

Atomic Structure of Chalcogen-Hydrogen Complexes in Silicon

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Abstract

The formation of complexes of hydrogen with the double donor impurities sulfur and selenium in silicon was studied by magnetic resonance. For both chalcogen impurities two spectra were observed by electron spin resonance. Applying in addition the double resonance techniques electron-nuclear double resonance (ENDOR) and field scanned ENDOR (FSE) the spin-Hamiltonian parameters could be determined. On this basis the atomic structure of the centers is elucidated. In the sulfur-doped silicon the two spectra (Si-NL54, Si-NL55) correspond to one-sulfur-one-hydrogen complexes, which are observed in a neutral paramagnetic state. In selenium-doped silicon a similar selenium-hydrogen complex is formed (spectrum Si-NL60), but the other spectrum (Si-NL61) corresponds to a structure involving two inequivalent hydrogen atoms. This latter center is observed in an ionized state. In all cases the chalcogen and hydrogen atoms form a center with the trigonal arrangement of the impurities. The centers can be ionized which implies that no full hydrogen passivation has taken place.

Introduction

From the early days of semiconductor research it has been recognized that interactions between impurities taking place in a semiconductor crystal are of utmost importance for the electronic properties of the material [1,2]. Only more recently a general awareness has grown that hydrogen can be present to high concentrations in semiconductors, including silicon, and is an active participant in pairing or complexing interactions. Such phenomena are enhanced by the easy introduction of hydrogen into silicon by standard processing technologies and by the high mobility of the atomic species. Interest in hydrogen interactions ranges from fundamental semiconductor science to practical application. Binding of hydrogen to dangling silicon bonds in the lattice vacancy is an example where progress of physical understanding of a basic intrinsic defect provides the driving force to research [3]. Passivation of bonds on surfaces and in amorphous materials, e.g. in upgrading solar cells, illustrates the relevance for technological purposes. Studies of hydrogen interactions were much stimulated by the discovery of the passivation of shallow acceptor states by hydrogen [4]. Due to binding energies near 1.4 eV the formed electronically passive complexes are stable to above room temperature. Generally the passivation of shallow donors in silicon is less complete and strong [5]. Given this situation the passivation of double donors is an interesting case. In a simple concept, a double donor can bind one or two hydrogen atoms with a correlated partial or full passivation. If electrostatic forces are providing a substantial contribution to the binding, the double core charge of a double donor might lead to stronger binding and thermally more stable passivated centers. Research as reported in this paper was stimulated by such considerations. In the present research the magnetic resonance technique was applied to investigate the process of passivation. In common with most other experimental research methods magnetic resonance is incapable to observe passivated centers, a handicap inherent to passivation. In contrast, a partially passivated double donor will have an odd number of electrons in its neutral charge state, will hence be paramagnetic and observable in magnetic resonance, allowing a study of the passivation process. The double donors sulfur and selenium in silicon and their passivation, studied by electron paramagnetic resonance (EPR), electron-nuclear double resonance (ENDOR) and field-scanned ENDOR (FSE), are the subject of this paper.

Analysis magnetic resonance data

In the chalcogen-doped samples, before hydrogenation, the spin resonances of sulfur and the sulfur pair, or of selenium and the selenium pair, are observed. These well-documented centers are identified by their g values and hyperfine interaction constants. Subsequent to the high-temperature hydrogen treatment these spectra have disappeared and new spectra are present. An illustration of the observed spectra, for magnetic field $\mathbf{B}$ parallel to a $\langle 100 \rangle$ crystal direction, is given in Figs 1 and 3 for sulfur and selenium, respectively. The central line of largest amplitude, near $B = 816$ mT in both cases, arises from centers formed from sulfur or selenium isotopes without nuclear spin. In each case pairs of smaller intensity resonances, symmetrically displaced with respect to the central component, are present. These are due to hyperfine interaction, either with isotope ^{33}S , nuclear spin $I = 3/2$, in the sulfur case or isotope ^{77}Se , $I = 1/2$, for the selenium samples. The total intensity in these hyperfine lines corresponds to the presence of these nuclear-magnetic isotopes, which was an enrichment to 25% for ^{33}S and the natural abundance of 7.6% for ^{77}Se . This fact suggests the identification with the chalcogen atom. To verify this point the spectra were as well produced in silicon doped with sulfur enriched to 99.5% and selenium of 99.1%. In the resulting spectra, shown in the Figs 2 and 4, the central component has disappeared and all intensity has moved to the hyperfine components. The hypothesis of sulfur/selenium hyperfine interaction is thus confirmed. The centers contain just one chalcogen atom, since if two such atoms were present in the centers the spectra would have had a different structure. If the two atoms are on an equivalent site a typical hyperfine structure with a 1:2:1 intensity ratio between three equidistant components must be observed. As this is not the case the possibility of two-chalcogen centers has to be discarded, even if chalcogen pair centers are present before hydrogenation. The ratio between resonance amplitudes of the pairs of side lines is not a constant, rather it depends on sample preparation conditions. This is most apparent in the selenium case comparing Figs 3 and 4. A fast quench promotes the formation of the outer pair of hyperfine lines. Also for the sulfur case the effect is present but much less pronounced, suggestive for a more equal thermal stability of the centers. Following this observation of lacking correlation in the quantitative generation, the pairs of satellites are interpreted as belonging to different independent centers. For sulfur, they are labeled Si-NL54 for the quartet with the larger hyperfine splitting, and Si-NL55 for the quartet with smaller splitting, see Figs 1 and 2. In the selenium case, the outer pair of lines in Figs 3 and 4 correspond to center Si-NL60, whereas the inner pair belongs to Si-NL61. As the result of nearly equal g tensor the resonances corresponding to $m_I = 0$ spin states, coincide rather precisely in the central line. Related structure in this central line due to this overlapping of the two spectra is observed, but is not resolved in the standard EPR measurement.

