

High-resolution EPR spectroscopy of the Si-NL10 thermal donor

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The Si-NL10 thermal donor has been studied with use of the high-frequency electron-paramagnetic-resonance technique. The experiment conducted at the far-infrared frequency band of ≈ 350 GHz proves the multispecies character of this center and gives a direct explanation of the so-called *g-shifting effect*. The experimental findings are in remarkable agreement with the predictions based on earlier advanced field-stepped electron-nuclear double-resonance measurements.

I. INTRODUCTION

It is a well-established phenomenon that when oxygen-rich silicon is subjected to annealing at temperatures in the vicinity of $\approx 450^\circ\text{C}$ electrically active, double-donor centers of shallow character are generated. These are termed thermal donors (TD's) and have been studied since the 1950s.¹ Although TD's are certainly among the most studied defect centers in silicon (for a more recent review see, e.g., Ref. 2) surprisingly few details concerning their microscopic structure have been revealed. Consequently, while many models for the center have been put forward, none of these is capable of explaining all the available experimental data. The confusion over the TD issue may be put in broader perspective by reference to the fact that very little is also understood in the closely related and much broader field of oxygen aggregation. For a long time no answer could be given even to a very basic question in this area, namely *why the aggregation should occur at all*. This particular problem has been addressed only very recently. Needels *et al.*³ have shown that the formation of $\langle 011 \rangle$ -elongated chains of interstitial oxygen in *staggered* arrangement is energetically favorable (in comparison with isolated oxygen interstitials) with approximately a 1-eV energy gain for every oxygen atom joining the cluster.

II. PRELIMINARIES

A. Multispecies character of thermal donors

One of the most puzzling features of TD formation is its multispecies character; there appears to exist not a single TD center but a whole family of very similar centers formed subsequently upon prolonged annealing. To date up to 11 different TD species with gradually decreasing ionization energies could be identified. The actual origin of this effect is not known. While the possibility of some (structural) reorientation mechanism giving rise to the variety of TD species cannot be ruled out, the more generally accepted opinion links the multispecies character of TD's to some kind of development mechanism

in which the defect cluster gradually increases its size. Such a model requires that the TD center is created in two steps: first an electrically active core of double-donor character and then subsequent decoration of the core with additional elements with only moderate influence on the electrical properties of the center. Out of these two steps the possibilities for the explanation of the development mechanism appear particularly limited; taking into account the components available in the silicon crystal, it seems obvious that such a process can only proceed in two ways, namely by the aggregation of oxygen atoms or silicon self-interstitials. Unfortunately, there are strong counterarguments in both cases, making the definitive acceptance of any of these mechanisms impossible at this stage.

1. *Oxygen aggregation.* Subsequent aggregation of oxygen atoms is assumed by the most prominent TD models.^{4,5} Since at least 11 different TD species have to be accounted for, this mechanism requires a very high number of oxygen atoms participating in the cluster. Assuming that the smallest oxygen core demands only two atoms, the number of oxygen atoms actually participating in the 11th species would be $2 + (10 \times 2) = 22$ for the case of persistent orthorhombic symmetry and $2 + (10 \times 1) = 12$ if the symmetry is allowed to be lowered. Both numbers are much too high with regard to the diffusion constant of interstitial oxygen in silicon. Nevertheless, it should be noted here that the recent work on oxygen precipitation³ seems to support the idea of the oxygen-based mechanism.

2. *Self-interstitial aggregation.* The idea that the oxygen core would be in the subsequent development procedure decorated with silicon self-interstitials has been introduced in order to cope with the low diffusivity of oxygen. It has again been put forward in a recent TD model by Deák, Snyder, and Corbett.⁶ However, such a mechanism would require an almost unlimited source of self-interstitials, whose origin is difficult to point out. (The most probable source for the generation of self-interstitials is, again, the oxygen aggregation.)

