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Comparative study of Si-NL8 and Si-NL10 thermal-donor-related EPR centers

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The current status of the electron-paramagnetic-resonance and electron-nuclear double-resonance (ENDOR) studies of thermal-donor (TD) centers in silicon is critically reviewed. The structural models developed for the TD-related Si-NL8 and Si-NL10 heat-treatment centers are presented. On the basis of the above, the possible identifications of these centers with special emphasis on the issue of the Si-NL10 center are given. It is shown that many of the apparent controversies in the recent ENDOR findings are of superficial nature, and a surprisingly uniform picture of the thermal-donor center is emerging.

I. INTRODUCTION

When oxygen-rich silicon is subjected to low-temperature annealing ($T_{\text{anneal}} < \sim 550\,^{\circ}\mathrm{C}$) electrically active centers of shallow double donor character are generated. The centers, usually termed thermal donors (TD's), have been discovered as early as 1954 (Ref. 1), and immediately the practical significance of the phenomenon for the rapidly developing silicon technology has been realized. Consequently, the properties of TD's have been thoroughly investigated and are currently known in great detail—for a recent review see, e.g., Ref. 2. As a result, in contemporary device applications the generation of TD's can be kept under control. However, in rather dramatic contrast, the physics of thermal donor centers provides a much lower level of understanding of the phenomenon. Here, especially, the structural model of TD's presents a controversial issue where on one side a vast wealth of experimental results and their interpretations has been gathered, while on the other no consensus as to the proposed atomic and electronic model seems to be possible. It is the aim of this paper to critically assess the available information with particular emphasis on separating the experimental evidence from its interpretation. It will be shown that many of the controversies concerning the TD model are of superficial nature and appear in larger part to be based on artifacts and overinterpretation rather than experimental evidence.

II. MAGNETIC RESONANCE STUDIES OF THERMAL DONORS

Already at a relatively early stage of the TD studies the magnetic resonance techniques have been employed. Muller *et al.*[3,4] were the first to report on a series of so-called paramagnetic "heat-treatment centers" whose generation has been observed to coincide with the formation of TD's. The studies of Muller *et al.* were later extended for a wide variety of materials and heat treatments,[5,6] and consequently the conclusions could become more detailed.

The extensive studies by electron paramagnetic resonance (EPR) revealed that two series of very similar paramagnetic heat-treatment centers labeled Si-NL8 and Si-NL10 of C_{2v} orthorhombic symmetry could be related to TD's. The angular dependence of the EPR spectra of both centers is depicted in Fig. 1. In *p*-type silicon both centers could be generated regardless of the particular dopant present in the material. The NL8 centers appeared for rather short annealing times, while the NL10 centers were generated later and clearly dominated for extended heat treatments, their concentration usually exceeding that of the NL8. In originally *n*-type silicon only the NL10 centers could be observed. EPR spectra of both NL8 and NL10 centers exhibited a very peculiar feature: their off-diagonal element g_{xy} of the $\overleftrightarrow{g}$ tensor was slightly changing upon prolonged annealing—a so-called "*g*-shifting effect." As a result both spectra exhibited the tendency of becoming more isotropic for longer heat-treatment durations (see Fig. 1).

One of the surprising results of the EPR studies of thermal donors was that, in spite of the fact that in some of the silicon used the concentration of the magnetic isotope ^{17}O of oxygen was as high as 3×10^{17} cm^{-3}, no hyperfine splitting due to that isotope could be observed, neither for NL8 nor for NL10 centers. Such a result, indicating absence of oxygen atoms in the heat-treatment centers, was clearly contradicted by evident dependence of both formation rate and maximum concentration of NL8 and NL10 centers on the initial interstitial oxygen concentration (in close resemblance to the generation kinetics of TD's). In view of that apparent contradiction of experimental data the electron-nuclear double-resonance (ENDOR) technique with its extremely high resolving power had been called upon. Here already rather preliminary experiments have proven to be very successful as the incorporation of oxygen atoms in the structure of the NL10 (Ref. 7) and NL8 (Ref. 8) centers was shown, establishing for the first time a direct link between the presence of oxygen in silicon and TD generation.