Switching over to hydrogen, structure revealing the hyperfine interaction with the $I = 1/2$ nuclear spin is just visible only for the selenium-related Si-NL60 center (Fig. 4). Apparently any existing hydrogen-induced splitting is small and requires ENDOR for its observation. ENDOR transitions were indeed observed on the EPR of the central line in the proper frequency range. For the magnetic field $B \approx 816$ mT and for the proton with $(g_n)_H = 5.5857$ the nuclear resonance frequency $(\nu_Z)_H = (g_n)_H \mu_n B/h$ is near 34.7 MHz. As the inspection of Figs 5 and 7 shows the ENDOR is observed at frequencies shifted, by equal amounts as required, to higher and lower values by the hyperfine interaction. The similar set of ENDOR observation was made in deuterated samples with the results shown in Figs 6 and 8. With $(g_n)_D = 0.85744$ the frequencies properly scale by the factor $(g_n)_H/(g_n)_D = 6.5144$. In the deuterium case the number of transitions has doubled due to the nuclear spin $I = 1$ of this hydrogen isotope. The higher nuclear spin implies that also quadrupole interactions are measured in the experiment. ENDOR transitions were recorded as a function of magnetic field orientation, for both protons and deuterons, rotating the field in a (011) plane from [100] to [011]. Rotational patterns are given in Figs 9 and 10 for the sulfur and selenium centers, respectively. Only patterns of frequencies below $(\nu_Z)_H$ are shown, but the similar set of data above the Larmor frequency was just as well available. For the sulfur case two such patterns were observed, for selenium there are three patterns. Each pattern, measuring a specific interaction strength, corresponds to a distinct site of a hydrogen atom in the structure of the center. The difference in observed hydrogen tensors represents a major difference in the passivation process of sulfur and selenium.

As all ENDOR was observed on the central component of the EPR spectrum, with its insufficient resolution, the allocation of ENDOR patterns to the distinct EPR centers is still not established. To this end the method of field-scanned ENDOR, which provides such correlation, was applied. Locking the NMR frequency in an FSE experiment to a selected transition, i.e., to a specific

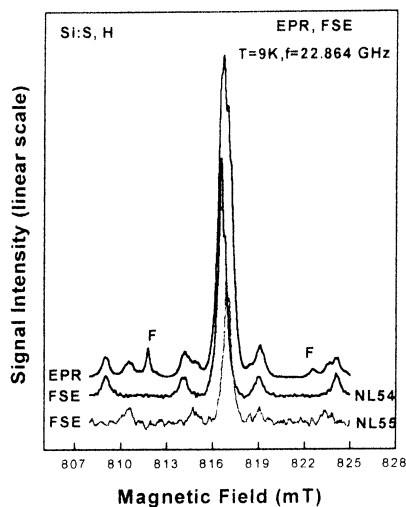


Fig. 1. EPR and FSE spectra Si-NL54 and Si-NL55 for $\mathbf{B} \parallel \langle 100 \rangle$. Sample doped with sulfur enriched to 25.5% in the ^{33}S isotope, nuclear spin $I = 3/2$.

