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HIGH-FIELD EPR SPECTROSCOPY OF THERMAL DONORS IN SILICON

Ruud Dirksen, F. Berg Rasmussen[1], T. Gregorkiewicz, and C.A.J. Ammerlaan

Van der Waals–Zeeman Institute, University of Amsterdam,
Valckenierstraat 65-67, NL-1018 XE Amsterdam, The Netherlands

[1]Risoe National Laboratory, DK-4000 Roskilde, Denmark

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Abstract Thermal donors generated in p-type boron-doped Czochralski-grown silicon by a 450 °C heat treatment have been studied by high-field magnetic resonance spectroscopy. In the experiments conducted at a microwave frequency of 140 GHz and in a magnetic field of approximately 5 T four individual thermal donors species could be resolved. These were observed in their singly ionized TD^+ charge state. For the first time in the four decades of thermal donor research the g tensor values for specific members of the Si-NL8 family are given. Also the symmetry of the observed species is discussed.

Introduction

Thermal donors (TD's) constitute a long-standing puzzle in the materials science of silicon. Ever since their first observation [1] they presented a challenge to both experiment and theory. At this moment, some 40 years after their discovery, there exists no microscopic model of their structure, which would be capable of accounting for all the available experimental data. Also the theoretical picture is not complete and basic questions remain unanswered. This situation continues to exist as new findings often contradict each other and complicate rather than converge our understanding of the problem. Little progress is achieved in spite of the fact that TD's are easily generated in large concentrations and, as such, can be readily observed by a variety of experimental techniques commonly used for defect characterization. At the same time the shallow electrical character and wide-spread abundance make TD's relevant for device development, performance and stability.

While numerous methods have been applied in the studies of TD's the infrared absorption and magnetic resonance proved to be among the most informative. The infrared absorption spectroscopy was the first to reveal the major problem which hinders the progress in the structure determination of these centers - the multispecies character. In a recent absorption study [2] it was shown that upon prolonged treatment of oxygen-rich silicon in the 450 °C temperature range a series of 16 very similar, yet distinct, shallow double donors develop, with each species having its own generation and decay properties. This very characteristic feature of TD centers could be also confirmed by the high-resolution deep-level transient spectroscopy (DLTS) technique [3]. The electrical structure of TD's was shown to be well described by the effective mass theory, with a series of helium-like levels within approximately 180 meV below the bottom of the conduction band. In addition to those findings, the two deepest members of TD family were shown to have bistable properties, thus further complicating the picture.

In electron paramagnetic resonance (EPR) two spectra were assigned to thermal donors [4,5]: one of them, Si-NL8, has been identified as a singly ionized charge state TD^+; the other one, Si-NL10, has recently been shown to incorporate a single hydrogen atom and, consequently, identified as a TD-H complex, although another structural variation, involving an aluminum acceptor, is also possible [6]. For both Si-NL8 and Si-NL10 centers participation of oxygen has been established proving in this way the relation between TD's and this dominant impurity [7,8]. Another important conclusion from magnetic resonance studies was the overall orthorhombic-I (C_{2v}) symmetry found for both TD-related centers.

Generally, in magnetic resonance each center is characterized by its g tensor which describes the Zeeman interaction between spin S of the center and the magnetic field. Experience shows that the g tensor in practice identifies the defect and forms its unique fingerprint. The multispecies character should then be readily observable as a series of similar EPR spectra. In practice the resonance lines of individual species overlap, resulting in line broadening. The annealing time development of TD species gives rise to a gradual, quasi-continuous change of line positions - the so called g-shifting effect. Such an effect leads to a lowering of anisotropy of the TD-related spectra for longer annealing times, in agreement with the simultaneous domination of the more shallow species. Actual EPR spectra of individual TD species could not be observed until now due to an insufficient resolving power of the available experimental setups, seriously hampering the value of the EPR technique in TD investigations. In view of the crucial role which magnetic resonance spectroscopy played in the past in the development of microscopic understanding of major defect centers, one may speculate that if this situation could be changed a flow of valuable information would follow. In this aspect the development of novel high-frequency magnetic resonance techniques offers new possibilities. These have been explored in the current study.

Experimental conditions

The experiments were performed with the newly constructed high-frequency D-band spectrometer operating at 140 Ghz. Its features and construction will be shortly described in the following.

