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ENDOR IDENTIFICATION OF A HYDROGEN-PASSIVATED THERMAL DONOR

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Abstract. Microscopic evidence of a prominent role of hydrogen in the structure of the Si-NL10 thermal donor (TD) is presented. Hyperfine interactions with the ^{1}H nucleus have been detected and analyzed by means of electron-nuclear double resonance (ENDOR). It has been established that the Si-NL10 defect incorporates one hydrogen atom. In deuterium-doped samples also the quadrupole interaction with the ^{2}H nucleus has been measured. On the basis of these measurements the direction of the bond formed by deuterium was concluded to be perpendicular to the $\langle 011 \rangle$ oxygen-containing symmetry plane of a TD. Based on the current results the Si-NL10 center was identified with a singly passivated TD in its neutral charge state.

Introduction

Thermal donors (TDs) are among the most challenging subjects in the defect physics of silicon. These centers, occurring after a heat treatment (HT) of Czochralski-grown silicon (Cz-Si) in the temperature range of 400-500°C, have been discovered in 1954 [1] but even now they lack satisfactory microscopic identification. Infrared absorption measurements revealed up to 17 different species of double-donor, effective-mass character [2]. Two prominent electron-paramagnetic-resonance (EPR) spectra of the same orthorhombic symmetry, labeled Si-NL8 and Si-NL10, were shown to be related to the TDs [3]. An electron-nuclear double resonance (ENDOR) study revealed interactions with oxygen for both centers [4, 5] and their local oxygen structure appeared to be identical. On the basis of the study of its alignment under uniaxial stress the Si-NL8 spectrum has been identified with a $(\mathrm{TD})^+$ charge state [6]. A microscopic identification of the Si-NL10 center was still unclear. The major problem follows from the fact that, when created in Al-doped material, the defect displays hyperfine (HF) interactions with Al, while in other materials no interactions either with residual Al or with other dopants have been found; the same defect can then either have an Al atom as a part of its structure or be created without it and still give rise to the same EPR spectrum.

In the past few years a very important role of hydrogen in the formation of defects in silicon has been recognized. It has been established that hydrogen can easily be introduced in silicon as a contamination, for example, during the crystal growth or by etching (for a recent review, see [7]). It has been found that hydrogen can significantly enhance oxygen diffusion and the rate of TD formation [8]. Recently also a series of hydrogen-related donors was found in Cz-Si after hydrogenation and heat treatment at 350°C [9].

Experiment

The samples for this study were prepared from *p*- and *n*-type Cz-Si with various dopants. The concentration of interstitial oxygen in all starting materials was about 1.2×10^{18} cm^{-3}. The

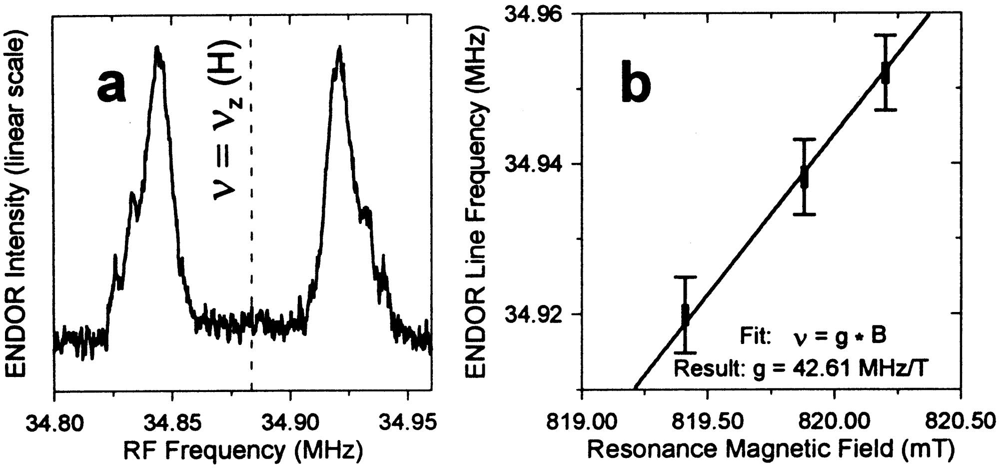

Figure 1: *Hydrogen ENDOR spectrum observed in a Cz-Si:Al sample after 470°C/55h HT. (a) - spectrum, recorded with* $\vec{B} \parallel \langle 110 \rangle$ *direction; (b) - displacement of the ENDOR line as a function of the magnetic field shift, fitted with a linear function. The value of the proportionality coefficient is equal within the experimental accuracy to the nuclear Zeeman frequency of a proton* $\nu(MHz)=42.5758B(T)$.

samples were diffused by hydrogen or deuterium in (heavy) water vapor atmosphere at 1250°C for 30 minutes and then rapidly quenched to room temperature. This procedure also served to disperse interstitial oxygen to ensure uniform starting conditions. Subsequently to the quench the samples were annealed at 470°C for various periods of time. An identical set of samples was given the same HT in (intentionally) hydrogen-free environment. The measurements were performed in a K-band EPR/ENDOR spectrometer in dispersion mode at a temperature of about 6.8-7 K, which appeared to be optimal for the ENDOR experiment. During the experiment the sample could be illuminated by white light in order to increase EPR intensity.

