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# Atomic and electronic structure of hydrogen-passivated double selenium donors in silicon

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## Abstract

Selenium–hydrogen-related defects in silicon have been investigated by magnetic resonance. Two new electron paramagnetic resonance (EPR) spectra Si-NL60 and Si-NL61 of selenium–hydrogen complexes were observed. By application of the electron nuclear double resonance (ENDOR) and field scanned ENDOR (FSE) techniques the symmetry and spin-Hamiltonian parameters of the centers were determined. Based on the obtained information the atomic and electronic structures of the centers are discussed with two different models: one–chalcogen – one-hydrogen and one–chalcogen – two-hydrogen complexes. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Silicon; Hydrogen passivation; Chalcogen; Magnetic resonance

## 1. Introduction

Over the last ten years, the passivation by hydrogen of shallow single donors and acceptors in silicon has been extensively investigated, both by experimental and theoretical methods; as a result these passivated dopants have become well-understood defects. In some contrast, the understanding of the more complex and varied processes of passivation of deep electronic centers is still not on a satisfactory level. The structure and corresponding electrical activity of hydrogen complexes with deep centers have proven to be intriguing; results are controversial in several cases. The interactions of hydrogen with the chalcogen double donors are good examples of this situation. Experiments using deep level transient spectroscopy (DLTS) [1], infrared absorption [2] and magnetic resonance [3] showed that hydrogen could passivate the sulfur double donor in silicon. However, there still is dispute about the number of hydrogen atoms per sulfur atom

participating in the passivation process, and about the question whether a S–H complex with a single hydrogen atom will behave as a, possibly shallow, single donor. In our experiments the hydrogen passivation of the double donor selenium was studied; new results were obtained.

In selenium-doped hydrogenated silicon two new electron paramagnetic resonance (EPR) spectra, labeled Si-NL60 and Si-NL61, were observed. The spectra, both revealing trigonal symmetry, have been investigated in detail by electron-nuclear double resonance (ENDOR) and field-scanned ENDOR (FSE). By the use of both natural and isotopically enriched selenium (isotope <sup>77</sup>Se, nuclear spin  $I = \frac{1}{2}$ , natural abundance 7.6%, enrichment 99.1%) the involvement of one selenium atom per center was conclusively established. From the hyperfine structure due to hydrogen or deuterium, using heavy water with 99.95% enrichment, the presence of hydrogen in the centers was concluded. The Si-NL60 spectrum displays the nuclear interaction due to one hydrogen atom. From the hyperfine and quadrupole interactions it is concluded that the corresponding center is very similar to the sulfur–hydrogen pairs (EPR spectra Si-NL54 and Si-NL55). The paramagnetic state most probably corresponds to the neutral charge state of a Si : Se, H single donor. The other spectrum, Si-NL61, reveals hyperfine interaction with two inequivalent hydrogen atoms. For this Si : Se,

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H<sub>2</sub> center no corresponding sulfur — two-hydrogen complex was reported. Models for atomic and electronic structure will be discussed on the basis of the current findings.

## 2. Sample preparation and K-band spectrometer

The samples were prepared by thermal diffusion of natural selenium (7.6% of the magnetic isotope <sup>77</sup>Se) or of selenium enriched to 99.1% of the <sup>77</sup>Se into p-type float-zone silicon boron-doped with the room-temperature resistivity between 75 and 125 Ω cm. The samples shaped as rectangular bars with typical dimensions 2 × 2 × 15 mm<sup>3</sup> were enclosed in quartz ampoules together with 0.5–1 mg of selenium powder mixed with an excess amount of silicon powder to create a SiSe atmosphere. They were heated to 1350°C for a period of 120–360 h. After the diffusion the rough surface layers of the samples were mechanically removed and the samples were etched in CP6 solution. Hydrogen or deuterium was introduced in a high-temperature treatment, at 1200–1350°C, in water vapor for 30–45 min, followed by a rapid quench to room temperature.

Magnetic resonance experiments were carried out using a superheterodyne spectrometer operating in the microwave K-band with the frequency near 23 GHz. For a more complete description of the equipment and the experimental techniques, see Ref. [4].

