

Magnetic resonance spectroscopy of hydrogen-passivated double donors in silicon

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Abstract

The microscopic aspects of hydrogen passivation of two double donor centers in silicon—substitutional sulfur and thermal donor—were investigated by the electron paramagnetic and electron nuclear double-resonance techniques. The passivation process was found to result in the formation of complexes involving a double donor and one hydrogen atom. Such complexes have single donor character and are therefore paramagnetic in their neutral charge state.

Keywords: Silicon; Hydrogen

1. Introduction

The influence of hydrogen doping on the characteristics of silicon single crystals is currently receiving much interest. This follows from the notion that hydrogen is easily introduced in a variety of ways, which include some standard techniques as used in silicon device manufacturing. It has been found that on interaction with (atomic) hydrogen the electrical activity of all kinds of impurities can be terminated. This process, known as passivation, was first reported by Pankove et al. [1] for shallow acceptors in silicon. Also hydrogen passivation of deep impurities, and among them double donor (DDs), has been reported. It is possible to imagine that a double donor may be passivated with one or two hydrogen atoms. This could create the situation that a passivated center would be accessible to magnetic resonance spectroscopy, since a singly passivated double donor in its neutral charge state would be paramagnetic with spin $S = 1/2$.

The effect of (hydrogen) passivation is also expected to be visible in IR absorption. Here, on passivation with one hydrogen atom, both effective mass theory (EMT) series of electronic transitions should vanish and, simultaneously, a new series of single-donor transitions should appear. In addition to these IR spectroscopy may reveal local vibrational modes of hydrogen atoms bonded within the complex. In this paper we report on EPR (electron paramagnetic reso-

nance), ENDOR (electron nuclear double resonance) and IR absorption investigations of two double-donor centers in silicon: substitutional sulfur and thermal donor (TD). The passivation effect for both centers has been observed earlier; the aim of the current study is to elucidate microscopic structural aspects of the impurity complexes formed during the passivation process.

2. Sulfur–hydrogen complexes

In the past chalcogen impurities in silicon and complexes between them have been subjected to intensive investigations. Among these isolated S and the S–S pair have been identified by EPR–ENDOR and DLTS (deep level transient spectroscopy). In particular Pensl et al. [2] reported on a variety of double-donor levels related to isolated chalcogens and their complexes. These could be passivated by exposure to hydrogen plasma. The kinetics of the passivation process was shown to be consistent with the participation of a single hydrogen atom. Theoretical analysis of the sulfur passivation process has been considered by Yapsir et al. [3], who examined various configurations of S–H and S–H₂ complexes. For the S–H defect the lowest-energy configuration was found with the hydrogen atom in a distorted bond-centered position of monoclinic symmetry, while local minima were also found for both antibonding positions of hydrogen on sulfur and the

nearest-neighbor silicon atoms respectively. It was further concluded that in an environment with an excess of sulfur the sulfur–hydrogen pair would be preferentially created. More recently the hydrogenation of sulfur donors was also investigated using IR absorption spectroscopy by Peale et al. [4]. They observed electronic transitions of new sulfur–hydrogen complexes of a single EMT donor character; these were apparently created on hydrogen passivation of sulfur-related double donors. The newly found centers were identified as singly passivated species and were suggested to be paramagnetic in their neutral charge state.

In the current study we used n-type, phosphorus-doped silicon of float-zoned (FZ) and Czochralski-grown (Cz) types. The samples were first diffused with sulfur (1370 °C, 48 h), subsequently with hydrogen or deuterium (1250 °C, 1/2 h), and finally quenched to room temperature. The EPR measurements on thus prepared samples revealed the presence of two new $S = 1/2$ EPR spectra [5]. These, labeled further Si-NL54 and Si-NL55, were partly overlapping and could be resolved only by the field-scanned ENDOR (FSE) technique. The observed spectra showed splitting in two components indicating the hyperfine interaction with hydrogen. This was confirmed by ENDOR measurements where spectra symmetric with respect to the Zeeman frequency of a free proton were observed. The involvement of hydrogen in the newly reported centers is also consistent with the measurements on samples doped with deuterium. Using the hydrogen hyperfine interaction the EPR spectra of Si-NL54 and Si-NL55 centers could be separated and their angular dependences, as depicted in Fig. 1, were measured. Both spectra have the same $\langle 111 \rangle$ axial symmetry but with a somewhat different degree of anisotropy. In order to establish conclusively the participation of sulfur in the Si-NL54 and Si-NL55 centers, samples doped with isotopically enriched sulfur (25% ^{33}S , $I = 3/2$) were also prepared. The EPR spectra recorded for these samples displayed a clearly resolved hyperfine interaction with one sulfur nucleus.

