

Role of Hydrogen in the Formation and Structure of the Si-NL10 Thermal Donor

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Microscopic evidence of a prominent role of hydrogen in the formation and structure of the Si-NL10 thermal donor is presented. Hyperfine interactions with the ^1H nucleus have been detected and analyzed by means of electron-nuclear double resonance (ENDOR) and field-scanned ENDOR. Based on the current results an identification of the Si-NL10 center as a singly passivated state of the thermal donor in its neutral charge state is proposed.

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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, were discovered in 1954 [1], but even now they lack satisfactory microscopic identification, although several experimentally based models have been proposed [2,3] and the issue has been thoroughly investigated theoretically [4,5]. Infrared and electrical measurements [6,7] revealed numerous (up to 17) different species of double-donor effective-mass character. Recently also vibrational modes of TD species have been finally identified [8]. 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 TD [9]. An electron-nuclear double resonance (ENDOR) study revealed interactions with oxygen for Si-NL10 [10] and later for Si-NL8 defect [11]. On the basis of production conditions and identical local oxygen structure, as established in ^{17}O ENDOR experiments, it has been suggested [12] that these defects are closely related. The g tensor of the Si-NL10 defect is less anisotropic than that of the Si-NL8 spectrum, suggesting that the paramagnetic electron binding of the Si-NL10 defect is weaker. On the basis of the study of its alignment under uniaxial stress the Si-NL8 spectrum has been identified with a $(\text{TD})^+$ charge state [13]. A microscopic identification of the Si-NL10 defect is still unclear. The major problem follows from the fact that, when created in Al-doped material, the defect displays hyperfine interactions with aluminum, while in other materials no interactions either with residual aluminum or with other dopants have been found; the same defect can then either have an aluminum atom as a part of its structure or be created without aluminum and still give rise to the same EPR spectrum.

In this situation an identification of the Si-NL10 spectrum with the negative charge state of TD [12] has been put forward. Although certainly plausible and capable to account for the spin value $S = 1/2$ and shallow character of the center, such an identification requires that the same center would have four different charge states in the band

gap of silicon—a rather improbable situation among the known defects (see discussion in Ref. [12]).

In the past few years a very important role of hydrogen in the formation of defects in silicon has been recognized. Moreover, 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 [14]). It has been found that hydrogen can significantly enhance oxygen diffusion and the rate of TD formation [15]. Recently it was also reported that hydrogen-plasma treatment of neutron-irradiated silicon leads to the formation of shallow donor centers [16]. Another series of hydrogen-related donors was found in Cz-Si after hydrogenation and heat treatment at 350 °C [17].

Being aware of these findings we decided to investigate the possible involvement of hydrogen in the structure of the Si-NL10 center. In a sample with a strong Si-NL10 EPR signal we have indeed detected a new ENDOR spectrum. Because the nuclear g value of a proton differs from that of the other magnetic nuclei, the new ENDOR lines appear in a different frequency region and require very different experimental conditions than the ones used in the previous study [18]. The observed ENDOR spectrum [see Fig. 1(a)] is symmetrical with respect to the Zeeman frequency of a free proton. By recording ENDOR spectra for different resonance field values [field-stepped ENDOR (FSE), see Ref. [10] for the details of the technique] and monitoring the frequency shift [Fig. 1(b)], we unambiguously identify hydrogen as being responsible for the detected hyperfine interaction (an example of such an identification can also be found in Ref. [19]). It should be emphasized that hydrogen has *not* been intentionally introduced into this material. In order to further investigate the influence of hydrogen on the formation of Si-NL10 centers, we prepared a series of samples intentionally doped with hydrogen. The samples were prepared from Cz-Si of four kinds. The first three were standard Cz-Si crystals: p type Al doped with room-temperature resistivity $\rho = 2.8\text{--}5.0\ \Omega\text{ cm}$; p type B doped, $\rho = 1.3\text{--}5.0\ \Omega\text{ cm}$; and n type P doped $\rho = 0.75\text{--}1.25\ \Omega\text{ cm}$. The concentration of interstitial oxygen in all three materi-