The 140 GHz microwaves are generated by a high-stability 18 times frequency multiplier which is externally driven by a tunable CW synthesizer (HP 8671B) running at a frequency of approximately 7.7 GHz. The multiplied signal is fed through a band pass filter and an injection locked amplifier delivering 30 mW output power to the homodyne microwave bridge. The attenuators in the bridge are electronically tuned PIN diodes. A helium-cooled InSb crystal detects the power reflected from the cavity. The cylindrical cavity (radius 1.41 mm) has an unloaded quality factor Q of approximately 4500 and can be tuned by repositioning of its bottom. The sample is glued to the bottom of the cavity and rotated for changing its orientation with respect to the magnetic field. Measurements are done when tuned to dispersion. The magnetic field is supplied by a 6 T superconducting magnet (Cryogenic) with provisions for linear scanning. Modulation of the magnetic field is achieved by an additional coil wound around the cavity allowing for phase-sensitive detection at about 100 kHz. The temperature of the sample and cavity-insert is kept stable by a helium flow cryostat combined with a heater (Cryogenic). In order to calibrate the magnetic field, markers with well known resonance lines, such as Si:P and manganese, are mounted in the cavity together with the sample under study.

Experimental results and discussion

A. Preliminaries

As already mentioned, the resolving power of conventional EPR is insufficient to reveal the individual TD species. Figure 1 presents the angular dependence of the Si-NL8 spectrum commonly assigned to TD$^+$; the thin and the thick lines correspond to the experimental results as obtained in a sample annealed, respectively, for 1.5 and 270 hours. A clear g-shifting effect can be concluded: upon prolonged annealing the spectrum of orthorhombic-I symmetry type undergoes, what is observed as, a continuous transformation and becomes more isotropic. In the g tensor description this

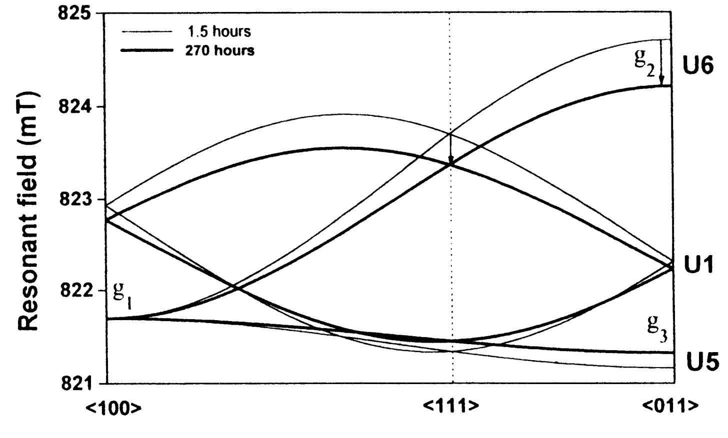

Figure 1: *The angular dependence of the Si-NL8 EPR spectrum as measured in the K microwave band for a Cz-Si:B sample annealed for 1.5 and 270 hrs - thin and thick lines, respectively.*

corresponds to a gradual change of tensor components, with the most pronounced variation of the off-diagonal element g_{xy}. A similar effect has also been concluded for the other TD-related Si-NL10 center [5].

The g-shifting effect illustrated in Fig.1 is readily explained if we assume that the actual EPR spectrum represents a superposition of unresolved contributions of individual species. The relative (but also absolute) concentrations of these change with the annealing time resulting in a somewhat different overall signal. Since the shallower species with the more isotropic g tensors dominate at a later heat-treatment stage, the superimposed spectrum also becomes less anisotropic, in agreement with the experimental result depicted in Fig.1.

B. Individual Si-NL8$_i$ species

Although up to now the EPR spectra of individual TD's could not be resolved, the distinction was possible by Electron Nuclear DOuble Resonance (ENDOR). Such experiments have, again, been performed for both TD-related centers. In ENDOR one observes hyperfine interactions between the electron spin of the center and nuclear spins of atoms on which it is localized.