Out of the two EPR centers discussed above the origin of the NL8 was quite soon disclosed[9] as a singly ionized (TD)$^+$ state of the thermal-donor center. This agreed well also with the observation conditions of the NL8 center; in *p*-type material the presence of acceptors allowed for partial ionization of double donor centers thus

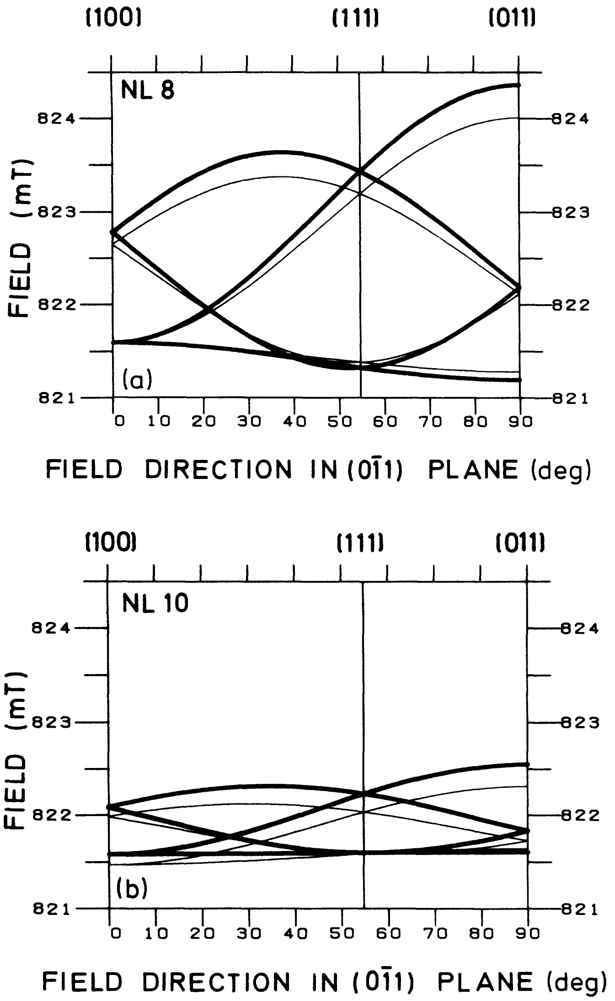

FIG. 1. Angular dependences for (a) the Si-NL8 and (b) Si-NL10 EPR spectra. Thick and thin lines correspond to heat-treatment times of 10 and 100 h, respectively.

converting them into the paramagnetic state. In case of *n*-type doping ionization was not possible, and therefore no NL8 spectrum could be observed. Following that identification, any structural information obtained for the NL8 center was directly relevant to the TD. Naturally a complete ENDOR experiment was attempted with the clear aim to determine the electronic and atomic configuration of the NL8 center and therefore finally establish the long-hidden structure of the thermal-donor center—both its core and the transformation mechanism.

The origin of the second prominent thermal-donor-related heat-treatment center NL10 remains still rather mysterious. The recent[10] suggestion based on the observation conditions rather spectacularly identified it with the overcharged $(\mathrm{TD})^-$ state of the thermal donor whose singly ionized $(\mathrm{TD})^+$ state yields the NL8 spectrum. That proposition seems however to be contradicted by the results of extensive ENDOR studies now available for both centers.[11–14] If the two spectra were generated by two different charge states of one and the same center, then the models of the atomic structures as deduced on basis of the ENDOR studies should be identical or very similar. As TD's constitute a series of very similar centers, such condition yields in detail that the structural models for both centers should have not only identical core, but also a similar transformation mechanism. In what follows the results of the ENDOR studies for both NL8 and NL10 centers will be briefly reviewed with particular emphasis on the differences of the models.

III. ENDOR STUDIES OF HEAT-TREATMENT CENTERS

A. Si-NL10 center

The ENDOR study of the NL10 center has been performed in aluminum-doped ^{17}O diffused silicon. It had an extensive character covering analysis of hyperfine interactions with ^{17}O, ^{29}Si, and ^{27}Al nuclei.[12,13] The results were further supplemented and then interconnected by means of the field-stepped ENDOR technique by which the interactions with different nuclei belonging to the same center could be recognized. On basis of the study a structural model for the NL10 center was proposed. The model is depicted in Fig. 2(a).

