

HYDROGEN PASSIVATION OF THE SULFUR DOUBLE DONOR IN SILICON INVESTIGATED BY EPR AND ENDOR

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Abstract. Hydrogen passivation of sulfur double donors in silicon led to the formation of two new centers, labeled Si-NL54 and Si-NL55, detected by means of EPR (electron paramagnetic resonance). The field-scanned ENDOR (electron nuclear double resonance) technique has been used to separate the spectra. The ratio of the intensities of both spectra remained the same after various quenching procedures, suggesting their formation to be of (almost) the same relative probability. Hyperfine interactions with sulfur and hydrogen disclosed the involvement of one sulfur atom and one hydrogen atom in each center. If hydrogen is substituted by deuterium, a quadrupole interaction on the latter could be determined in deuterium ENDOR. Based on the experimental evidence the defects are identified as two forms of a (substitutional) sulfur double donor in the neutral charge state, passivated with a single hydrogen atom, i.e., (S-H)⁰ pairs.

Introduction

Hydrogen passivation of electronic centers is among the interesting topics in defect physics. Passivation with hydrogen can terminate the electrical activity of both shallow and deep centers influencing their detection by spin-sensitive techniques. The passivation mechanism of single donors and the structure of thus created hydrogen-dopant pairs have been extensively studied both by experiment and theory. For double donors the situation is considerably less known. One could expect their electrical activity to be terminated by two hydrogen atoms. However, formation of a double donor-single hydrogen pair might convert a double donor into a single donor and render it paramagnetic in its neutral charge state. Indeed such an effect has lately been reported. In a recent study by EPR (electron paramagnetic resonance) and ENDOR (electron nuclear double resonance) Martynov *et al.* concluded that hydrogen passivation of a thermal double donor leads to formation of a more shallow single donor center (Si-NL10 defect) [1].

A typical and well-studied double donor in silicon is substitutional sulfur. In the past substitutional sulfur as well as sulfur-pair centers in silicon have been identified by EPR/ENDOR [2-4]. Upon interaction with hydrogen, passivation of sulfur-related centers has been concluded; in deep level transient spectroscopy (DLTS) hydrogen passivation of S₂⁰ and S₂⁺ in silicon has been observed by Pensl *et al.* [5,6]. In infrared absorption a series of single donors related to sulfur-hydrogen complexes was established by Peale *et al.* [7]. In this communication we report on an EPR/ENDOR and a field-scanned ENDOR (FSE) identification of the singly passivated sulfur double donor.

Experiment

The study has been performed on $1.4 \times 1.4 \times 10 \text{ mm}^3$ n-type float-zoned (FZ) and Czochralski (Cz) samples. The FZ samples, doped with $6 \times 10^{14} \text{ cm}^{-3}$ phosphorus and having a room-temperature resistivity of $8.2 \text{ } \Omega\text{cm}$ were diffused with hydrogen and natural sulfur and the Cz samples, containing $5.3 \times 10^{13} \text{ cm}^{-3}$ phosphorus and with a room-temperature resistivity of $100 \text{ } \Omega\text{cm}$, were diffused with hydrogen and natural sulfur or deuterium and natural sulfur or hydrogen and isotopically enriched sulfur containing 25.54 at.% of the magnetic isotope ^{33}S which has nuclear spin $I = 3/2$. To diffuse the sulfur, the samples were closed in quartz ampoules together with 0.5 mg of sulfur mixed with excess silicon powder to create a silicon-sulfur-rich atmosphere, and kept for a period of 48 hours at $1370 \text{ } ^\circ\text{C}$. After this diffusion hydrogen was introduced in the sample by annealing in quartz ampoules with water for a period of 0.5 hour at $1250 \text{ } ^\circ\text{C}$. Finally, the samples were quenched to room temperature in 3 seconds. To check the formation kinetics also different quenching times of 15 and 20 seconds were used.

The measurements were performed with an EPR/ENDOR superheterodyne spectrometer operating at 23 GHz (K-band) and adjusted to detect the dispersion part of the EPR signal. The magnetic field was modulated at 175 Hz. During the experiments the samples were kept at a temperature of 9 K.