In spite of the aforementioned problems, it seems absolutely clear that understanding of the multispecies nature

is essential for the solution of the TD puzzle. Therefore, any additional information in this field will be particularly welcome. The most direct evidence of the multispecies character of the TD center has, until now, been provided by infrared-absorption (ir) studies. Following earlier reports, recent ir results⁷ show the existence of 11 very similar but distinctly different centers. These can be distinguished by slightly different binding energies ranging from 69.9 to 49.9 meV and 156.3 to 116 meV for the first and second ionization series, respectively. No further insight into the origin of differentiation between the species could be provided. Further confirmation of the multispecies character of TD came from photoluminescence (PL). Steele and Thewalt⁸ identified PL bands due to recombination of excitons bound to TD centers in their neutral charge state. Eighteen different PL bands could be identified, indicating nine TD species. Also in this experiment no insight into the mechanism responsible for the creation of the TD variety could be gained.

B. Magnetic-resonance studies of thermal donors

The magnetic-resonance technique has been applied at a relatively early stage of TD studies and several *heat-treatment centers* have been discovered.⁹ Two of them, labeled Si-NL8 and Si-NL10, were later found¹⁰ to be directly related to TD's. The Si-NL8 was identified as a singly ionized charge state (TD)⁺,¹¹ the precise identification of the other TD-related EPR spectrum, Si-NL10, is still in dispute.¹² The existing controversy concerns the question of whether both spectra should be related to two different paramagnetic states of (structurally) the same center or whether the Si-NL10 spectrum corresponds to a center whose core is somewhat different from that of the NL8-TD (e.g., by substituting a silicon interstitial with an aluminum one⁶). Apart from this issue, there appears to be no doubt that both centers are oxygen-based thermal donors of a multispecies character with an oxygen-dependent development mechanism. Taking into account all the similarities between the two centers,¹² it becomes evident that, while some difference between the cores of the two centers cannot (yet) be conclusively ruled out, there must exist only one development mechanism giving rise, under similar condition of heat treatment, to a comparable number of species of similar concentrations. Therefore, information regarding the growth mechanism, regardless of whether it was actually obtained for the Si-NL8 or Si-NL10 center, is of equal importance for the TD issue.

By its very nature, the magnetic resonance technique—EPR and, even more so, electron-nuclear double resonance (ENDOR)—is very suitable for the subtle studies of the microscopic structure of defect centers. It is then not unreasonable to expect that magnetic-resonance studies are potentially capable of revealing a wealth of information on the TD development mechanism. Consequently, such studies have been executed for both NL8 and NL10 centers with the aim of developing an atomic model of the thermal donor. The multispecies character of thermal-donor centers is visualized in EPR by the so-called *g-shifting effect*. The effect,

itself, has been observed earlier^{13,14} but at that time no clear explanation could be offered and the importance of the finding was underestimated. In Fig. 1 the *g*-shifting effect is shown for the Si-NL10 spectrum; it manifests itself in a quasicontinuous change of the *g* tensor of the spectrum as a function of the heat-treatment time. Upon its discovery, the most plausible explanation for the effect was given in terms of continuous accumulation by the silicon lattice of the stress generated by the oxygen aggregation.

The later ENDOR experiments revealed many structural details of both centers.^{15,16} In particular, with respect to the development mechanism, it has been found that there existed a variety of the Si-NL10 centers with their individual EPR spectra hidden in an overall, inhomogeneously broadened resonance line. The advanced ENDOR study executed for the aluminum-doped Czochralski-grown silicon¹⁷ revealed the presence of at least ten different Si-NL10 centers; for all of these, but one, small deviations from the orthorhombic symmetry type toward monoclinic have been traced. The generation kinetics for various species could also be followed. Figure 2 shows the result obtained by the field-stepped ENDOR (FSENDOR) technique for the aluminum-doped Czochralski-grown silicon sample annealed for 48 h at 470°C: in Fig. 2(a) an ENDOR spectrum is shown with individual resonance lines belonging to different species, while in Fig. 2(b) the subcomponents of the total EPR line as determined for these ENDOR resonances are depicted. The experiment has been performed with the magnetic field **B** parallel to the [011] direction, at the U_6 point of the C_{2v} symmetry, where the separation of individual species reaches a maximum (see Fig. 1). In this way the separation between the EPR lines of the most prominent species giving rise to Al-*T* and Al-*Mbc*3 ENDOR shells¹⁵ was determined to be ≈ 0.06 mT.