The most important conclusion from the study was the multiplicity of the NL10 center species. On basis of the experiment it was unambiguously established that a series of very similar, but different, centers existed; each one of them was characterized by its own EPR spectrum with slightly different g-tensor values. The EPR spectra of individual species were superimposed, resulting in one inhomogeneously broadened NL10 spectrum. Moreover, it was discovered that while the overall symmetry of the superimposed spectrum remained orthorhombic, the actual symmetry of all the components, but one, was of lower, monoclinic type. Due to a very delocalized character of the center, the lowering of the symmetry gave only a very small effect which could be exclusively observed through aluminum ENDOR.

As has been mentioned before, the preliminary measurements established incorporation of oxygen in the center. The full analysis of the ^{17}O ENDOR results has shown that the NL10 centers contained at least two oxygen atoms and that all the oxygen atoms, whose hyperfine interactions could be observed, incorporated in any of the NL10 species were always positioned on only one of the two (different) (011) symmetry mirror planes of the defect. The measured values of the quadrupole interaction were shown to be consistent with the bonded interstitial position of the oxygen atoms with the silicon-oxygen bonds also lying in the mirror plane of the defect. Such position is remarkably similar to the usual site of oxygen in the silicon lattice. The smallest NL10 center found for the aluminum doped material had orthorhombic symmetry and contained two oxygen atoms and a single aluminum atom (on the symmetry axis). From the experimental data it could not be decided whether the position of the aluminum atom was interstitial or substitutional. The other NL10 species were of monoclinic symmetry and also contained one aluminum atom. The origin of

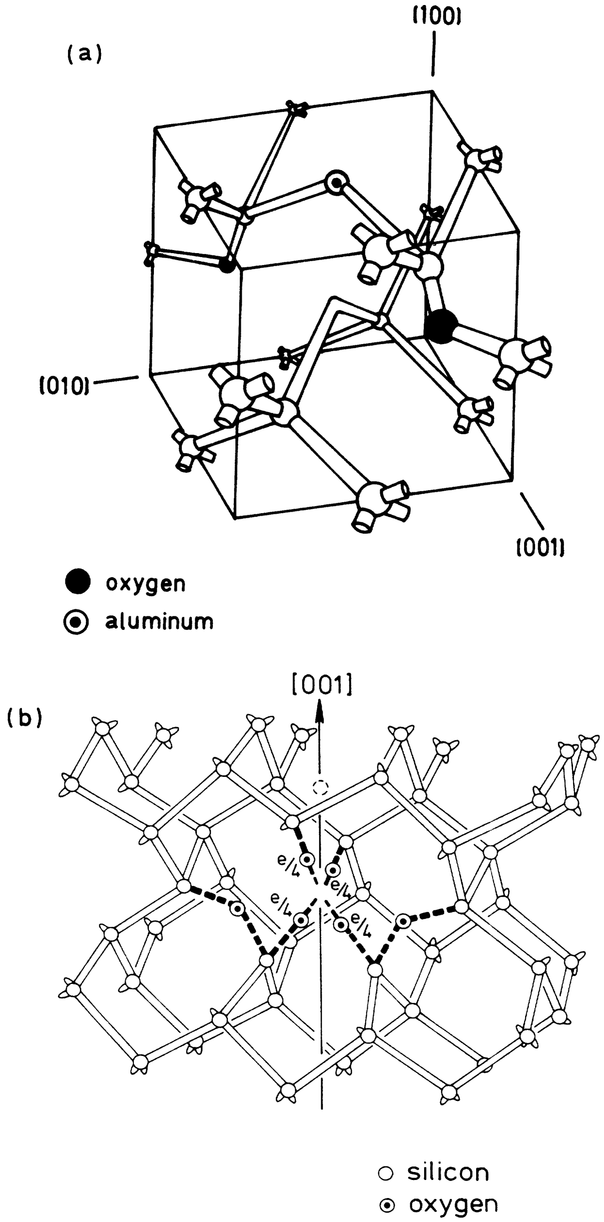

FIG. 2. Structural models derived from ENDOR investigations of (a) the Si-NL10 center (Ref. 12), and (b) the Si-NL8 center (Ref. 14).

lowering of the symmetry was not directly determined in the experiment; it could, however, be explained if the later NL10 species were generated by the transformation mechanism in which a single oxygen atom would be added to the core of originally orthorhombic symmetry. It should be pointed out that the developing oxygen chain should then always be contained within only one of the two mirror planes.