Based on the current results we identify the Si-NL54 and Si-NL55 centers as two configurations of a sulfur–hydrogen pair, i.e. a substitutional sulfur (double) donor passivated by one hydrogen atom. Consistent with the $S = 1/2$ spin value we assign the spectra to the neutral charge state of such a complex. Our identification is supported by IR absorption measurements carried out on the sample used for the magnetic resonance experiment. The observed spectrum, as depicted in Fig. 2, reveals the presence of the characteristic $1s \leftrightarrow 2p$ electronic transitions assigned earlier to the S–H donors [4]. The proposed substitutional position of sulfur follows rather naturally from the studies on isolated sulfur and also from the donor character of the observed centers. Following the experimental findings

the position of the hydrogen atom has to be along a $\langle 111 \rangle$ direction with respect to sulfur. This leaves three possibilities: bond-centered (BC), and two antibonding (AB) sites on S and on a nearest-neighbor Si respectively. We note here that our results do not support the conclusions of Yapsir et al. [3] who predicted a distorted BC site for hydrogen in the S–H complex. However, they are consistent with the first-order kinetics of sulfur donor passivation, as concluded from the DLTS studies.

3. Thermal donor–hydrogen complexes

TDs are among the most complicated defect centers in silicon and an established model of their microscopic structure is still lacking. Among many techniques, magnetic resonance spectroscopy has also been used to study these centers. As a result two EPR spectra,

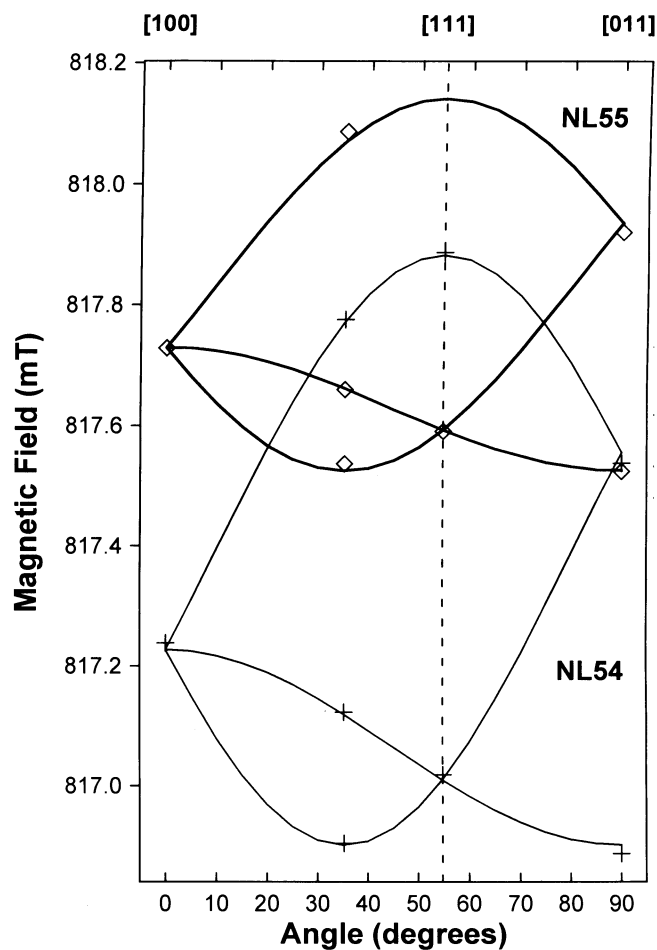


Fig. 1. Angular dependence of the FSE spectra of Si-NL54 and Si-NL55 centers observed in the sample diffused with hydrogen and natural sulfur. Experimental data averaged over the hydrogen hyperfine splitting are used together with a simulation based on a computer fit. The measurements were taken at a microwave frequency $\nu = 22.8809$ GHz.