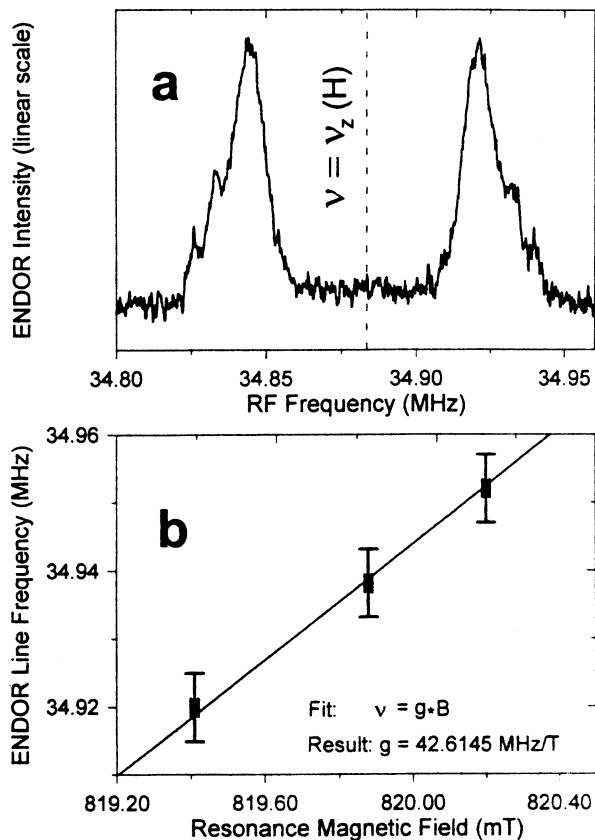


FIG. 1. The hydrogen ENDOR spectrum observed in a Cz-Si:Al sample after 470 °C/55 h HT. (a) Spectrum, recorded with $\vec{B} \parallel \langle 110 \rangle$ direction, $B = 819.324 \text{ mT}$; (b) displacement of the ENDOR line as a function of the magnetic field shift, fitted with a linear function. The value of the proportionality coefficient is equal within the experimental accuracy to the nuclear Zeeman frequency of a proton $\nu(\text{MHz}) = 42.5758B(\text{T})$.

als was about $1.2 \times 10^{18} \text{ cm}^{-3}$. The fourth material was high-resistivity boron-doped Cz-Si crystal, doped in the melt with nitrogen ($[O_i] = 8.7 \times 10^{17} \text{ cm}^{-3}$; $[N] = 1.4 \times 10^{15} \text{ cm}^{-3}$), kindly provided by Dr. P. Wagner of Wacker Heliotronic GmbH. The interest in N-doped silicon was stimulated by the works of Hara *et al.* [20] where the observation of paramagnetic defects, similar to Si-NL10, in nitrogen-diffused Cz-Si has been reported. The samples were sealed in quartz ampoules, containing argon atmosphere and a few milligrams of water. An identical set of samples without any water in the ampoules was also prepared. All the samples, with or without water, were subjected to a standard procedure of heat treatment at 1250 °C, followed by a quench to room temperature. This procedure served to disperse interstitial oxygen to ensure uniform starting conditions and/or to diffuse hydrogen. Subsequent to the quench the samples were annealed at 470 °C for various periods of time. 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.

In all the samples diffused with hydrogen, an ENDOR spectrum, similar to that depicted in Fig. 1(a), was observed. Its traces were also observed in almost all the samples that were not intentionally diffused with hydrogen, confirming the hydrogen contamination of commercially available high-grade silicon [17].

In the N-doped sample no nitrogen ENDOR was observed. Therefore, we conclude that nitrogen is not a part of the Si-NL10 defect structure. However, in this material, and also in Cz-Si:P samples, a very strong hydrogen ENDOR could be seen even for the samples prepared in a dry environment. We conclude that these materials were very effectively contaminated with hydrogen during the crystal growth. It is also plausible that in Cz-Si:Al or Cz-Si:B material, where the concentration of acceptors was higher, the contaminative hydrogen passivated them. Therefore, in the Cz-Si:P and Cz-Si:N samples more hydrogen was available for Si-NL10 formation.

The multispecies character of the Si-NL10 defect was established in Ref. [18]. We performed FSE studies of Si-NL10 in a hydrogen-diffused Cz-Si:Al sample. In this technique (also known as ENDOR-induced EPR [21]) one obtains the EPR "image" of a center responsible for a certain ENDOR line. We could resolve two species with different anisotropy of a g tensor related to different hydrogen ENDOR lines [see Fig. 2(a)]. It can also be seen from the same figure that the hydrogen-containing EPR species have a higher anisotropy of the g tensor than that of the net EPR spectrum. This means that not all of the Si-NL10 defects in aluminum-doped material are hydrogen-containing. In the same sample ^{27}Al FSE revealed the species with lower anisotropy [see Fig. 2(b)].