B. Si-NL8 center

For the NL8 $(TD)^+$ center the results of ^{29}Si (Ref. 11) and ^{17}O (Refs. 8 and 14) ENDOR studies are currently available. In both cases the experiments have been performed on boron-doped oxygen-rich silicon. Here also, as in the case of NL10, several different species were found to be contained within the NL8 EPR spectrum and ENDOR-ir absorption correlation has been attempted. The major conclusion from the analysis of the silicon hyperfine interactions was that the so-called Ourmazd-Schröter-Bourret (OSB) model of the thermal donor[15] was not confirmed; in that model a prominent interaction with a silicon interstitial was postulated, and the experiment failed to detect it. Another important conclusion concerned the symmetry of different NL8 species; according to the presented results, all the NL8 species, and therefore all different thermal-donor species, were of orthorhombic symmetry. Assuming an oxygen growth mechanism, this conclusion could only be interpreted as an indication that the addition of oxygen atoms during the transformation procedure of the TD had to occur in pairs. On basis of the ^{17}O ENDOR results a structural model for the thermal donor core was proposed. It involved four oxygen atoms in a vacancy, two in each symmetry plane. The proposed model is depicted in Fig. 2(b). No hyperfine interactions with any other kind of nuclei were discovered; this in particular means that the incorporation of boron (and later also aluminum) atoms in the structure of the NL8 center was excluded.

IV. IDENTIFICATION OF THE Si-NL10 CENTER

As already mentioned, the NL8 spectrum had been unambiguously identified with the singly ionized $(TD)^+$ state of the thermal donor center. The microscopic identification of the NL10 center is by far less clear. It is nevertheless of utmost importance in the TD studies as the amount of structural information available for this center is very extensive and therefore could amend our present level of understanding of the TD issue. In the following, various possibilities of NL10 identification will be presented and discussed.

A. Relation of NL10 centers with TD's

The basic question which has to be addressed prior to any further more detailed considerations is the relation of NL10 centers with TD's. Here already the production conditions leave very little if any doubt as to their mutual correlation. The generation of TD's, which can be monitored by resistivity changes, ir absorption or (in case of *p*-type material) also by EPR of NL8 centers, will always lead to generation of NL10 centers; in every case when the spectrum of NL8 centers appears in the sample (indicating TD generation), it is followed by later formation of the NL10 centers. In a much similar manner the liquidation of TD's (as observed by resistivity measurements) coincides with annihilation of NL10 EPR spectrum. Another important notion is that in case of aluminum-doped Czochralski silicon for which the generation of TD's (resistivity measurements) is enhanced, a similarly increased generation of NL10 centers occurs.[5] Such mutual correlation can only be explained if the NL10 spectrum is the EPR image of TD centers themselves or originates from some other centers whose creation accompanies the generation of TD's. Since at the same time electrical measurements of heat-treated samples indicate donor center generation of smooth, asymptotic character the NL10 centers cannot be of acceptor character (no compensation effects), nor can they constitute a later, finally transformed, and electrically neutral form of TD's (no loss of donor character is observed as the concentration of the NL10 centers grows). In light of this, it appears that the only remaining possibility would be that for longer annealing time TD's are being transformed into some different kind of donor centers ("new donors"?), and those give rise to the Si-NL10 EPR spectrum. Since in n-type material the NL10 centers can be observed without illumination, then their electrical character should most likely be that of a single donor. Moreover, since the silicon sample in which the NL10 centers can be observed shows at room temperature n-type conductivity, the single-donor ionization level should be rather shallow. This is further supported by the g value of the NL10 center which is very close to 2, and therefore characteristic for shallow, effective-mass-like donors with very small spin-orbit coupling.[16] The possibility to identify the NL10 center with thermal-donor centers different from those related to the well-known ir series of TD's is discussed in more detail in the next paragraph.

B. Relation of NL10 centers with NL8 TD's

Let us first consider the possibility of identifying the NL10 center with a (thermal) donor different from NL8 TD's. The idea of relating the NL10 spectrum to some novel kind of thermally generated donor centers implies that their structure should be different from that of the "classic" thermal donors which, in their singly ionized charge state, give rise to the NL8 spectrum. This, in turn, requires that the microscopic models derived from the ENDOR experiments for the NL10 and NL8 centers should be significantly different and, indeed, such conclusion has been reached; the proposed models, as reviewed in the previous paragraphs, differ both in the core and the proposed development mechanism. However, when closely inspected, the differences appear to be of superficial nature. In the following subsections the apparent differences are more systematically examined.

