

Hydrogen passivation of double donors in silicon: A comparison of selenium versus sulfur

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Magnetic resonance measurements on hydrogen-passivated selenium-doped silicon have revealed two new EPR spectra of two different paramagnetic centers labeled Si-NL60 and Si-NL61. The centers show clearly <111>-axial trigonal symmetry in the angular dependence patterns of EPR, ENDOR and FSE and are identified as complexes including hydrogen and selenium atoms in the atomic structure. Based on analysis of the experimental data two different atomic configurations have been proposed for Si-NL60 and Si-NL61 as a pair of one-hydrogen – one-selenium, and a two-hydrogen – one-selenium complex, respectively. A comparison of the new centers to the experimental and theoretical data available for the sulfur-hydrogen system (EPR centers Si-NL54 and Si-NL55) is presented.

1. Introduction

In the successful experimental observation of hydrogen passivation of the sulfur double donors in silicon by Zevenbergen *et al.* [1], two new EPR (electron paramagnetic resonance) spectra, labeled Si-NL54 and Si-NL55, of hydrogen-sulfur centers have been reported. Recently, magnetic resonance studies on hydrogen passivation of the selenium double donors in silicon resulted also in the observation of two new EPR spectra, Si-NL60 and Si-NL61, related to hydrogen-selenium complexes [2]. As belonging both to the group of chalcogen elements, the same behavior of sulfur and selenium as dopant impurities and as reactant with hydrogen in silicon are expected. However, experimental results show that besides many similar characteristics differences also are apparent in the spectra. The constituents, i.e., number of hydrogen atoms in the centers are different leading to a difference in creation probability of the centers. The three centers Si-NL54, Si-NL55 and Si-NL60 are very similar and proved to be a one-hydrogen – one-chalcogen pair. An unambiguous picture of the Si-NL61 spectrum can not yet be presented.

In this paper, results for the hydrogen-selenium system, with conclusions for the Si-NL60 and Si-NL61 centers are briefly presented with a comparison to the hydrogen-sulfur system.

2. Experimental results

The sample preparation procedures for sulfur and selenium are similar with two crucial separate steps of diffusion: (1) thermal diffusion of sulfur or selenium at a temperature of 1200°C to 1370°C for 100 to 350 hours in SiS/SiSe atmosphere, (2) short diffusion in water vapor at a temperature of 1200-1300°C. Details about sample preparation are described in Refs [1,2]. 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. [3].

In the samples doped only with sulfur or selenium, the spectra of isolated sulfur and sulfur pairs for sulfur-doped samples or isolated selenium and selenium pairs for selenium-doped samples were observed. The intensity of these spectra was quite weak; the g values determined for these spectra corresponded to the well-known g values in the literature. After diffusion with hydrogen new centers were created with intensity some ten times higher. The central spectral lines corresponding to components with nuclear spin $I = 0$ are superposition of the centers Si-NL54 and Si-NL55 for sulfur or Si-NL60 and Si-NL61 for selenium. Typical spectra are depicted in Figs 1 and 2 for sulfur and selenium, respectively. The FSE (field scanned ENDOR) spectra of individual components of the centers are shown as lower thin resolved lines. The hydrogen hyperfine interaction is clearly observed for Si-NL54, Si-NL55 and Si-NL60 with a splitting of about 0.25 mT. No splitting is observed for Si-NL61; this implies that the hydrogen hyperfine tensor A for this center must be smaller than that of the others.

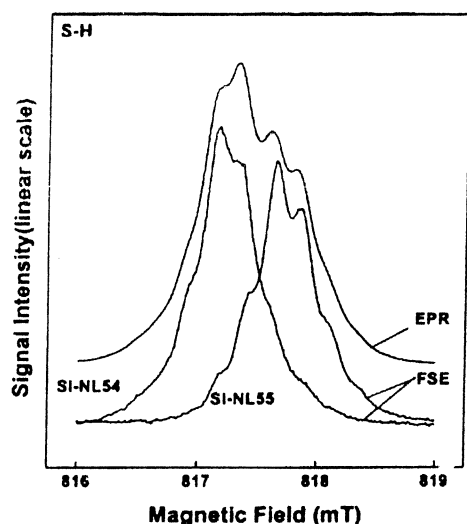


Fig. 1: The EPR and FSE spectra of Si-NL54 and Si-NL55 centers for magnetic field $B \parallel \langle 100 \rangle$, recorded at temperature $T = 9$ K, microwave frequency $f = 22.8809$ GHz.