## 3. Resonance spectra of the defects

The two EPR spectra Si-NL60 and Si-NL61 of Se–H defects observed in the hydrogenated selenium-doped samples are given in Fig. 1 for magnetic field *B* parallel to a  $\langle 100 \rangle$  crystal direction. The spectra of both centers are well characterized with pairs of satellites, symmetrically displaced with respect to the central component, which are due to the hyperfine interaction with isotope <sup>77</sup>Se, nuclear spin  $I = \frac{1}{2}$ . The total intensity of these hyperfine components fits precisely with the isotopic composition of natural selenium identifying the presence of one selenium atom in the structure of the defects. The central resonance is a superposition of two spectra, which can only be separated by the FSE technique. The superimposed EPR and the FSE spectra are given in Fig. 1. In order to confirm the conclusion on selenium participation, samples diffused with selenium enriched to 99.1% of <sup>77</sup>Se were prepared. The spectra of Si-NL60 and Si-NL61 are well reproduced in these samples with the central components almost absent and all intensity in the hyperfine components. The trigonal,  $\langle 111 \rangle$ -axial symmetry, of both central components (by FSE) and hyperfine components (by EPR) is observed for the Si-NL60 and Si-NL61 centers. The angular dependence patterns of the

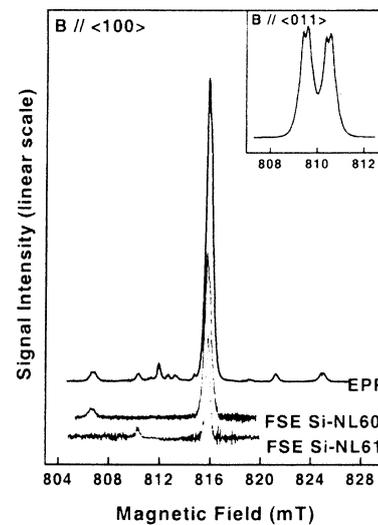


Fig. 1. EPR over full range and FSE spectra of Si-NL60 and Si-NL61 for  $B \parallel \langle 100 \rangle$ , microwave frequency  $f = 22.7536$  GHz,  $T = 4.2$  K. The inset shows low-field hyperfine lines of Si-NL60 for  $B \parallel \langle 011 \rangle$  and  $f = 22.8768$  GHz.

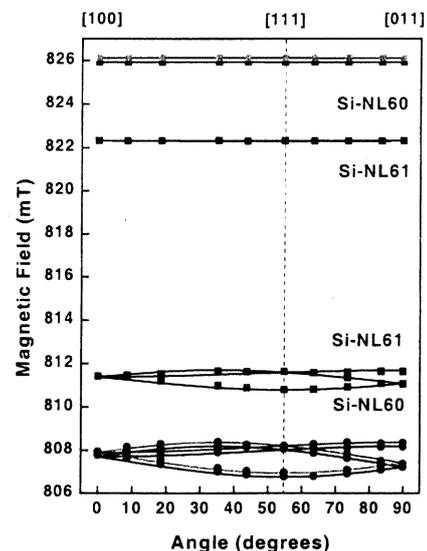


Fig. 2. EPR angular dependence of the <sup>77</sup>Se patterns,  $T = 1.5$  K,  $f = 22.8152$  GHz. The double loops observed for Si-NL60 are due to hydrogen hyperfine interaction.

resonance spectra when rotating the field from  $[100]$  to  $[011]$  in the  $(0\bar{1}1)$  plane are given in Fig. 2.