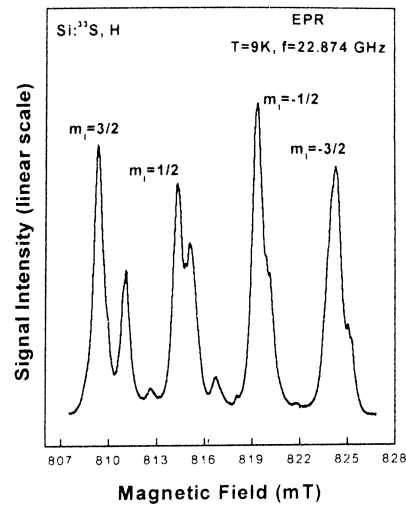


Fig. 2. EPR spectra Si-NL54 and Si-NL55 for $\mathbf{B} \parallel \langle 100 \rangle$. Sample doped with sulfur enriched to 99.5% in the ^{33}S isotope, nuclear spin $I = 3/2$.

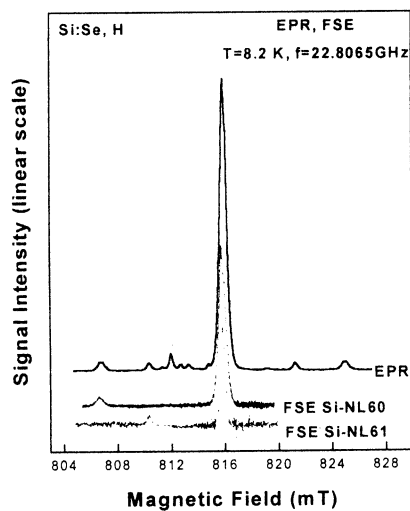


Fig. 3. EPR and FSE spectra Si-NL60 and Si-NL61 for $\mathbf{B} \parallel \langle 100 \rangle$. Sample doped with natural selenium with 7.6% of the isotope ^{77}Se , nuclear spin $I = 1/2$.

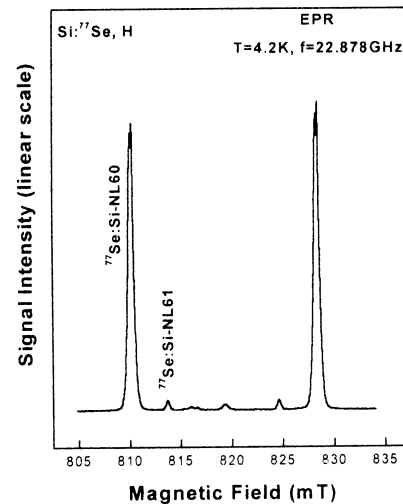


Fig. 4. EPR spectra Si-NL60 and Si-NL61 for $\mathbf{B} \parallel \langle 100 \rangle$. Sample doped with selenium enriched to 99.1% in the isotope ^{77}Se , nuclear spin $I = 1/2$.

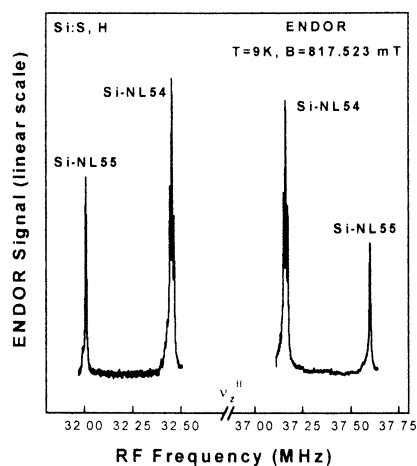


Fig. 5. Hydrogen ENDOR of EPR spectra Si-NL54 and Si-NL55 observed on transitions $m_l = 0$ at $B = 817.52\text{ mT}$, $B \parallel \langle 100 \rangle$. Zeeman frequency for hydrogen $(\nu_z)_H = 34.807\text{ MHz}$.

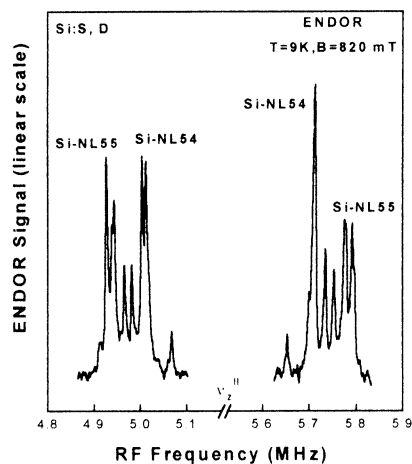


Fig. 6. Deuterium ENDOR of EPR spectra Si-NL54 and Si-NL55 observed on transitions $m_l = 0$ at $B = 820.03\text{ mT}$, $B \parallel \langle 100 \rangle$. Zeeman frequency for deuterium $(\nu_z)_D = 5.359\text{ MHz}$.