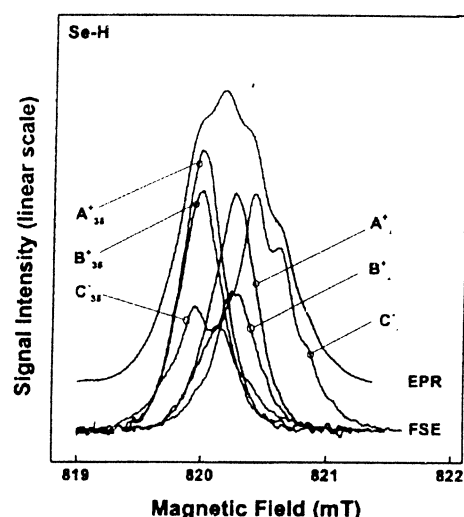


Fig. 2: The EPR and FSE spectra of Si-NL60 and Si-NL61 centers for $B \parallel \langle 011 \rangle$, recorded at $T = 9$ K. The labels A and B correspond to the Si-NL61 center, label C corresponds to the Si-NL60 center.

By measuring FSE over a wide field range covering the hyperfine lines of either sulfur or selenium, the intensity ratio of the central resonance and hyperfine line has proved that only one chalcogen atom is involved in the centers. Consistent results are observed in the samples doped with enriched ^{33}S or ^{77}Se as shown in Figs 3 and 4. From experiments as can be seen from Figs 3 and 4, the creation probabilities of Si-NL54 and Si-NL55 for sulfur are high and about the same. The concentration of Si-NL54 is slightly higher than Si-NL55. For selenium, the Si-NL60 center is observable in all samples with high concentration whereas the Si-NL61 center has low creation probability and is observable only in rapidly quenched samples, with a concentration about a few ten times lower than that of the Si-NL60 center. Hydrogen participation into the centers is deduced from several pieces of evidence: the lines split into two components or the line width broadens in the sample doped with hydrogen. No splitting is observed in the samples doped with deuterium. The ENDOR (electron nuclear double resonance) measurements in the range of hydrogen interaction frequencies have detected strong resonance spectral lines symmetrically displaced with respect to the free proton Zeeman frequency. Two different

angular dependence patterns are observed as depicted in Fig. 5 for sulfur, three patterns are found for selenium, Fig. 6.

By measuring FSE on these ENDOR lines, the participation of one hydrogen atom in the microscopic structure of the Si-NL54, Si-NL55 and Si-NL60 centers is established. The Si-NL61 center is assembled from two different hydrogen atoms labeled A and B whose hyperfine interactions are very similar, with the A tensors only about 10% different. This means that this center might belong to a complex of two-hydrogen – one-selenium atoms.

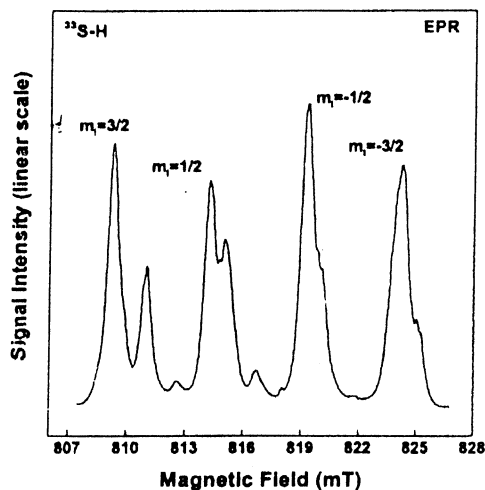


Fig. 3: EPR spectra Si-NL54 and Si-NL55 for $\mathbf{B} \parallel \langle 100 \rangle$ using sulfur enriched to 99.5% in the ^{33}S isotope, $I = 3/2$. $T = 4.2 \text{ K}$, $f = 22.874 \text{ GHz}$.

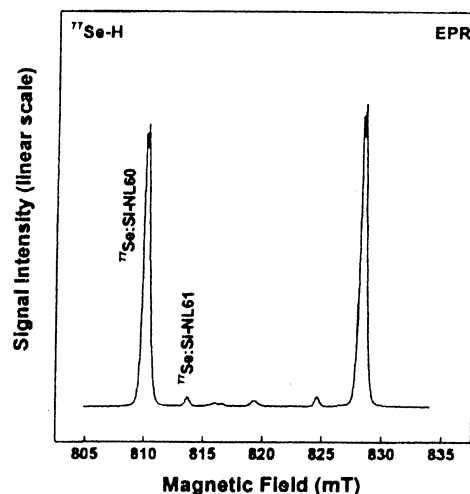


Fig. 4: EPR spectra Si-NL60 and Si-NL61 for $\mathbf{B} \parallel \langle 100 \rangle$ using selenium enriched to 99.1% in the ^{77}Se isotope, $I = 1/2$. $T = 4.2 \text{ K}$, $f = 22.878 \text{ GHz}$.

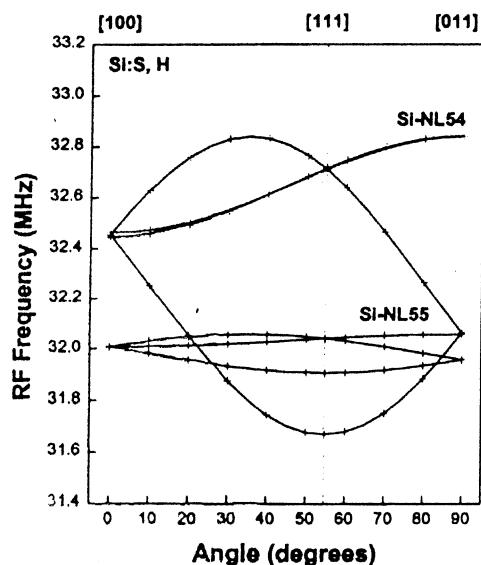


Fig. 5: Angular dependence of the hydrogen ENDOR for the spectra Si-NL54 and Si-NL55 in the low-frequency region with respect to the nuclear Zeeman frequency of free proton. A small misorientation is observed in the $\langle 100 \rangle$ direction.