For the Si-NL8 center a ^{29}Si [9] and ^{17}O ENDOR [8] has been done revealing hyperfine interactions with ligand silicon atoms as well as with oxygen atoms forming (presumably) the essential part of the TD structure. In both cases different "shells" have been found and these have been postulated to arise from different TD species. A direct relation between a selected hyperfine interaction and the EPR center can be obtained in the so-called field-swept ENDOR (FSE); in case of Si-NL8 studies the available conditions did not allow for such a measurement. On the other hand, an attempt was made to correlate different ENDOR shells with TD species detected by IR absorption [10].

Also for the Si-NL10 center a vast body of experimental evidence has been collected. Similarly to Si-NL8, the individual species were resolved in ENDOR [11]. In this case, however, successful FSE measurements could identify several members of the Si-NL10 family. Although the separation of individual contributions was only possible for the single most anisotropic orientation and only close to the <011> crystal direction, i.e., in the vicinity of the U6 point indicated in Fig.1, the FSE technique was in that case capable of providing a very valuable structural information. Among the few separated species only one was found to have the "true" orthorhombic-I symmetry; for all the other ones a small monoclinic distortion was inferred. This finding is of crucial importance for the modeling of the TD structure, and will be further discussed in the next section.

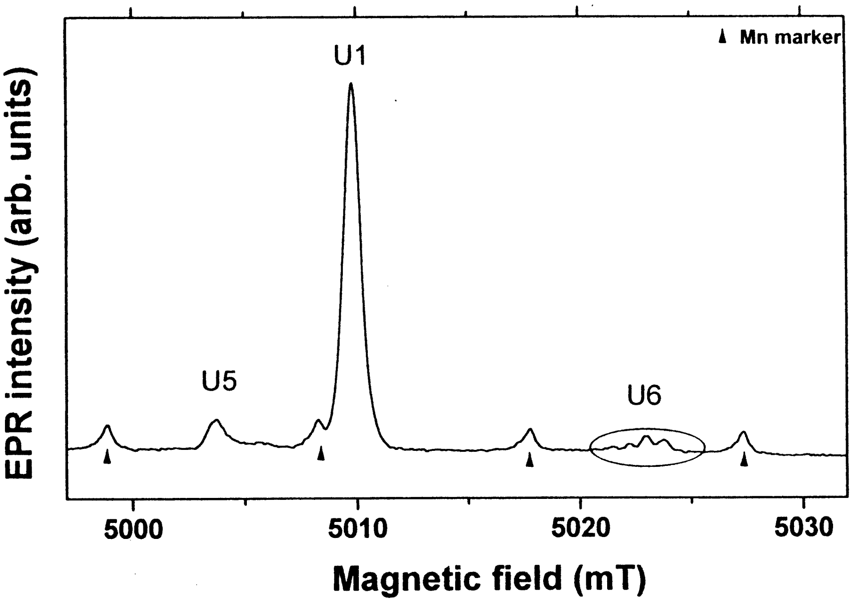

Figure 2: *The Si-NL8 EPR spectrum as obtained in the D-microwave band at 140 GHz with magnetic field parallel to <011>. The indicated splitting of the high-field component U6 shows the contributions of individual TD species. Mn markers are indicated.*

In addition to the ENDOR/FSE studies the Si-NL10 species were also investigated by high-field magneto-absorption [12]. In the experiment conducted for an Al-doped Czochralski-grown Si sample in a magnetic field of 12 T three different species were resolved. However, in view of a poor signal-to-noise ratio, the distinction was possible only for the U6 point, where the separation between the individual spectra is most pronounced; this allowed for an estimation of the specific g tensors.

Since the individual species are characterized by specific g tensors, the spectral separation between them is proportional to magnetic field. In the current study we take full advantage of that effect. Figure 2 shows the EPR spectrum as measured in the studied sample with the magnetic field of approximately 5 T parallel to the <011> crystallographic direction. The four evenly spaced resonances of equal intensity are due to manganese and serve as field markers. For a center of orthorhombic-I symmetry the spectrum in this direction contains three lines with 1:4:1 intensity ratio. Instead, in the figure the high-field line U6 is split into at least four components of different magnitude; their total integrated intensity is equal to that of the low-field resonance U5 at 5003.701 mT. We conclude that the observed splitting represents contributions of individual TD species whose spectra are well resolved in the high-field U6 point, and coincide for the low-field line (U5). Such a behavior is in good agreement with that expected from the g-shifting effect, as depicted in Fig.1. The measurement presented in Fig.2 is the first direct EPR identification of individual TD species observed here in their singly ionized charge state TD$^+$. We label these species Si-NL8$_1$–Si-NL8$_4$.

