

## Electron-paramagnetic-resonance identification of hydrogen-passivated sulfur centers in silicon

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Two centers are detected in hydrogenated sulfur-doped silicon by means of electron paramagnetic resonance. Both defects, labeled for further reference Si-NL54 and Si-NL55, are very similar and have trigonal symmetry; to better resolve the spectra, the field-scanned electron nuclear double resonance (ENDOR) technique has been used. The ratio of the intensities of both spectra remained the same after various quenching procedures, suggesting their formation to be (almost) of the same relative probability. Isotopically enriched sulfur was used and disclosed the involvement of one sulfur atom in each center. In ENDOR hyperfine interactions with hydrogen, one atom per center, have been observed. Extra evidence of the involvement of hydrogen in these defects was found by doping with deuterium. 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.,  $(\text{S-H})^0$  pairs. Such an identification is supported by infrared absorption measurements.

The role of hydrogen remains one of the most interesting topics in the study of electrically active defects in silicon. Hydrogen can easily be introduced into silicon by a variety of methods and is also present as a common contaminant in commercially available silicon.<sup>1</sup> In the past it has been found that hydrogen has a drastic effect on the electronic properties of the material. Upon hydrogen passivation of single donors and acceptors the electrical activity of these defects is terminated,<sup>2</sup> and their detection by spin-sensitive techniques is not possible. The passivation mechanism and the structure of thus created hydrogen-dopant pairs have been extensively studied by both experiment and theory. For double donors the situation is considerably less well known. One would expect that their electrical activity could be terminated by two hydrogen atoms. However, formation of a double-donor-single-hydrogen pair could convert a double donor into a single donor and lead to its paramagnetism in a neutral charge state. Indeed, such an effect has lately been reported. In a recent study by electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR) Martynov *et al.* concluded that hydrogen passivation of a thermal double donor leads to formation of a shallower single donor center (Si-NL10 defect).<sup>3</sup>

Chalcogens present a classic example of double donors in silicon; they were extensively studied and, as a result, their structure is well understood. In the past substitutional sulfur as well as sulfur-pair centers in silicon have been identified by EPR/ENDOR.<sup>4-6</sup> Upon interaction with hydrogen, passivation of sulfur-related centers has been concluded; in deep level transient spectroscopy (DLTS) hydrogen passivation of  $\text{S}_2^0$  and  $\text{S}_2^+$  in silicon has been observed by Pensl *et al.*<sup>7,8</sup> In infrared absorption a series of single donors related to sulfur-hydrogen complexes was established by Peale *et al.*<sup>9</sup> In this communication we report on an EPR and a field-scanned ENDOR (FSE) identification of the singly passivated sulfur double donor.

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

The magnetic resonance experiments were carried out in an EPR/ENDOR superheterodyne spectrometer operating at 23 GHz (*K* band) and tuned to dispersion. The magnetic field was modulated at 175 Hz and the radio-frequency for ENDOR measurements was on-off modulated at a rate of 3.3 Hz. The measurements were performed at 9 K.

Similar results have been found for Cz and FZ material. In the samples diffused with natural sulfur and hydrogen two 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 which could indicate the hyperfine interaction with hydrogen which has nuclear spin  $I = 1/2$  and a 100% natural abundance. This preliminary conclusion was fully confirmed in ENDOR measurements which revealed hyperfine interactions with hydrogen nuclei. By