Results

Similar results have been found for Cz and FZ material. In the samples diffused with natural sulfur and hydrogen two new EPR spectra were observed. The spectra, labeled for further reference Si-NL54 and Si-NL55, were not well resolved but they showed clear g-tensor anisotropy. The observed pattern showed splitting in two components; this could indicate the hyperfine interaction with hydrogen which has nuclear spin $I = 1/2$ and a 100% natural abundance. Indeed, at temperatures of 9 K, hydrogen ENDOR on both EPR spectra could be observed. A symmetrical pattern around the Zeeman frequency of a free proton indicates that hydrogen is responsible for the hyperfine interactions. Analysis of the ENDOR spectra revealed that the Si-NL54 and Si-NL55 defects are both of the same, $\langle 111 \rangle$ axial, symmetry, as can be seen in Figure 1(a).

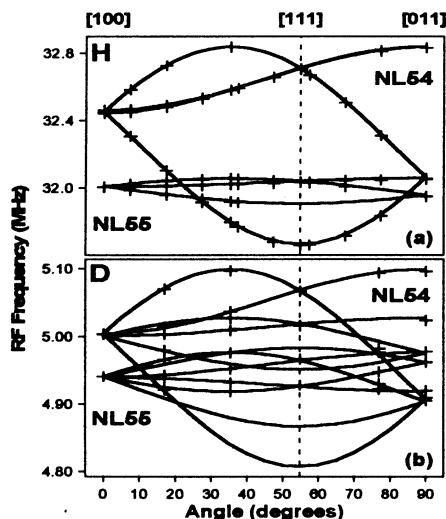


Figure 1: (a) Angular dependence of the hydrogen-ENDOR spectra of Si-NL54 and Si-NL55 observed in the sample diffused with hydrogen and natural sulfur and (b) angular dependence of the deuterium-ENDOR spectra of Si-NL54 and Si-NL55 observed in the sample diffused with deuterium and natural sulfur. Average experimental data is used together with a simulation with the spin-Hamiltonian parameters as given in Table 1.

The FSE technique was applied on the different ENDOR spectra of both defects to separate their overlapping EPR signals. In the FSE experiment the radio frequency is locked to an NMR line while the magnetic field is scanned. In this case the observed spectrum resembles ordinary EPR, while only transitions connected to the levels involved in the selected NMR transition are being detected. The comparison of EPR and FSE spectra of the Si-NL54 and Si-NL55 defects for the magnetic field $\vec{B} \parallel \langle 100 \rangle$ is presented in Figure 2(a). Subsequently, using the FSE technique, the full angular dependence for both newly reported centers could be measured. Both defects have trigonal symmetry and their g-values are summarized in Table 1.

If hydrogen is substituted by deuterium the nucleus of the latter will experience a quadrupole interaction with the gradient of the local electrostatic field, which can be determined in ENDOR. Figure 1(b) shows the angular dependence of the deuterium-ENDOR spectra of a sample doped with deuterium and sulfur. In Figure 2(b) EPR and FSE spectra of the Si-NL54 and Si-NL55 defects with deuterium are shown. The results clearly confirm the involvement of hydrogen in the structure of the relevant centers: in the deuterated samples the EPR spectra split into three components due to the hyperfine interaction with a nucleus having a nuclear spin $I = 1$ and a 100% abundance. The spacing between the lines is smaller, $\mu_D/2\mu_H \approx 15\%$, i.e., about 6.5 times less than for hydrogen, and consequently the structure is not resolved.

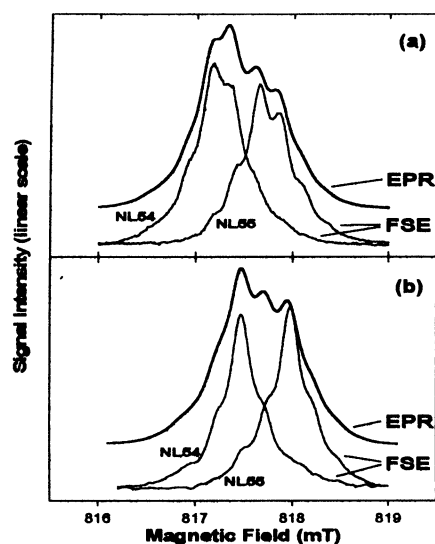


Figure 2: EPR and FSE spectra of Si-NL54 and Si-NL55 for magnetic field $\vec{B} \parallel \langle 100 \rangle$, recorded at a temperature of 9 K. (a) Spectra of the sample diffused with hydrogen and natural sulfur, recorded at a microwave frequency of 22.8809 GHz and (b) spectra of the sample diffused with deuterium and natural sulfur, recorded at a microwave frequency of 22.8851 GHz.