However, in spite of its great resolving power, the ENDOR technique has an indirect character; although the ENDOR effect usually represents a certain percentage of

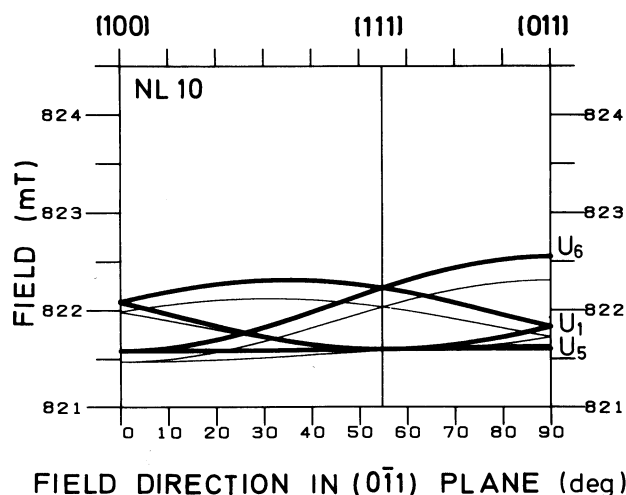


FIG. 1. Time dependence of the Si-NL10 EPR spectrum, or *g*-value shifting effect (23 GHz). The thick and thin lines correspond to 470°C annealing of 10 and 100 h, respectively. The U_1 , U_5 , and U_6 high-symmetry points are marked.

the EPR signal, the actual intensity of the observed resonance line depends not only on the actual concentration of the paramagnetic centers but also on the relaxation effects. Therefore, the results obtained from FSENDOR produce no absolute quantitative information on concentrations and have to be treated with a certain reserve.¹⁷ Such limitations are much less applicable to the direct EPR experiment, where the signal intensity is proportional to the concentration of centers. Therefore, if the EPR experiment could reach the resolution of ENDOR, the generation kinetics of various TD species as measured by magnetic resonance could be compared with those obtained by other techniques, and especially ir absorption. In such a case, a direct one-to-one correspondence could be established; a precise ir identification of EPR centers would allow one to assign the wealth of structural information available from advanced ENDOR studies to a clearly identified TD-related energy level, thus providing a unique insight into the TD development mechanism. At the same time, in the case of the Si-NL10 center,

whose ir series is not yet identified, important clues concerning its identification could be obtained.

III. EXPERIMENTAL DETAILS

In order to actualize the above-outlined idea, a high-frequency, high-field EPR (HF-EPR) experiment has been conducted. The details of the experiment setup have been described elsewhere.¹⁸ It uses an optically (CO_2) pumped far-infrared laser as the submillimeter source. The magnetic field is provided by a high-homogeneity superconducting coil. In the experiment the intensity of the radiation transmitted through the sample is registered as a function of the magnetic field (magnetotransmission). The magnetic field is modulated to allow for the usual lock-in detection technique. The sample for the experiment has been prepared from high-grade Czochralski-grown aluminum-doped ($[\text{Al}] \approx 9 \times 10^{15} \text{ cm}^{-3}$) silicon. The sample has been given a TD-generating heat treatment of ≈ 200 h at 470°C . The HF-EPR experiment has been conducted at a pumped helium temperature of 2 K.

IV. RESULTS AND DISCUSSION

Following the heat treatment, a strong Si-NL10 EPR signal could be detected; the EPR spectrum of the sample, as measured in the *K*-microwave band at 23 GHz at liquid-helium temperature with the magnetic field oriented along the [011] crystallographic direction, is depicted in Fig. 3(a). The U_6 point has been marked. As already mentioned, from the dependence of the anisotropy of the Si-NL10 spectrum on the annealing time (Fig. 1), it could be concluded that the most pronounced separation of the EPR spectra of individual species could be expected for this point—the largest *g* shifting is observed at U_6 .¹³ Therefore, this orientation has been selected for the high-frequency experiment.

In Fig. 3(b) the ENDOR spectrum obtained for this sample in the *K* band at the microwave frequency of approximately 23 GHz is presented. The individual resonances can be assigned to different species; the species are identified according to the convention introduced in Ref. 15. In the FSENDOR measurements performed on this material, the exact positions of the EPR lines corresponding to the separate Si-NL10 species could be determined. Additionally, the results of the FSENDOR confirmed the generation kinetics as reported in Ref. 17, with the species denoted as Al-*T* and Al-*Mbc3* being present in the highest and second-highest concentration, respectively.