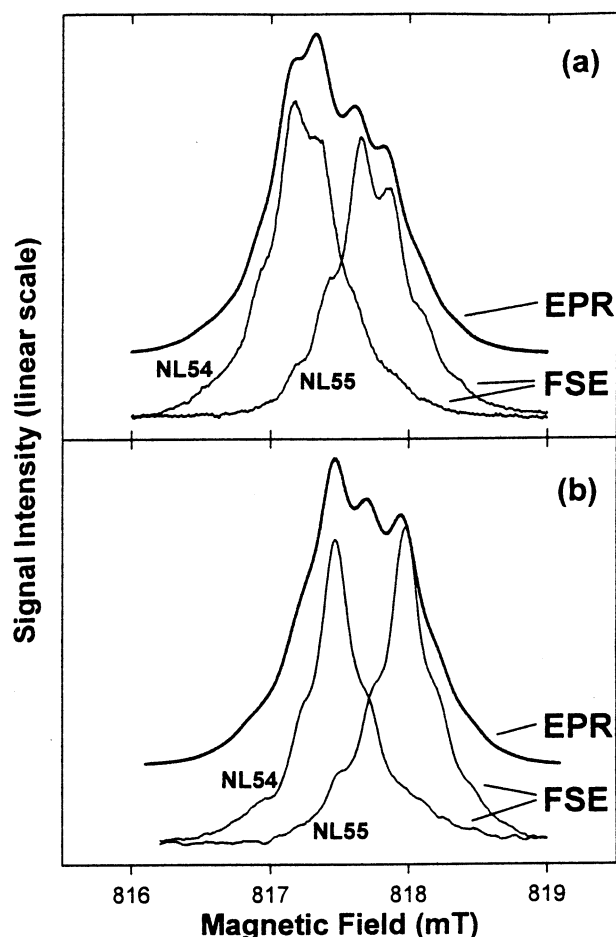


FIG. 1. The EPR and FSE spectra of Si-NL54 and Si-NL55 for magnetic field  $\vec{B} \parallel \langle 100 \rangle$ , recorded at a temperature of 9 K. (a) Spectra of the sample diffused with hydrogen and natural sulfur, recorded at a microwave frequency of 22.8809 GHz and (b) spectra of the sample diffused with deuterium and natural sulfur, recorded at a microwave frequency of 22.8851 GHz.

recording ENDOR spectra below and above the Zeeman frequency of a free proton the presence of hydrogen in the studied defect has been unambiguously established. Analysis of the ENDOR spectra revealed the presence of two centers, characterized by a somewhat different hyperfine interaction with hydrogen; both of the same  $\langle 111 \rangle$  axial symmetry but differing by the degree of anisotropy. Details of the hydrogen ENDOR analysis will be published in a separate paper.<sup>10</sup> Different ENDOR spectra of both defects were subsequently used in a FSE experiment to separate their overlapping EPR signals. In the FSE experiment the radio-frequency is locked to a 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  $\vec{B} \parallel [100]$  is presented in Fig. 1(a). Consequently, using the FSE technique, the full angular dependence for both newly reported centers could be measured; the result is shown in Fig. 2. Both defects have trigonal symmetry and their  $g$  values are