Results

Hydrogen ENDOR. In all the samples diffused with hydrogen as well as in most of the control samples we observed a new ENDOR spectrum. The spectrum (see Fig. 1(a)) is symmetrical with respect to the Zeeman frequency of a free proton. By recording ENDOR spectra for different resonance magnetic field values and monitoring the frequency shift (Fig. 1(b)), we unambiguously identify hydrogen as being responsible for the detected HF interaction.

The angular dependence of the hydrogen ENDOR has been studied. In all the samples we observed two similar HF tensors of a triclinic symmetry, labelled H-*G*1 and H-*G*2. In a Cz-Si:In sample the intensity of the H-*G*2 tensor was higher than that of H-*G*1 allowing accurate determination of its parameters (see Table I). The isotropic part of the HF tensor is proportional to the localization of the paramagnetic electron on hydrogen. Using the parameters of the hydrogen 1*s* wave function, we arrive at the localization $\eta \approx 6 \times 10^{-3}\%$. Extremely small as it may appear, the value of localization is, nevertheless, comparable to that found for oxygen [10].

Symmetry of the Si-NL10 center. The triclinic symmetry of the Si-NL10 hydrogen HF interaction is lower than that of its EPR g-tensor; the latter was concluded to be orthorhombic [3]. Generally, that would mean that the hydrogen shell contains four nuclei on equivalent sites.

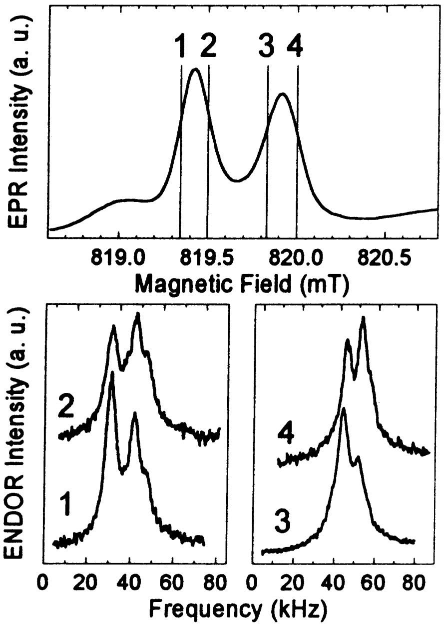

Figure 2: *Determination of the true symmetry of the Si-NL10 defect. Top panel - EPR spectrum with $\vec{B} \parallel \langle 111\rangle$ direction. Vertical lines, numbered 1 to 4 indicate the magnetic field values where ENDOR spectra were recorded. Bottom left and bottom right panels present ENDOR spectra, recorded on low-field- and high-field EPR lines respectively and plotted with respect to the Zeeman frequency of a proton. When the magnetic field is shifted from the value 1 to the value 2 the intensity ratio of the two ENDOR peaks in the spectrum changes, indicating that these peaks are due to two distinct EPR lines. The same holds for the ENDOR spectra, recorded with the magnetic field values 3 and 4. In total the EPR spectrum in the $\langle 111\rangle$ direction consists of 4 lines and thus has triclinic symmetry.*

However, in EPR a small triclinic distortion of the otherwise almost orthorhombic tensor can easily be missed due to the insufficient resolution of this technique. We can now use a higher resolution of Field-Stepped ENDOR (FSt-ENDOR) to determine the actual symmetry of the Si-NL10 center. The measurements were carried out for $\vec{B} \parallel \langle 111\rangle$. The EPR spectrum in this direction consists of two lines, each of them giving rise to two ENDOR peaks. Changes of relative intensities of the peaks in ENDOR spectra upon shifting of the magnetic field were observed for both EPR lines (see Figure 2) which serves as an indication that these two peaks correspond to two unresolved EPR lines with slightly different positions of maximum intensity. Thus we conclude that the symmetry of the Si-NL10 is, in fact, triclinic and each defect contains only one hydrogen atom.

Deuterium ENDOR. While the HF interaction carries the information about the symmetry of the whole center, the quadrupole interaction is determined by electric field gradient and can therefore be indicative for local arrangements around the magnetic nucleus. To study these the samples doped with deuterium were prepared. Deuterium has a nuclear magnetic spin $I = 1$ and, consequently, a quadrupole moment. If such a nucleus is placed in an inhomogeneous electric field additional energy splitting, detectable in an ENDOR experiment, can occur. In the sample treated in a heavy-water-vapor atmosphere an ENDOR spectrum, symmetrical with respect to the nuclear Zeeman frequency of a deuteron, was observed. This, together with the notion that the spectrum was only found in the samples treated in a D_2O atmosphere allows us to identify deuterium as being responsible for the observed interaction. The angular dependence of deuterium ENDOR was measured (see Figure 3). It was fitted with an isotropic HF and an orthorhombic quadrupole term with the parameters as summarized in Table I.