Since the samples were intentionally doped with hydrogen at high temperature, the participation of hydrogen in the centers is anticipated. In EPR, the hyperfine interaction with hydrogen with nuclear spin  $I = \frac{1}{2}$  is visible only for the Si-NL60 center. This splitting is about 0.24 mT creating the two loops in the angular

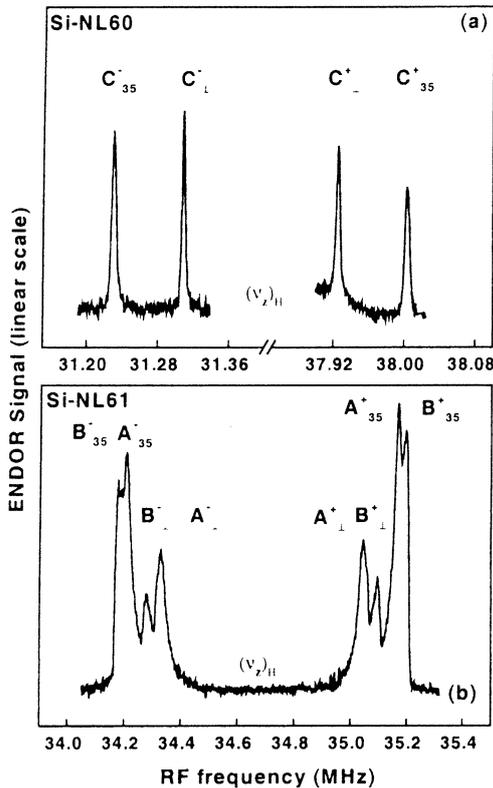


Fig. 3. ENDOR hydrogen spectra for  $B \langle 0 1 1 \rangle$  of (3a) Si-NL60.  $B = 813.168$  mT,  $f = 22.7067$  GHz. and (3b) Si-NL61.  $B = 814.812$  mT,  $f = 22.7553$  GHz.  $T = 8.2$  K.

dependence pattern of the Si-NL60 center, see Fig. 2. Such a splitting is not observed in deuterated samples. A closer view on the hydrogen hyperfine splitting of Si-NL60 for  $B \langle 0 1 1 \rangle$  is given in the inset in Fig. 1.

To further verify the hydrogen involvement, ENDOR experiments have been performed. Typical hydrogen-ENDOR spectra are given in Fig. 3 for the magnetic field  $B \langle 0 1 1 \rangle$  mT. For the proton with  $(g_n)_H = 5.58556$  the nuclear resonance frequency  $(\nu_z)_H = (g_n)_H \mu_n B/h$  is near 34.7 MHz. The observed ENDOR spectra have two different groups of lines marked with A, B and C that correspond to ENDOR of three different hydrogen atoms. The first group (C lines) is, as seen in Fig. 3a, located about 3.3 MHz from the proton Zeeman frequency  $(\nu_z)_H$ . The second group (A and B lines), as given in Fig. 3b, is very close to  $(\nu_z)_H$  with the hyperfine interaction being about 8 times smaller. Both groups of spectra are symmetric with respect to  $(\nu_z)_H$  identifying the observed hyperfine interaction as being due to hydrogen. Detailed analysis of ENDOR and FSE spectra is given in Ref. [5]. The far group of spectra corresponds to a hyperfine interaction of about 6.7 MHz. In the EPR such a hyperfine interaction gives a splitting of 0.24 mT, which

is indeed observed for the EPR spectrum Si-NL60. The other group of lines corresponds to two hydrogen atoms belonging to the Si-NL61 center: the hyperfine interaction constant of approximately 0.8 MHz leads to an EPR splitting of 0.03 mT which is too small to be observed in EPR. By measuring the hydrogen ENDOR and FSE angular patterns the trigonal symmetry of the centers is confirmed. The spin-Hamiltonian parameters are given in Table 1 of Ref. [5]