In Fig. 4 the HF-EPR spectrum of the sample is shown. The measurement has been performed at the frequency of 349 GHz with [Fig. 4(a)] and without [Fig. 4(b)] an additional phosphorus-doped silicon crystal for *g*-value determination. The phosphorus signals could be easily distinguished from TD-related resonances because of the fact that their relative intensity changes during subsequent magnetic-field sweeps. This is due to the effect of the dynamic nuclear polarization which becomes very efficient in high magnetic fields.¹⁹ In view of the expected splitting of the individual EPR spectra, the sample

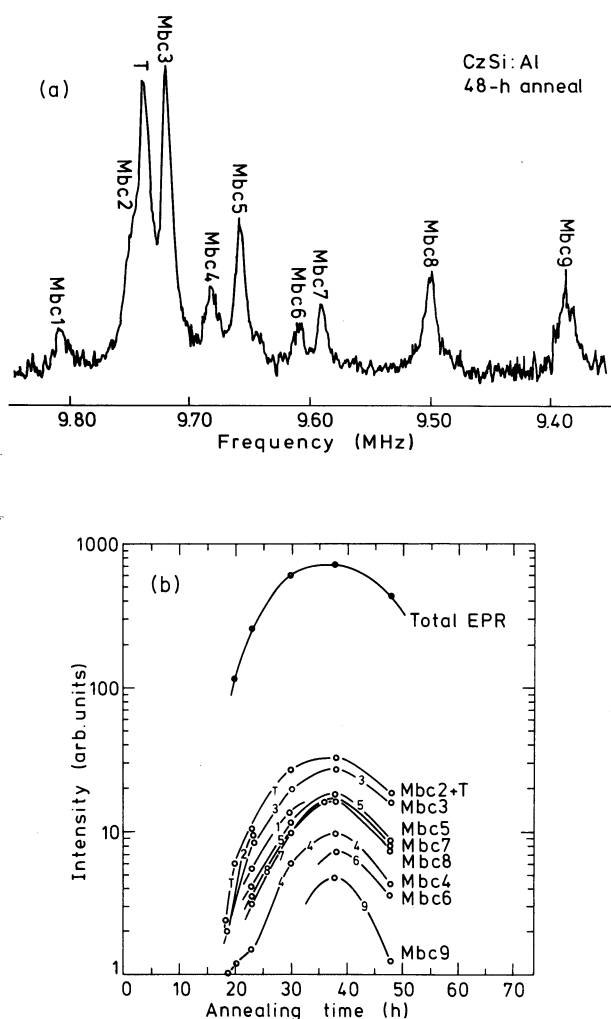


FIG. 2. FSENDOR results for the Al-doped Czochralski-grown silicon sample following annealing at 470°C for 48 h; (a) ENDOR spectrum with individual resonance lines corresponding to different species; (b) intensity of the overall EPR line and individual components corresponding to different species.

was oriented with the [011] direction parallel to the external magnetic field; the value of the magnetic field was in the 12-T range. As can be seen from the figure, the HF-EPR experiment has proven to be very successful, fully confirming the ENDOR-derived concept of the multispecies character of the Si-NL10 center. The individual species could clearly be resolved in the so-called U_6 symmetry point along the [011] direction. The actual effective g values of the individual U_6 points corresponding to the individual species are summarized in Table I. For easy comparison, the corresponding values as determined from the FSENDOR measurements at 23 GHz are also given. These have been calculated for the same sample which has also been studied in the HF-EPR experiment. Additionally, the g values obtained on similar samples with, however, shorter heat-treatment times¹⁷ are also given.