In view of the high magnitude of the quadrupole interaction we neglect the contribution of the paramagnetic electron and in a usual manner [10] interpret this interaction as arising from the unbalanced charge density on the deuteron which, in turn, is determined by the bond(s) that deuterium is forming with neighboring atom(s). The quadrupole interaction tensor

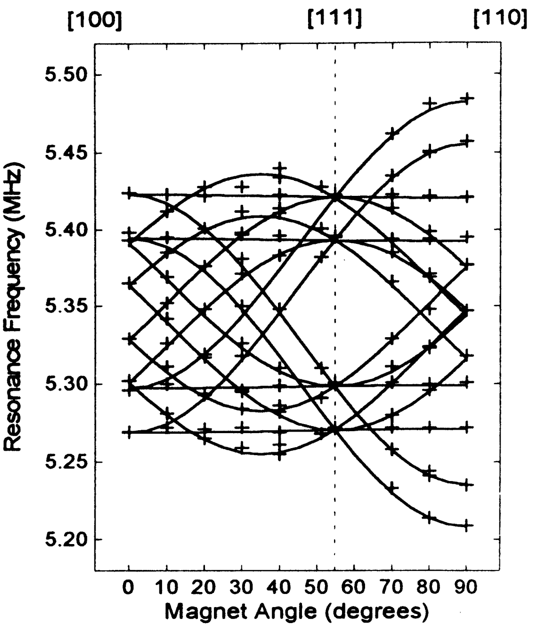

Figure 3: *Angular dependence of ENDOR line positions of Si-NL10 in Cz-Si:In sample, treated 1/2 h at 1250°C in D_2O atmosphere and annealed 42 h at 470°C. + represent experimental points; solid lines are computer simulation with the parameters as summarized in Table I.*

appears to be almost axial, consistent with the expectation that hydrogen would form a single bond. However, the direction of the tensor axis (and therefore of the bond) is very surprisingly along $\langle 011 \rangle$ crystalline direction, perpendicular to the oxygen-containing symmetry plane (see Table I).

Discussion

In the light of the new findings we propose to identify the Si-NL10 center as a neutral thermal double donor with one of its two electrons passivated by hydrogen. Upon passivation the symmetry of a TD is lowered from C_{2v} to C_1. In this model Si-NL8 and Si-NL10 would have an identical oxygen core, determining their symmetry and HF interactions with the ^{17}O nucleus. However, the fact that one of the TD electrons is passivated, and not lost to the conduction band, would mean that the remaining electron is weaker bound than in the case of the $(TD)^+$ state that gives rise to the Si-NL8 spectrum.

Finally, we come back to the question of aluminum incorporation in the Si-NL10 center. So

Nucleus	Shell	Tensor	i	T_i (kHz)	$\mathbf{n}_i$
^1H	H-$G2$	A	1	55.2	(0.681, 0.652, 0.333)
			2	101.8	(-0.371, 0.700, -0.610)
			3	83.4	(-0.631, 0.292, 0.719)
^2H	D-$T1$	A		28	
		Q	1	-41.8	(1.000, 0.000, 0.000)
			2	-40.5	(0.000, -0.707, 0.707)
			3	82.3	(0.000, 0.707, 0.707)

Table I: *The principal values and the associated eigenvectors of the HF and quadrupole tensors, as obtained from the measurements on the Cz-Si:In samples, doped with hydrogen or deuterium. The format is similar to that used in Ref. [10].*

far aluminum was the only nucleus having a characteristic HF interaction with the paramagnetic electron of the Si-NL10 defect, apart from silicon and oxygen. Following the current result the roles of aluminum and hydrogen in the defect structure seem, somehow, similar. An aluminum atom can be removed from its substitutional position by a self-interstitial, created during the process of oxygen aggregation. Once made interstitial, aluminum, similar to hydrogen, is a fast diffuser. It would be able to diffuse towards the core of a TD, where it might eventually compensate one of the two TD's electrons.

Conclusions

Summarizing, we have observed the hydrogen HF interaction of the Si-NL10 defect in (hydrogen-diffused) crucible-grown silicon. By performing a FSt-ENDOR experiment we have established that the actual symmetry of the center is triclinic and that it contains one hydrogen atom. From the study of the quadrupole interaction with deuterium we have concluded that this atom forms a single bond perpendicular to the oxygen-containing $\langle 011 \rangle$ symmetry plane of the center. We propose a possible structural model of the Si-NL10 center, identifying it with a singly passivated thermal double donor. With the current finding the problem of the mutual relation between the Si-NL8 and Si-NL10 EPR spectra and thermal donors in silicon appears to be resolved.

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