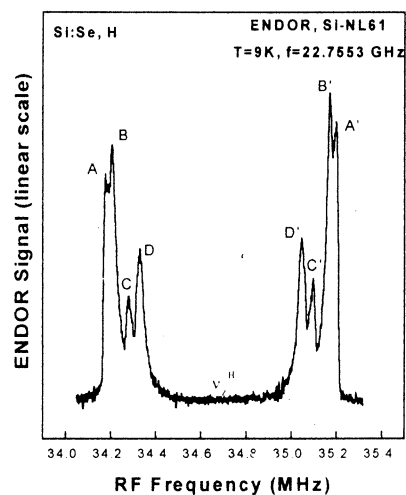


Fig. 7. Hydrogen ENDOR of EPR spectrum Si-NL61 observed on transitions $m_l = 0$ at $B = 814.812\text{ mT}$, $B \parallel \langle 011 \rangle$. Zeeman frequency for hydrogen $(\nu_z)_H = 34.693\text{ MHz}$.

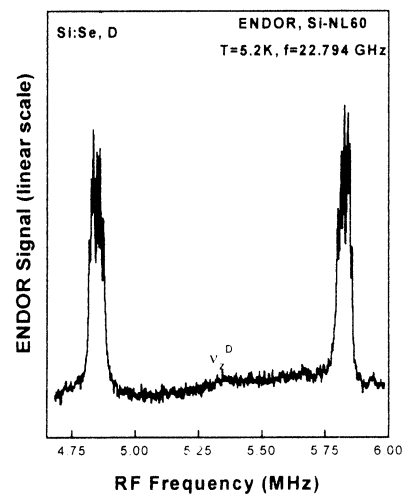


Fig. 8. Deuterium ENDOR of EPR spectrum Si-NL60 observed on transitions $m_l = 0$ at $B = 813.168\text{ mT}$, $B \approx 40^\circ$ away from $\langle 100 \rangle$. Zeeman frequency for deuterium 5.334 MHz .

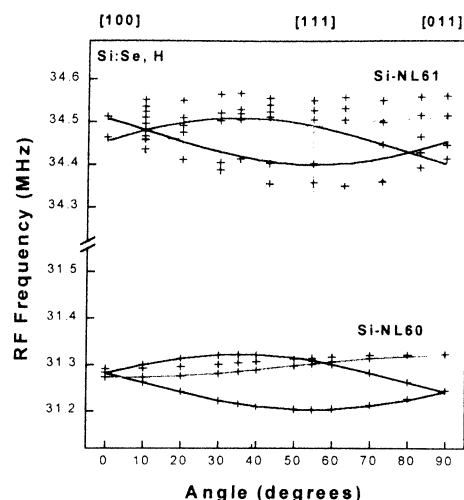


Fig. 10. Angular variation of the hydrogen ENDOR for the selenium-related spectra Si-NL60 and Si-NL61.

A quantitative analysis of these experimental data was made using a spin Hamiltonian, including all relevant spin-related energies: electron Zeeman energy, nuclear Zeeman energy for hydrogen/deuterium, hyperfine interaction with sulfur/selenium and hydrogen/deuterium, and quadrupole interaction for deuterium. All coupling tensors have the trigonal symmetry, as shown for the hydrogen ENDOR results in Figs 9 and 10. A summary of spin-Hamiltonian constants is given in Table 1. A more detailed presentation of data and discussion is given in Refs 6 and 7.

Spectrum	$g_{\parallel}$	$g_{\perp}$	(A _{S/se}) _#	(A _{S/se}) _⊥	(Q _s) _#	(Q _s) _⊥	(A _H) _#	(A _H) _⊥
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 1.020	0.816 0.735

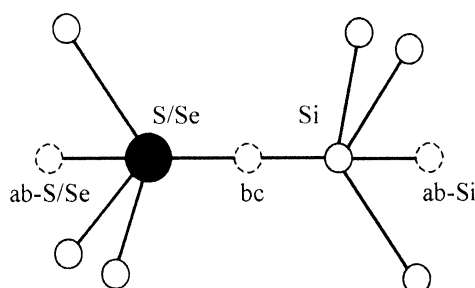


Fig. 11. Atomic structure model for the chalcogen-hydrogen centers. Possible positions for the hydrogen atom are indicated by bc for a bond-centered site, ab-S/Se for an anti-bonding site next to the chalcogen atom and ab-Si for the silicon anti-bonding site.

Atomic model

All tensors reflecting interactions with the defect electron and nuclei involved have the trigonal symmetry. Specifically, this applies to the g tensor and the chalcogen hyperfine interaction. As there is only one chalcogen atom in the centers, this atom must have its position on the $\langle 111 \rangle$ axis of the center. In all known cases chalcogen atoms in silicon occupy a substitutional lattice site. This is assumed to be also the case for the complexes with hydrogen. 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. Such a linear model is shown in Fig. 11. The 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 results from advanced theoretical calculations are required to unambiguously conclude on the actual positions taken by the hydrogen atoms.

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