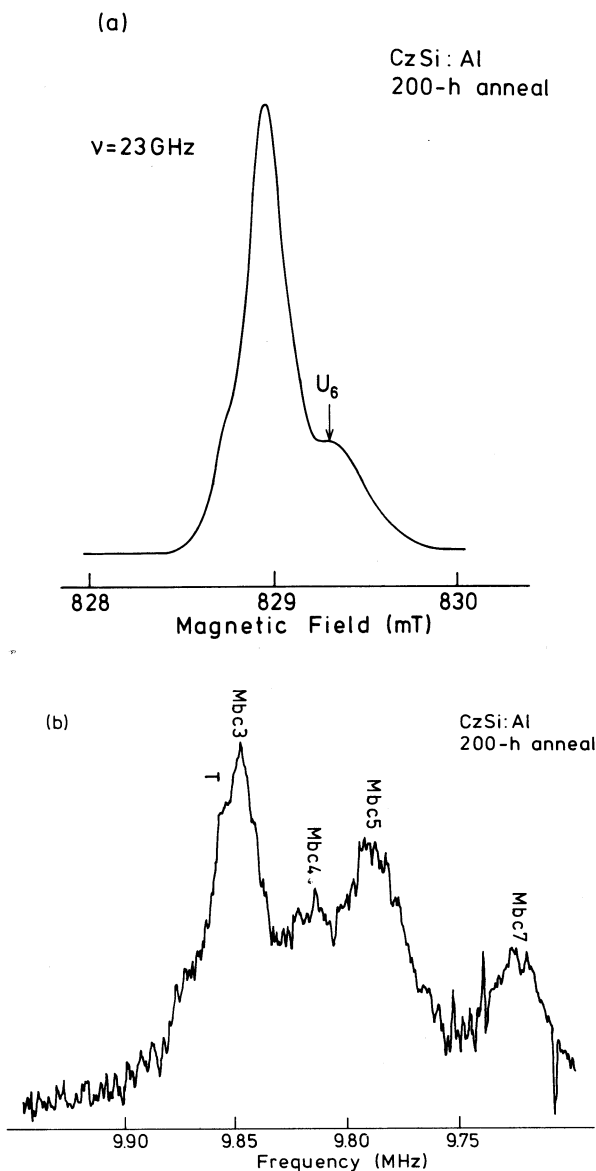


FIG. 3. (a) EPR and (b) ENDOR spectra of the CzSi:Al sample annealed at 470°C for 200 h as measured for 23-GHz microwave frequency. Magnetic field is along the [011] crystallographic direction. The same sample was used for the HF-EPR experiment (see Fig. 4).

The results, as presented in Table I, show remarkable agreement between the g values obtained by the HF-EPR and FSENDOR techniques. The agreement can be compared only for the mostly separated species which appear in the highest concentration, i.e., Al- T , Al- $Mbc3$, and Al- $Mbc5$; the other species have even more similar g values and therefore cannot be resolved either in FSENDOR or in HF-EPR. On the other hand, the “early” Si-NL10 species Al- $Mbc1$ and Al- $Mbc2$ of a not fully understood nature¹⁵ could not be observed in the HF-EPR due to the long annealing time of the sample used in that experiment. Table I also provides conclusive evidence that the g values of individual species remain unchanged during the annealing procedure; the overall g -shifting effect can therefore be related entirely to the inhomogeneous character of the spectrum. The above conclusion is derived here for the Si-NL10 center but is certainly also