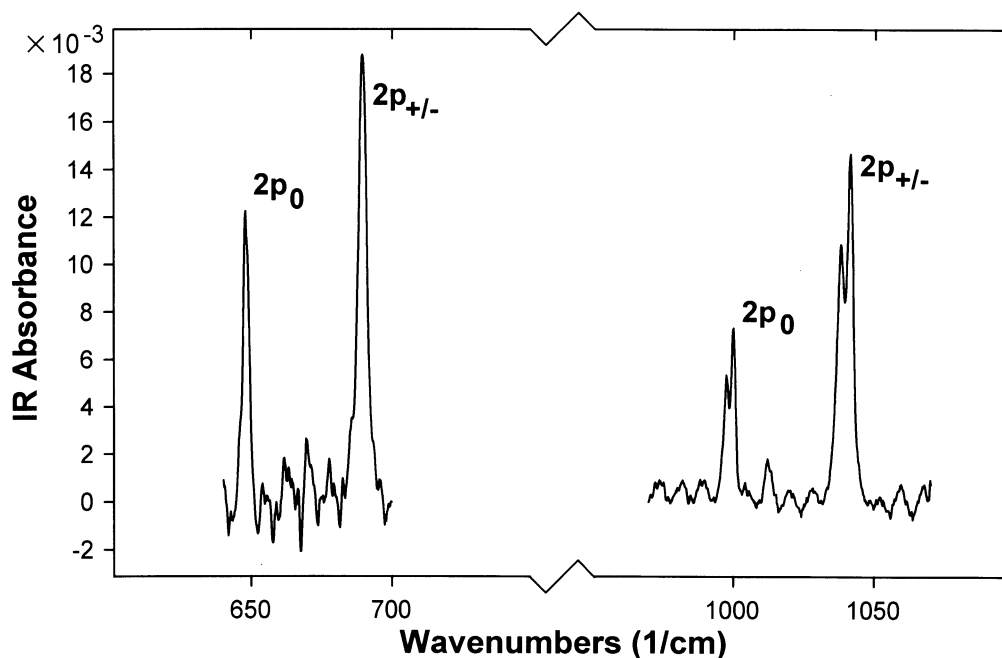


Fig. 2. IR absorption spectrum for the sample doped with hydrogen and natural sulfur, for which Si-NL54 and Si-NL55 EPR spectra were observed. The $1s \leftrightarrow 2p$ transitions as observed also by Peale et al. [4] are indicated. The measurements were taken at a temperature $T = 8$ K and with a resolution of 1 cm^{-1} . The sample thickness was 1.8 mm.

Si-NL8 and Si-NL10, both of orthorhombic-I symmetry are now associated with TDs. The first, Si-NL8, has been identified as a singly ionized state TD^+ ; the microscopic identification of the Si-NL10 center is still debated [6].

The influence of hydrogen on TDs was investigated and their passivation has been reported [7]. Also an enhanced TD formation for Cz-Si exposed to hydrogen plasma has been observed [8]. A possible explanation of the latter effect was offered by Estreicher [9]. The proposed mechanism involved enhanced oxygen diffusion mediated by atomic hydrogen. If true, this would allow for a situation in which the formation of a donor center and its passivation are accomplished in a single step.

Being aware of the above findings we undertook to investigate a possible involvement of hydrogen in the structure of the Si-NL10 center. In a sample with a strong Si-NL10 signal but not intentionally doped with hydrogen we have indeed detected a new ENDOR spectrum which appeared to be symmetric with respect to the Zeeman frequency of a free proton [10]. By recording the ENDOR spectra for different resonance field values and monitoring the frequency shift, further evidence for hydrogen being responsible for the detected hyperfine interaction was obtained. Having established that, we intentionally doped a series of samples with hydrogen following the procedure described earlier for sulfur. In all thus prepared samples a

similar hydrogen ENDOR spectrum was observed. By the FSE technique the ENDOR spectrum was found to be a superposition of independent components related to different Si-NL10 species. The angular dependence of the hydrogen ENDOR was studied in a hydrogen-doped Cz-Si:P sample and is depicted in Fig. 3. Preliminary analysis revealed in this case the presence of two similar hyperfine tensors of triclinic symmetry; they could be assigned to two different Si-NL10 species. The hyperfine interaction was found to be very small explaining that its presence could not be observed in an EPR experiment.