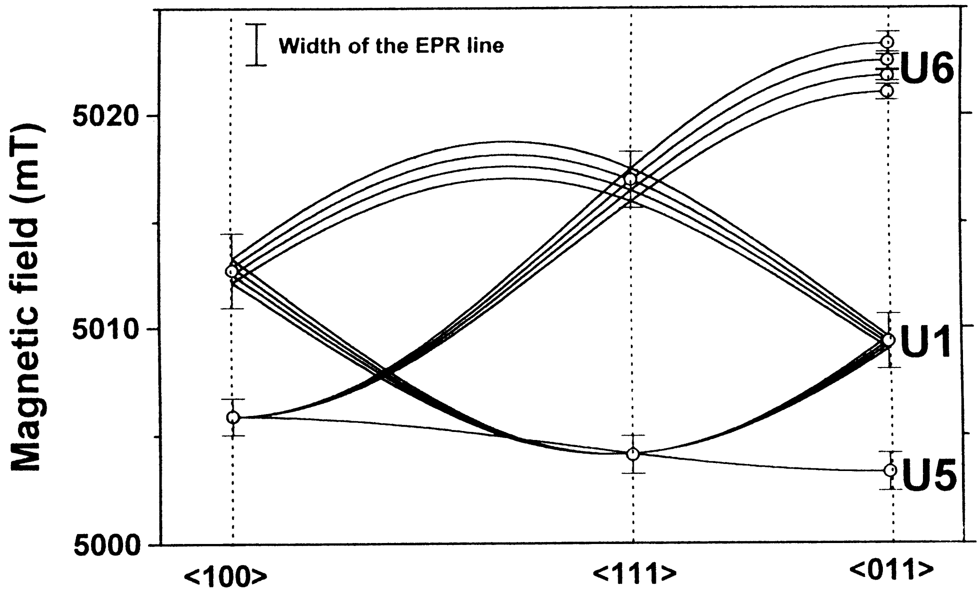

Figure 3: *The angular dependence of the Si-NL8 EPR spectrum as obtained in the D-microwave band at 140 GHz. Solid lines represent simulations for the individual TD species Si-NL8$_1$ to Si-NL8$_4$ with the parameters as summarized in Table I.*

Subsequently the whole angular dependence was measured. The result is illustrated in Fig.3 where experimental data are shown together with the computer fit under the assumption of orthorhombic-I symmetry. The resulting g tensors for the four species are summarized in Table I. Following the earlier discussion we identify the most anisotropic Si-NL8$_1$ as the basic TD present in our sample; it should be characterized by the most simple microscopic structure with (possibly) the smallest number of participating oxygen atoms and the lowest ionization energy level. The "later", less anisotropic species - Si-NL8$_2$–Si-NL8$_4$ - should represent larger structures, with gradually shallower electric levels. Careful inspection of the high-field line in Fig.2 reveals a possible presence of still further species; their presence can also be concluded from a broad high-field shoulder of the middle component - U1. Their field shift is, however, insufficient to determine the g tensors.

Table I: *g values of individual species of Si-NL8*

	Si-NL8_1	Si-NL8_3	Si-NL8_3	Si-NL8_4
g_1	1.99980	1.99980	1.99980	1.99980
g_2	1.99285	1.99317	1.99346	1.99376
g_3	2.00084	2.00084	2.00084	2.00084

C. Symmetry aspects

In the fitting of the angular dependence illustrated in Fig.3 the orthorhombic-I symmetry has been assumed, in line with the generally accepted symmetry properties of TD centers. However, when one considers now that in the current experiment individual species are separately probed, the natural assumption of the C_{2v} symmetry appears much less certain. In detail, if one accepts a general model that the TD development process comprises (interstitial) oxygen aggregation around a characteristic core of precisely orthorhombic-I symmetry and electrical character of a double donor, then it appears highly unlikely that this symmetry type would be preserved in the TD growth process. In order to maintain the orthorhombic-I symmetry for all the species the growth process would either have to take place along a <100> crystallographic direction (the two-fold defect axis), or would require the simultaneous addition of at least two oxygen atoms on symmetry-equivalent sites on both sides of the cluster. The first possibility is contradicted by the experimental data which indicate <011> as the growth direction; the latter one is highly improbable in view of the large number of components involved. Consequently, it is plausible that, when investigated separately, the majority of TD species would disclose symmetries lower than orthorhombic-I: monoclinic or general. We note here that such a growth-induced symmetry lowering has been concluded in case of the other TD-related EPR spectrum, Si-NL10, from the FSE studies [10]. In that case, among the four species investigated in some detail only one was determined to have a true C_{2v} symmetry type; for the other ones a small splitting of the orientations which coincide in U6 has been concluded. The magnitude of this splitting was shown to be (far) below the resolution of a K-band EPR experiment.