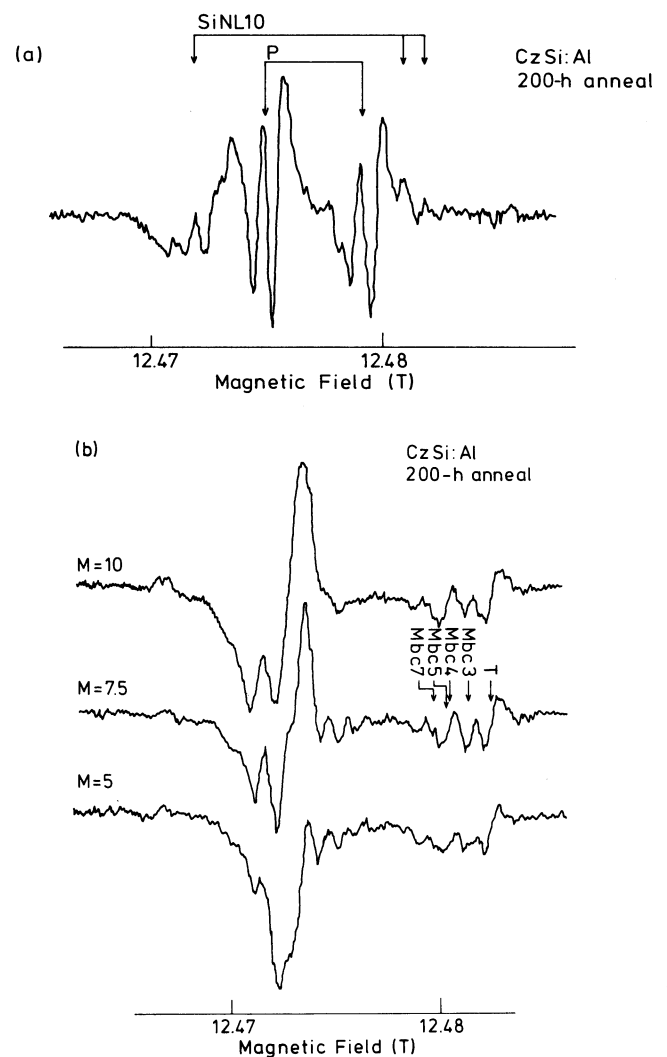


FIG. 4. HF-EPR spectrum of the CzSi:Al sample heat-treated for 200 h at 470°C (a) with and (b) without additional Si:P field marker. The frequency is 349 GHz and the magnetic field of around 12-T magnitude is along the [011] crystallographic direction. The well-resolved EPR lines corresponding to individual Si-NL10 species are indicated. Different spectra in (b) were obtained for three different field modulation values.

TABLE I. Precise positions of the U_6 high-symmetry points for the EPR spectra of individual Si-NL10 species.

Si-NL10 Species	HF-EPR (349 GHz)		FS-ENDOR (23 GHz)	
	Magnetic field (T)	g (200 h)	g (200 h)	g (48 h)
Al-Mbc1				1.99 741
Al-Mbc2				1.99 755
Al-T	12.48 254	1.99 765	1.99 767	1.99 762
Al-Mbc3	12.48 162	1.99 779	1.99 785	1.99 781
Al-Mbc4	12.48 077	1.99 793		1.99 792
Al-Mbc5	12.48 055	1.99 797	1.99 810	1.99 797
Al-Mbc7	12.47 954	1.99 813	1.99 833	1.99 807
Al-Mbc8				1.99 807

applicable to the other TD-related Si-NL8 spectrum. A close inspection of Fig. 4(b) also gives two other important pieces of information.

(1) The lowest trace in Fig. 4(b) corresponding to the smallest field-modulation value clearly shows that splitting of the U_1 high symmetry point also takes place. Although this result could be anticipated from the g shifting effect (see Fig. 1), its size was, however, too small—judging by the signal-to-noise ratio—to be revealed by FSENDOR experiments performed at 23 GHz. Unfortunately, at this stage, a concurrent identification of the U_1 and U_6 points corresponding to the same species is not possible; more experiments will be necessary in order to establish this correlation and to give the full g tensors for individual Si-NL10 species. Also, the lowering of the (originally) orthorhombic-I symmetry for the “later” species found in the FSENDOR¹⁵ cannot be confirmed.

(2) The intensity of the individual EPR spectra which can be *directly* related to the concentration of the various species appears to be in agreement with the generation kinetics as derived from FSENDOR. In this way convincing evidence is presented that, in spite of all the reservations,¹⁷ the ENDOR technique is also capable of providing, in some cases quantitative information of at least relative character.

V. CONCLUSIONS

While further studies are clearly needed for a full exploration of the possibilities which the HF-EPR technique offers for gaining information on the silicon

thermal-donor system, the data already existing at this point provide additional insight into this field of research. The results presented in this study give a direct experimental confirmation of the multispecies character of the Si-NL10 thermal donor. Both the spectral separation between individual species and their relative concentrations could be determined; these appear to be in remarkable agreement with the predictions based on the earlier indirect FSENDOR investigations. In this sense, the present experiment clearly shows that the advanced FSENDOR technique is capable of delivering reliable information not only of qualitative but also of quantitative character.

The results presented in this paper indicate that future HF-EPR studies could reveal information directly related to the essence of the thermal-donor transformation mechanism. Such information is inaccessible by any other experimental technique currently applied in the thermal-donor field of research. This very special position of HF-EPR is due to its remarkable resolving power (for TD studies it matches that of the ir absorption), combined with the symmetry and concentration information characteristic for standard EPR.

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