The presence of a hydrogen component poses again the question of the microscopic structure of the Si-NL10 center and its relation to TDs. From the current measurements we conclude that hydrogen plays an important role. A crucial point for the microscopic identification of the Si-NL10 center is the number of hydrogen atoms involved. Such information can be deduced from symmetry considerations of EPR and ENDOR spectra. As already mentioned, the symmetry of the hydrogen ENDOR shell has been established as triclinic. In order to determine the number of hydrogen atoms participating in the structure of the center it is necessary to establish (with the same precision) the real symmetry of the corresponding EPR spectrum. The FSE experiment based on the hydrogen hyperfine interaction showed the presence of an unresolved splitting of the EPR spectrum indicating its true triclinic symmetry.

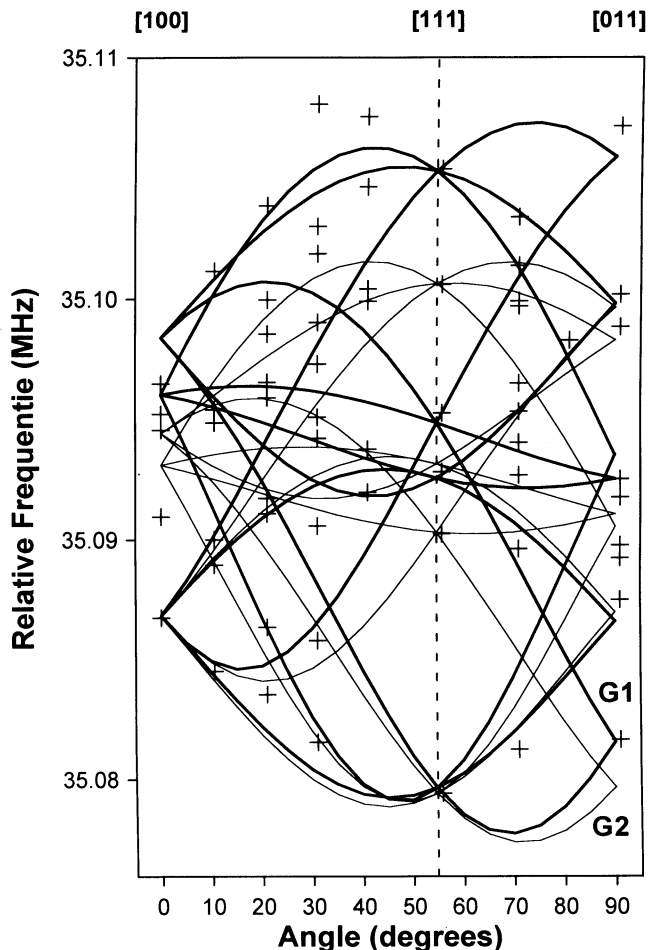


Fig. 3. Angular dependence of the hydrogen ENDOR spectra observed for a Cz-Si:P sample after 470 °C, 64 h heat treatment: + represent experimental points, bold and thin lines represent simulation for two different tensors, G_1 and G_2 , corresponding to individual Si-NL10 species.

Based on this result we conclude that only a single hydrogen atom is present in the structure of the defect. The current findings allow us to identify the Si-NL10 center as the neutral charge state of a singly passivated TD. Such an identification is consistent also with all the reported characteristic features of the Si-NL10 structure and its similarities with Si-NL8 [6].

4. Conclusions

We have shown that the passivation process of the double donor centers in silicon may proceed via the formation of DD-H pairs which have single-donor character and are therefore paramagnetic in their neutral charge state. Two examples of such complexes, S-H and TD-H pairs, were detected and studied by EPR-ENDOR and also IR spectroscopies. We note that, although similar in nature, both complexes must differ significantly in the detailed bonding configuration of hydrogen, as evidenced by their different thermal stability.

Acknowledgments

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