Although in the current study the experimental data could be satisfactorily fitted with orthorhombic g tensors, a possible lowering of the symmetry type has been given further attention. This is illustrated in Fig.4.

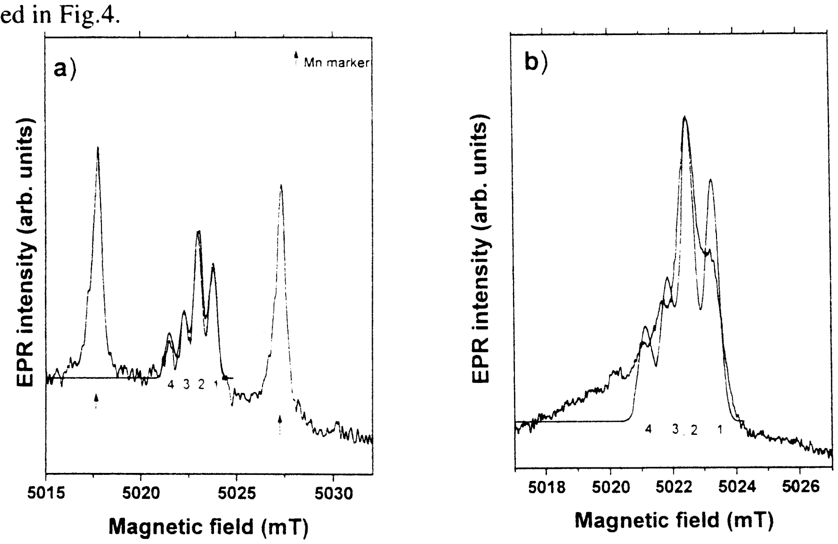

Figure 4: *Comparison of the measured and the simulated spectra with magnetic field oriented* **(a)** *along a <011> direction and* **(b)** *16° away from <011>. Only the resonance U6 from a single TD orientation is shown. A clear disagreement for the off-main-direction measurement can be observed.*

Figure 4(a) shows the EPR spectrum as experimentally observed in the high-symmetry U6 point. This measurement has been used to determine the intensity of individual components, and a simulation of the signal has been made. As can be seen the experimental form of the spectrum can be very well reproduced. Subsequently, the intensity and the linewidth established in this way have been used to simulate the spectrum expected 16° away from the main direction. In Fig.4(b) this simulation is compared with the actual measurement: in this case the agreement is rather poor. The experimental result can be readily reproduced if we assume a small, unresolved splitting of components related to Si-NL8_1, Si-NL8_3, and Si-NL8_4. Therefore the current study offers strong indications that the growth process lowers the overall symmetry of the TD center from orthorhombic to, at least, monoclinic. However, even when performed at the frequency of 140 GHz, the experimental resolution of EPR appears insufficient to decide on the precise symmetry of the individual species.

In follow-up experiments currently on the way the growth/development of TD's will be further investigated. We hope that these studies will finally unravel the symmetry changes and, in this way, contribute to the understanding of the whole process.

Conclusions

The individual species of silicon TD's were for the first time resolved in EPR. They were observed in their singly-ionized charge state TD^+. From the measurements performed in a magnetic field of approximately 5 T and a microwave frequency of 140 GHz the g tensors for four centers, labeled Si-NL8_1–Si-NL8_4, have been determined. From an analysis of the form of the spectrum observed at approximately 16° away from the <011> main direction the true symmetry of the TD centers has been investigated; some indication has been found that some of the species present in the investigated crystal were of a symmetry lower than orthorhombic-I usually assigned to TD's.

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