The angular dependence of the hydrogen ENDOR was studied in hydrogen-doped Cz-Si:P. While the detailed analysis is still in progress we were already able to identify at least two similar hyperfine tensors of a (most probably) triclinic symmetry with the parameters as listed in Table I. In view of the small value of the hyperfine interaction it is understandable that it cannot be observed in EPR. The isotropic part of the hyperfine tensor is proportional to the localization of the paramagnetic electron on hydrogen. Using the parameters of the hydrogen $1s$ wave function, we arrive at the localization $\eta \approx 6 \times 10^{-3}\%$ for both species. Extremely small as it may appear, the value of localization is, nevertheless, comparable to that found for oxygen [18]. That means that hydrogen plays an important role in the Si-NL10 defect structure.

As mentioned in the introduction the identification of Si-NL10 is an issue of a considerable dispute. The current finding adds here an important clue. The earlier revealed features of Si-NL10 include the following: (1) the center is closely related to TDs; (2) it is created subsequently to Si-NL8; (3) its oxygen structure is identical to that of Si-NL8; (4) the electron spin value is $S = 1/2$; and (5) the

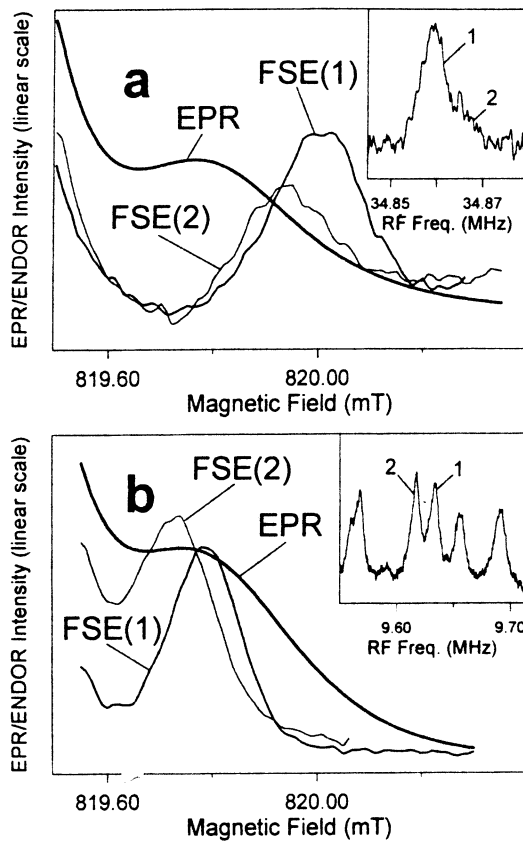


FIG. 2. The hydrogen (a) and aluminum (b) FSE spectra in a Cz-Si:Al sample after hydrogen diffusion and $470^{\circ}\text{C}/55$ h HT, compared to the EPR spectrum. Shown in the insets are fragments of the respective ENDOR spectra, two lines of which (1 and 2) were used to make FSE scans. $T = 7$ K, $\nu = 22.923$ GHz, $\vec{B} \parallel \langle 110 \rangle$.

wave function of the Si-NL10 paramagnetic electron has a more shallow character than that of Si-NL8.

Consistent with the above-listed features and in light of the new finding we propose to identify the Si-NL10 center as a neutral thermal double donor with one of its two electrons passivated by hydrogen, rather than with a $(\text{TD})^{-}$ state [12]. In this model Si-NL8 and Si-NL10 would have an identical oxygen core, determining their symmetry and hyperfine 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

TABLE I. Hyperfine parameters for the fitted hydrogen tensors. The format is similar to that used in Ref. [18].

Tensor	i	A_i , kHz	\mathbf{n}_i
H-G1	1	55.0	(0.727, 0.606, 0.322)
	2	114.7	(-0.280, 0.690, -0.667)
	3	84.3	(-0.627, 0.395, 0.672)
H-G2	1	54.3	(0.735, 0.616, 0.286)
	2	103.4	(-0.392, 0.729, -0.562)
	3	84.3	(-0.554, 0.301, 0.777)

mean that the remaining electron is weaker bound than in the case of the $(\text{TD})^{+}$ state that gives rise to the Si-NL8 spectrum.