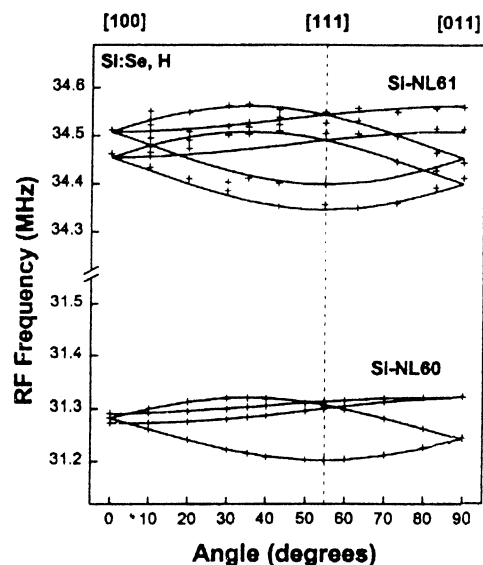


Fig. 6: Angular dependence of the hydrogen ENDOR for the spectra Si-NL60 and Si-NL61. Trigonal symmetry is observed for both centers. Double pattern of Si-NL61 indicates the hyperfine interaction of two different hydrogen atoms.

The spin-Hamiltonian parameters for the selenium- and sulfur-hydrogen spin $S = 1/2$ centers as observed in EPR, ENDOR and FSE and fitted with experimental data are given in table 1.

Table 1: Spin-Hamiltonian parameters for the chalcogen-hydrogen spin $S = 1/2$ centers. All tensors have the $\langle 111 \rangle$ axial form. Units are MHz except for g which is dimensionless.

Spectrum	$g_{//}$	$g_{\perp}$	$(A_{S/Se})_{//}$	$(A_{S/Se})_{\perp}$	$(Q_S)_{//}$	$(Q_S)_{\perp}$	$(A_H)_{//}$	$(A_H)_{\perp}$
Si-NL54	1.99886	2.00126	143.1	137.7	6.6	-3.3	6.281	3.936
Si-NL55	1.99823	1.99974	124.0	117.9	5.0	-2.5	5.801	5.500
Si-NL60	1.99635	1.99459	535.6	495.3			6.782	6.603
Si-NL61	1.99627	1.99512	321.5	296.8			1.060	0.816
							1.020	0.735

3. Atomic configurations

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. The atomic configuration of the Si-NL54 and Si-NL55 centers has already been proposed in Ref. 1 where hydrogen is placed at the bond-centered site and anti-bonded to one of silicon neighbors, respectively. A similar atomic configuration is described for the Si-NL60 center. Since all observed tensors, which reflect interaction of the defect electron with nuclei involved, have trigonal symmetry, the $\langle 111 \rangle$ 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 $\langle 111 \rangle$ 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 $\langle 111 \rangle$ -oriented line passing through the chalcogen atom. In such a linear model possible positions for hydrogen are a bond-centered site and anti-bonding sites with respect to chalcogen or silicon atoms. For the Si-NL61 centers, as concluded above, with two constituent hydrogen atoms two such sites must be occupied. However, an alternative atomic configuration of two centers of one-hydrogen – one-selenium atoms but will similar g tensor can not be excluded. A more detailed analysis of resonance data or theoretical modeling is required to unambiguously conclude on the actual positions of the hydrogen atoms.

4. Conclusion

By magnetic resonance, the very similar paramagnetic centers of sulfur and selenium with hydrogen are characterized and a comparison of their atomic and electronic structures is made. Four EPR spectra labeled Si-NL54, Si-NL55, Si-NL60 and Si-NL61 identified by particular g and A -tensors have proved the involvement of hydrogen and sulfur/selenium atoms in the microscopic structure. The first three centers are very similar and are described by a model with the structure of a one-hydrogen – one-chalcogen pair in which chalcogen and hydrogen atoms occupy sites along a $\langle 111 \rangle$ axial direction. The hydrogen atom might occupy the bond-centered site, anti-bonded to S/Se or anti-bonded to one of the silicon neighbors. The Si-NL61 center has two hydrogen atoms in the microstructure, with hyperfine interaction tensors about six times smaller and much lower creation probability compared to the others. The atomic model for this center is still disputed; a theoretical calculation is needed to bring out a proper atomic configuration.

References

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- [2] P. T. Huy, C. A. J. Ammerlaan, T. Gregorkiewicz and D. T. Don, submitted for publication Phys. Rev. B.
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