I = +1$
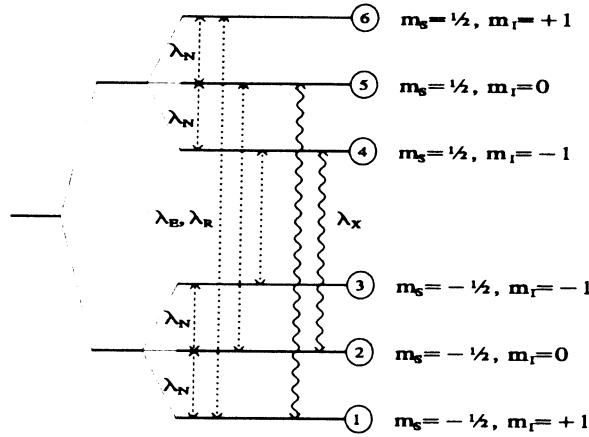
Figure 4 *Level diagram of the Hamiltonian as in equation 1. The relaxations are indicated with λ_N, λ_E and λ_X for nuclear, electronic and cross-relaxations, respectively. Resonant (EPR) transitions are labeled with λ_R.*

Without an external resonant (microwave) field, the steady-state solution of the coupled set of equations is the thermal equilibrium distribution: $N_1=N_2=N_3 = xN/(3+3x)$ and $N_4=N_5=N_6 = N/(3+3x)$, with N being the total number of spin systems. When the external field is resonant, two extra terms are added. For example, the resonance 1↔6 gives an extra transition:

$$
\begin{aligned}
dN_1/dt' &= dN_1/dt + \lambda_R(N_6 - N_1)\\
dN_6/dt' &= dN_6/dt - \lambda_R(N_6 - N_1),
\end{aligned}
\tag{3}
$$

where λ_R is the quasi relaxation, depending on the power of the applied microwave field. The intensity of the EPR signal is linearly proportional to the number of resonant transitions:

$$
I_{EPR} \sim \lambda_R(N_6 - N_1).
\tag{4}
$$

As an example, the numerical solution of the equations as described above, with $x=4$, $\lambda_N=10^{-6}$, $\lambda_E=10^{-4}$, $\lambda_X=10^{-2}$, and $\lambda_R=0.1$ yields an EPR intensity ratio of 1.55:0.86:0.59. The saturation of the EPR lines distorts the normal ratio (1:1:1) in an asymmetrical way. In Figure 5a this distortion is depicted in comparison with the low-microwave-power spectrum, while Figure 5b shows the line intensities as a function of the stimulated-transition probability, which is a measure of the microwave power. Other values of the relaxation parameters λ_N, λ_E, and λ_X will give different ratios, but the asymmetry always remains. This is not observed for Si-NL52, thus ruling out NCP as a possible cause for the changing of the relative intensities of the Si-NL52 components.
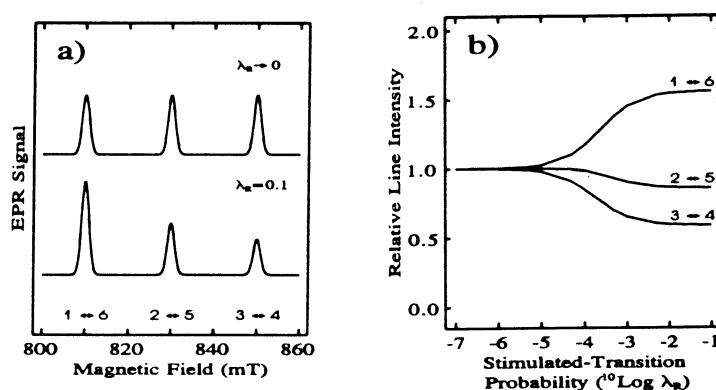

Figure 5 *a) Low power spectrum (top trace) and saturated spectrum (bottom trace). The nuclear spin is polarized by the microwaves. b) Microwave-power dependence of the individual line intensities.*

Ortho and para hydrogen. Molecular hydrogen has two forms: ortho hydrogen with parallel nuclear spins ($I=1$) and para hydrogen with anti parallel spins ($I=0$). Assuming Si-NL52 arises from a (charged) hydrogen molecule, the changing of relative intensities of the parts of the spectrum can be explained as an induced conversion of the ortho-hydrogen molecules, responsible for a HF triplet spectrum, to para-H_2, producing a Zeeman singlet spectrum, and *vice versa*.

FIELD-SCANNED ELECTRON NUCLEAR DOUBLE RESONANCE

The method of field-scanned ENDOR (FSE) provides a way to increase the resolution of the EPR spectrum, because it distills that part of the EPR spectrum which has nuclear magnetic resonance (NMR) at a selected frequency [8]. This simplifies the complicated lineshape of the Si-NL52 spectrum, as can be seen in Figure 6. Here an FSE scan is shown in comparison with the original EPR spectrum for a direction of the magnetic field close to <011>. The FSE scan shows the Zeeman line (825.0 mT), an HF line (829.6 mT) and two sets of SHF lines. The distance of the two outermost SHF lines is 1.60 mT (A=45 MHz), while their intensities indicate an interaction with a shell of two silicon atoms. This is consistent with the model as depicted in the right part of Figure 1, where the first SHF shell contains two Si atoms on the extended <111> H-H bond axis.
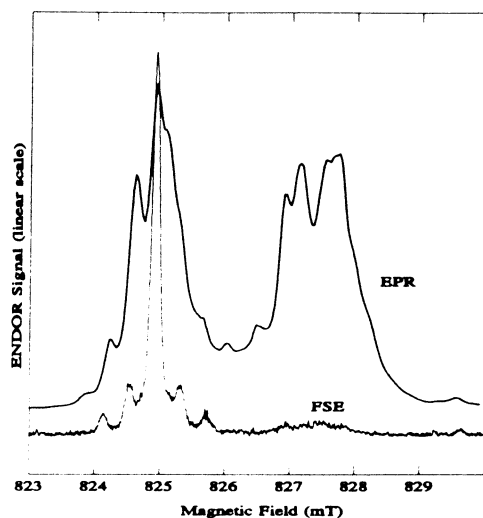
Figure 6 *EPR (thick trace) and FSE (thin trace) of Si-NL52 at a magnetic field angle 5° from <011>.*

CONCLUSIONS

The Si-NL52 and P_b spectra show remarkable similarities, because: 1) they have the same spin Hamiltonian and spin-Hamiltonian parameters, resulting in a similar angular dependence (Fig. 2), 2) show the same anomalous varying of the HF-to-Zeeman intensity ratio, and 3) have identical SHF structure. The distance of the SHF lines is equal to the distance observed for P_b, while their intensity, now measured accurately, is within the error margins as mentioned before [5]. We therefore conclude that Si-NL52 and P_b both represent basically the same defect.

On the other hand the experimental data can be better explained in the framework of the model of a paramagnetic hydrogen molecule located at an interstitial site as indicated in Figure 1. Namely, the new model can explain the varying of the HF-to-Zeeman intensity ratio, by assuming a conversion between ortho and para H_2, and it can explain the symmetry and the intensity of the SHF structure. We therefore propose the same model of interstitial H_2 for P_b. Since P_b is detected at Si/SiO_2 interfaces and porous silicon, such a conclusion implies evidence for the presence of hydrogen at such places.

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