To follow on our hypothetical identification we have studied the influence of hydrogen on the formation of both Si-NL8 and Si-NL10 spectra. In this case we used B-doped material, where the process of Si-NL10 formation is known to be rather slow [9]. The intensities of the Si-NL8 and Si-NL10 spectra in hydrogen-diffused and hydrogen-free Cz-Si:B samples were studied for various annealing times. In the samples diffused with hydrogen, the production of the Si-NL10 spectrum was significantly enhanced, while the formation of Si-NL8 was suppressed [see Fig. 3]. We also could not detect any hydrogen ENDOR on the Si-NL8 spectrum. This brings us to the conclusion that hydrogen is not involved in the Si-NL8 defect formation, consistent with its assignment to $(\text{TD})^{+}$ and in line with the infrared absorption measurements [17].

Being a dominant defect in Cz-Si after prolonged HT, a singly passivated TD should manifest itself in a series of infrared-absorption lines due to transitions to the excited states of a shallow single donor and possibly already has been observed [17].

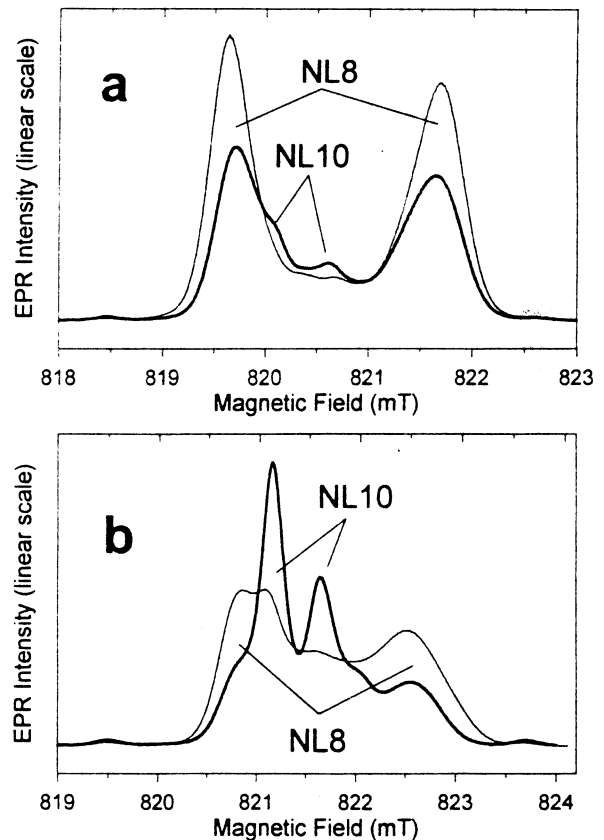


FIG. 3. The influence of hydrogen on the intensity of Si-NL10 and Si-NL8 EPR spectra in Cz-Si:B silicon after 11.5 (a) and 64 h (b) HT at 470°C . Bold and thin lines correspond to the samples treated with and without water vapor, respectively. Both spectra are recorded under white-light illumination at the temperature of 7 K with $\vec{B} \parallel \langle 110 \rangle$ direction.

Finally, we come back to the question of aluminum incorporation in the Si-NL10 center. So far aluminum was the only nucleus having a characteristic hyperfine 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 clustering (Watkins kick-out mechanism [22]). 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 compensate one of the two TD's electrons. Such aluminum-containing single donors were discussed in Ref. [5].

It is not yet clear whether the Si-NL10 defect is always either hydrogen- or aluminum-containing; our model requires the presence of a passivating element in the structure of the Si-NL10. More experiments are on the way.

Summarizing, we have observed the hydrogen hyperfine interaction of the Si-NL10 defect in (hydrogen-diffused) crucible-grown silicon. We have concluded that hydrogen plays an important role in the structure of this defect. We have proposed a possible structural model of the Si-NL10 center, identifying it with a singly passivated thermal double donor. With the current finding the long-standing puzzle of the mutual relation between the Si-NL8 and Si-NL10 EPR spectra and thermal donors in silicon appears to be resolved. A second important conclusion is the convincing evidence of the fact that hydrogen in substantial (10^{14} – 10^{15} cm $^{-3}$) concentration is present in commercially available silicon and that its influence on the properties of the material cannot be neglected.

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