To establish the role of sulfur in the defects, samples diffused with hydrogen and isotopically enriched sulfur were prepared. In these samples the same two new spectra were found; they displayed a clearly resolved hyperfine interaction with the ^{33}S nucleus (nuclear spin $I = 3/2$). The identity of the centers was further confirmed by FSE measurements on hydrogen ENDOR which showed that the sulfur hyperfine interaction had also trigonal symmetry for both defects. EPR and FSE spectra are presented in Figure 3; a fourfold split spectrum ($I = 3/2$) belongs to each central line ($I = 0$). Relative intensities of the components in each spectrum demonstrate the involvement of one sulfur nucleus for both detected centers.

The Si-NL54 and Si-NL55 defects can be described with the following spin-Hamiltonian:

$$\mathcal{H}_S = \mu_B \vec{B} \cdot \vec{g} \cdot \vec{S} + \vec{S} \cdot \vec{A}^S \cdot \vec{I}^S + \vec{I}^S \cdot \vec{Q}^S \cdot \vec{I}^S + g_N^S \mu_N \vec{B} \cdot \vec{I}^S + \vec{S} \cdot \vec{A}^H \cdot \vec{I}^H + g_N^H \mu_N \vec{B} \cdot \vec{I}^H + \vec{I}^D \cdot \vec{Q}^D \cdot \vec{I}^D, \quad (1)$$

where $\vec{A}^S$ and $\vec{Q}^S$ represent the hyperfine and the quadrupole interactions with the ^{33}S nucleus,

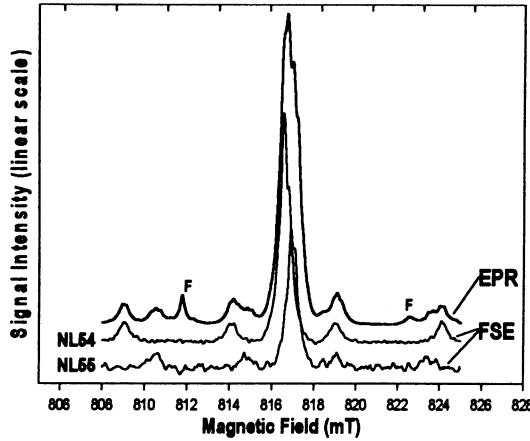


Figure 3: The EPR and FSE spectra of Si-NL54 and Si-NL55 for $\vec{B} \parallel \langle 100 \rangle$ in the sample diffused with hydrogen and isotopically enriched sulfur. To each central line ($I = 0$) belongs a fourfold spectrum ($I = 3/2$) showing the involvement of one ^{33}S nucleus (the lines indicated with F belong to a different spectrum). The spectra were recorded at a microwave frequency of 22.8637 GHz and at a temperature of 9 K.

respectively, A^H represents the hyperfine interactions with the H nucleus, and the electron spin is $S = 1/2$. The hyperfine and quadrupole tensor values for the hydrogen, deuterium and sulfur nucleus are listed in Table 1.

Discussion

The hyperfine interaction tensors can provide information about the electronic distribution in the defect. In the conventional one-electron linear combination of atomic orbitals (LCAO) approximation the wave function is taken as the superposition of the atomic wave functions. With the atomic wavefunction parameters [8], the localization η^2 of the electron on a nucleus and the s - and p -character, α^2 and β^2 , respectively, can be derived. These are presented in Table 2.

Table 1: Spin-Hamiltonian parameters for Si-NL54 and Si-NL55, as obtained from computer fits of the ENDOR angular dependencies (H and D) and the FSE angular dependencies (S). Electron spin $S = 1/2$; $A_{\parallel}^{H,D,S}$, $A_{\perp}^{H,D,S}$, $Q_{\parallel}^{D,S}$ and $Q_{\perp}^{D,S}$ are hyperfine and quadrupole tensor principal values for the H, D and ^{33}S nuclei.