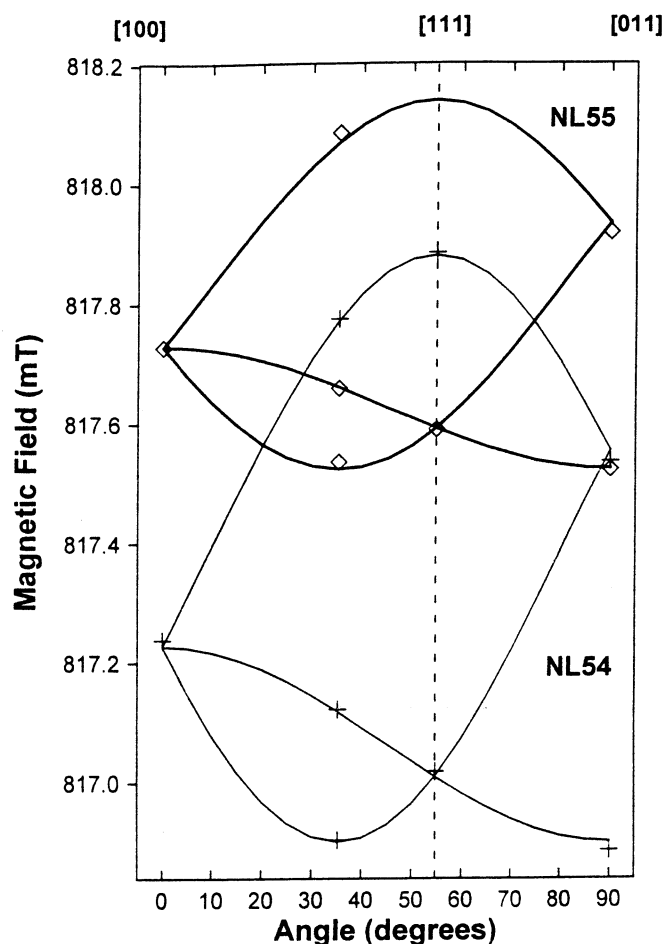


FIG. 2. Angular dependence of the FSE spectra of Si-NL54 and Si-NL55 observed in the sample diffused with hydrogen and natural sulfur. Average experimental data are used together with a simulation with the spin-Hamiltonian parameters as given in Table I. The measurements were done at a microwave frequency of 22.8809 GHz.

summarized in Table I.

Hydrogen participation in the structure of the centers was further investigated by doping the silicon samples with sulfur and deuterium. In this case the deuterium nucleus will experience a quadrupole interaction with the gradient of the local electrostatic field, which can be determined in deuterium ENDOR. In Fig. 1(b)

TABLE I. Spin-Hamiltonian parameters for Si-NL54 and Si-NL55, as obtained from computer fits of the FSE angular dependencies. Electron spin  $S = 1/2$ ;  $A_{\parallel}^S$ ,  $A_{\perp}^S$  and  $Q_{\parallel}^S$ ,  $Q_{\perp}^S$  are hyperfine and quadrupole tensor principal values, respectively, for the  $^{33}\text{S}$  nucleus.

| Parameter         | NL54                           | NL55                           | unit |
|-------------------|--------------------------------|--------------------------------|------|
| $g_{\parallel}$   | $1.99886 \pm 4 \times 10^{-5}$ | $1.99823 \pm 4 \times 10^{-5}$ |      |
| $g_{\perp}$       | $2.00126 \pm 4 \times 10^{-5}$ | $1.99974 \pm 4 \times 10^{-5}$ |      |
| $A_{\parallel}^S$ | $143.1 \pm 2.7$                | $124.0 \pm 2.6$                | MHz  |
| $A_{\perp}^S$     | $137.7 \pm 2.7$                | $117.9 \pm 2.6$                | MHz  |
| $Q_{\parallel}^S$ | $6.6 \pm 2.7$                  | $5.0 \pm 2.6$                  | MHz  |
| $Q_{\perp}^S$     | $-3.3 \pm 2.7$                 | $-2.5 \pm 2.6$                 | MHz  |

EPR and FSE spectra of the Si-NL54 and Si-NL55 defects with deuterium are shown. The results clearly confirm involvement of hydrogen in the structure of the relevant centers: in the deuterated samples the EPR spectra should 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 should be 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. The full analyses of the deuterium ENDOR measurements which reveal the deuterium-related hyperfine and quadrupole interactions will be published separately.<sup>10</sup>

While the involvement of hydrogen in both centers has been clearly established the participation of sulfur, whose natural composition has practically no magnetic isotopes, could only be postulated based on production conditions. In order 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  $^{33}\text{S}$  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 also had trigonal symmetry for both defects. The EPR and FSE spectra are presented in Fig. 3; a fourfold 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. Since the quadrupole interaction with this nucleus constitutes only a second-order effect for the EPR spectrum it could barely be observed in the EPR/FSE experiments. For its more accurate determination sulfur ENDOR measurements are required. These are currently in progress. The observed FSE spectra could be fitted with the following spin Hamiltonian:

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

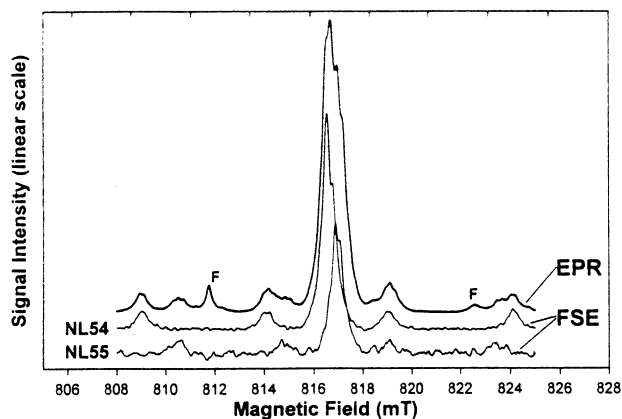


FIG. 3. The EPR and FSE spectra of Si-NL54 and Si-NL55 for  $\vec{B} \parallel \langle 100 \rangle$  in the sample diffused with hydrogen and isotopically enriched sulfur. To each central line ( $I = 0$ ) belongs a fourfold spectrum ( $I = 3/2$ ) showing the involvement of one  $^{33}\text{S}$  nucleus (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.

where  $\vec{A}^S$  and  $\vec{Q}^S$  represent the hyperfine and the quadrupole interactions with the  $^{33}\text{S}$  nucleus, respectively, and the electron spin is  $S = 1/2$ . The  $S = 1/2$  value is consistent with the available ENDOR data. The results of the computer fit are summarized in Table I.

While full analysis of the experimental data is required before detailed microscopic models of the Si-NL54 and Si-NL55 centers can be proposed some conclusions can already be drawn at this stage of the study. The available data certainly allow one 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 positions for the hydrogen nucleus would then be the bond centered, antibonded on a sulfur nucleus, or antibonded on a 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.<sup>11</sup> 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 theory (EMT) states of the S-H pairs.<sup>9</sup> The intensities of both spectra have a similar behavior with temperature, as given in Fig. 4, 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 s, the two EPR spectra appear in the same intensity ratio of Si-NL54:Si-NL55  $\approx 3:2$  as in the fast-quenched

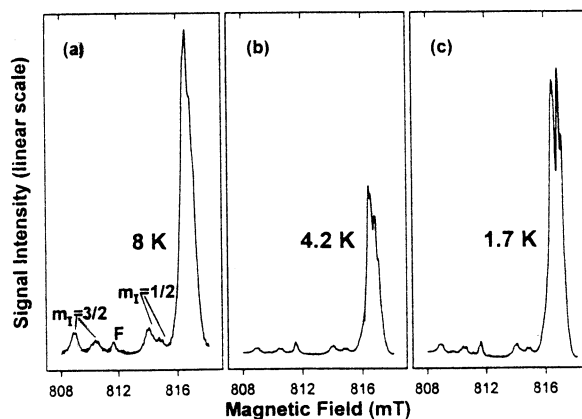


FIG. 4. Temperature dependencies of Si-NL54 and Si-NL55 for  $\vec{B} \parallel \langle 100 \rangle$ . The intensities of both spectra decrease if the temperature is lowered to 4.2 K, and grow again if the temperature is decreased further to 1.7 K.

samples, suggesting that the relative probability of their formation is (almost) the same. However, the intensities of these spectra were lowered so much (four times after 15 s and five times after 20 s) that we can expect that the spectra would disappear completely if the samples were cooled slowly. This is in agreement with van Oosten and Ammerlaan who concluded that rapid quenching in water was necessary to form isolated sulfur; slower quenching would promote the formation of sulfur-sulfur pairs rather than the isolated sulfur defect.<sup>5</sup> The detailed models and

the identification of the origin of the apparent distinction between the two centers can only be proposed upon full analysis of the ENDOR data<sup>10</sup> and the simultaneous development of theoretical calculations.

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

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<sup>10</sup> I. S. Zevenbergen, T. Gregorkiewicz, and C. A. J. Ammerlaan (unpublished).

<sup>11</sup> P. Kaczor and M. Godlewski (private communication).