#### 4. Atomic structure of the defects

From the experiment the participation of a single selenium and a single hydrogen atom in the microscopic structure of the Si-NL60, and a single selenium and two hydrogen atoms in the microscopic structure of Si-NL61 is established. As the isolated chalcogen (sulfur, selenium) is known to occupy a substitutional position in silicon (either in their single form or in  $S_2$ ,  $Se_2$  pairs), the substitutional position is also assumed to be true for the selenium-hydrogen complexes observed in this study. Since all observed tensors, which reflect interaction of the defect electron with nuclei involved, have trigonal symmetry, the  $\langle 1 1 1 \rangle$  direction must be assumed as the axis of the defect structure. Hyperfine interactions with the hydrogen or deuterium atoms, reflecting the local symmetry around these impurities, also have the perfect trigonal symmetry. It implies that the hydrogen/deuterium impurities are on the  $\langle 1 1 1 \rangle$  axis of the center. As the centers cannot have inversion symmetry, only one position is available in shells of the trigonal type. The defects as a whole therefore have an axial structure with the hydrogen impurities along a  $\langle 1 1 1 \rangle$ -oriented line passing through the chalcogen atom. Such a linear model is shown in Fig. 4. Possible positions for hydrogen are a bond-centered site and anti-bonding sites with respect to chalcogen or silicon atoms. More detailed analysis of resonance data or advanced theoretical modeling are required to unambiguously conclude on the actual positions of the hydrogen atoms.

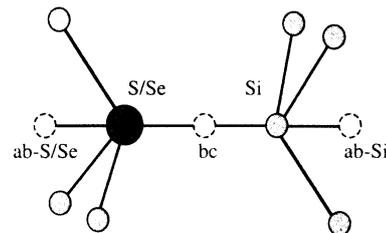


Fig. 4. Atomic model for chalcogen-hydrogen centers. Possible positions for the hydrogen atom are indicated by bc for a bond-centered site, ab-S/Se for anti-bonding site next to the chalcogen atom and ab-Si for the silicon anti-bonding site.

Table 1

Parameters related to the analysis of hyperfine interactions of the Si : Se, H spectra Si-NL60 and Si-NL61 and of the Si : S, H spectra Si-NL54 and Si-NL55

Parameter	Si-NL60	Si-NL61		Si-NL54	Si-NL55	Unit
Nucleus	$^{77}\text{Se}$	$^{77}\text{Se}$		$^{33}\text{S}$	$^{33}\text{S}$	
$a$	508.7	305.0		139.5	119.9	MHz
$b$	13.4	8.2		1.8	2.0	MHz
$\eta^2$	5.67	3.43		5.89	5.54	%
$\alpha^2$	52	51		70	64	%
$\beta^2$	48	49		30	36	%
Nucleus	$^1\text{H}$	$^1\text{H}$	$^1\text{H}$	$^1\text{H}$	$^1\text{H}$	
$a$	6.663	0.897	0.830	4.718	5.600	MHz
$b$	0.060	0.081	0.095	0.782	0.100	MHz
$\eta^2$	0.47	0.063	0.058	0.33	0.39	%

### 5. Electronic structure of the defects

Based on LCAO analysis of observed values for the isotropic part  $a$  and anisotropic part  $b$  of the hyperfine interactions, the total localization  $\eta^2$  of the electron, the s-character  $\alpha^2$  and p-character  $\beta^2$  for selenium and hydrogen are calculated. As given in Table 1, the small localization of the paramagnetic electron ( $\eta_{\text{Se}} \approx 5.7\%$  for Si-NL60,  $\eta_{\text{Se}} \approx 3.4\%$  for Si-NL61,  $\eta_{\text{H}} \approx 0.5\%$  for Si-NL60,  $\eta_{\text{H}} \approx 0.06\%$  for Si-NL61) places the Si-NL60 and Si-NL61 in the group of the shallow single donors such as phosphorus, arsenic and antimony. For Si-NL60, the combination of single donor character and participation of a single hydrogen atom in the microscopic structure is very much similar to the Si-NL54 and Si-NL55 centers, which were identified with sulfur–hydrogen complexes [3]. Consequently, we identify this center as a form of a substitutional selenium double donor in the neutral charge state, passivated with a single hydrogen atom, i.e., (Se–H) pair. For the Si-NL61 center, evidence of the

involvement of two hydrogen atoms has clearly been obtained leading to a conclusion that the center is observed most probably in an ionized state. With the trigonal arrangement of the impurities (hydrogen, selenium) this implies that no full passivation has taken place and the center is still electrically active regardless of complexing with two hydrogen atoms.

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