	Si-NL54	Si-NL55	S_2^+	unit
$g_{\parallel}$	$1.99886 \pm 4 \times 10^{-5}$	$1.99823 \pm 4 \times 10^{-5}$	1.99992	
$g_{\perp}$	$2.00126 \pm 4 \times 10^{-5}$	$1.99974 \pm 4 \times 10^{-5}$	2.00115	
$A_{\parallel}^{(H)}$	$6.281 \pm 9 \times 10^{-3}$	$5.801 \pm 8 \times 10^{-3}$		MHz
$A_{\perp}^{(H)}$	$3.936 \pm 9 \times 10^{-3}$	$5.500 \pm 8 \times 10^{-3}$		MHz
$A_{\parallel}^{(D)}$	$0.959 \pm 3 \times 10^{-3}$	$0.867 \pm 2 \times 10^{-3}$		MHz
$A_{\perp}^{(D)}$	$0.591 \pm 3 \times 10^{-3}$	$0.823 \pm 2 \times 10^{-3}$		MHz
$Q_{xy}^{(D)}$	$0.024 \pm 3 \times 10^{-3}$	$0.019 \pm 2 \times 10^{-3}$		MHz
$A_{\parallel}^{(S)}$	143.1 ± 2.7	124.0 ± 2.6	115.0	MHz
$A_{\perp}^{(S)}$	137.7 ± 2.7	117.9 ± 2.6	112.3	MHz
$Q_{xy}^{(S)}$	3.3 ± 2.7	2.5 ± 2.6	2.3	MHz

The available data certainly allow to identify both centers as sulfur-hydrogen pairs with $\langle 111 \rangle$ axial symmetry. Since the intensity of the spectra is the same in the float-zoned ($[\text{O}_i] < 10^{16} \text{ cm}^{-3}$) and in the Czochralski-grown samples ($[\text{O}_i] \approx 10^{18} \text{ cm}^{-3}$) we conclude that oxygen is not involved in the formation of the Si-NL54 and Si-NL55 centers. Since the isolated sulfur is known to occupy a substitutional position in silicon, we assume that it is also substitutional in the Si-NL54 and Si-NL55 centers. From the trigonal symmetry of hydrogen ENDOR it can

be concluded that in both defects the hydrogen nucleus is situated along a $\langle 111 \rangle$ -axis of the crystal with respect to sulfur. Three possible nearest positions for the hydrogen nucleus would then be bond-centered, anti-bonded on a sulfur nucleus or anti-bonded on a nearest neighbor silicon nucleus. In view of the $S = 1/2$ value of both centers we identify them as sulfur-hydrogen pairs in the neutral charge state. Such an identification of the Si-NL54 and the Si-NL55 centers as singly passivated substitutional sulfur donors is further supported by infrared absorption measurements [9]. The infrared absorption spectra of the same samples which are studied here by magnetic resonance techniques, reveal the presence of the bands assigned earlier to the transition

between the $1s$ and $2p$ effective-mass states of the S-H pairs [7]. The intensities of both spectra have a similar behavior with temperature which indicates that the two EPR centers are different and not due to the ground state and a thermalized excited state of the same defect. For two Cz samples quenched to room temperature in respectively 15 and 20 seconds, the two EPR spectra appear in the same intensity ratio as in the fast-quenched samples, suggesting that the relative probability of their formation is (almost) the same. However, the intensities of these spectra decreased very much and the spectra disappeared completely when the samples were cooled slowly. The detailed models and the identification of the origin of the apparent distinction between both centers can only be proposed upon the development of theoretical calculations.

Summary

Summarizing, we have established that hydrogen passivation of the isolated sulfur double donor in silicon leads to the formation of two new paramagnetic defects, Si-NL54 and Si-NL55. Each defect has trigonal symmetry and consists of one sulfur nucleus and one hydrogen nucleus situated along a $\langle 111 \rangle$ -axis of the crystal.

Table 2: For hydrogen, deuterium and sulfur respectively: the observed values for a and b , the localization η^2 of the electron, the s -character α^2 and the p -character β^2 .

Parameter	Si-NL54	Si-NL55	S_2^+	
$a^{(H)}$	4.719	5.600		MHz
$b^{(H)}$	0.783	0.100		MHz
$\eta^2^{(H)}$	0.33	0.39		%
$a^{(D)}$	0.714	0.838		MHz
$b^{(D)}$	0.123	0.015		MHz
$\eta^2^{(D)}$	0.33	0.38		%
$a^{(S)}$	139.500	119.933	113.200	MHz
$b^{(S)}$	1.800	2.033	0.878	MHz
$\eta^2^{(S)}$	5.82	5.49	4.14	%
$\alpha^2^{(S)}$	69.2	63.1	78.9	%
$\beta^2^{(S)}$	30.8	36.9	21.1	%

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