1. Oxygen structure of the core

The core of the NL10 center involves two oxygen atoms in one (011) plane, while the model of the NL8 center core puts forward the presence of two similar pairs of oxygen atoms on two perpendicular symmetry planes. To comment on that it is necessary to recall that since the C_{2v} symmetry, characteristic for the NL8 center as well as for one of the NL10 centers, possesses a twofold and not a fourfold-symmetry axis, then the two mirror planes constituting that symmetry are *not* equivalent. Therefore, for the centers with the exact C_{2v} symmetry, the ENDOR experiment can distinguish between interactions arising from nuclei contained in different planes; such a distinction follows directly from the experiment and does not require any further assumption for its interpretation. However, for an unambiguous shell assignment, an adequate experimental resolution is required. In the NL10 center ENDOR study the frequency resolution was sufficient, and therefore the experiment provided a definitive answer determining "planar" structure of the investigated center [i.e., all the oxygen atoms whose hyperfine interactions could be unraveled were contained within only one of the two (011) mirror planes of the center]. One has to note here that this conclusion is valid also for the NL10 centers of the lower C_{1h} symmetry type, as also in such case the ENDOR experiment of sufficient resolution provides direct distinction between the oxygen atoms positioned in the symmetry plane and outside it. On the other hand the authors of the NL8 ^{17}O ENDOR study clearly state that in their case the resolution was not sufficient to identify the symmetry type of the observed shells of oxygen atoms.[14] It is therefore possible that also for the NL8 center all the oxygen atoms are contained within the same mirror plane yielding a planar oxygen structure similar to that proposed for the NL10.

The detailed argument leading to the conclusion of the oxygen core with two pairs of oxygen atoms in two perpendicular mirror planes is presented in (Ref. 17). It is not based on the analysis of the ^{17}O hyperfine interactions (which, as discussed before, provides an unambiguous answer), but on the following indirect reasoning.

(1) The structure of the TD center is *a priori* assumed to consist of a central core common for every TD species and a peripheral part which is changing during the development process.

(2) From the fact that two similar ^{17}O hyperfine tensors are observed, the conclusion is derived that the corresponding two oxygen shells must have similar position within the TD center (not one in the core and the other one outside), and hence both oxygen shells are in the core.

(3) As the observed oxygen hyperfine interactions are approximately $\langle 111 \rangle$ axial, then the oxygen atoms must be placed along $\langle 111 \rangle$ directions and the positions closest to the center of the defect are found on the two (011) mirror planes.

(4) Since two oxygen shells are observed, then the smallest number of oxygen atoms involved is two.

(5) The situation, when in the TD core two nonequivalent oxygen atoms are located along $\langle 111 \rangle$ in different (011) planes, results in lowering the symmetry of the center below C_{2v} and that is contradicted by the ^{29}Si ENDOR measurements. Therefore, in order to maintain the orthorhombic symmetry of the TD center, two oxygens must be incorporated in each shell.

The above way of reasoning is vulnerable, as it requires the arguments [(1)–(5)] to be unconditionally correct. One has to note that the ^{17}O hyperfine tensors are indeed similar, and therefore positions of the relevant oxygen atoms can be expected to be also similar. There seems, however, to be no reason for assuming the positions within the "core" (in this case in a vacancy); both oxygen shells can as well be placed in the same TD center outside the "core". Furthermore, it has to be noticed that the NL8 study has been performed in the X microwave band

and the authors failed to resolve various NL8 species by the field-stepped ENDOR (ENDOR-induced EPR) technique. Therefore, it is conceivable that two oxygen shells originating from two different NL8 species could have been erroneously assigned to the same center. For various experimental reasons the NL10 study could be performed with higher resolution of both g value and ENDOR frequency allowing, therefore, for clear distinction of various species. In view of that also a different number of oxygen atoms participating in the cores of the proposed models does not provide an established structural difference between the two centers.

Considering argument (3) of the above-mentioned reasoning, it is necessary to point out that the hyperfine interaction as probed on a given atom site is often but not always axial in the direction to the center of the defect. The examples when this is not the case can be found, e.g., in the study of the negative charge state of the vacancy by Sprenger *et al.*[18] or in the data for the oxygen-vacancy center by van Kemp *et al.*[19,20] Therefore, in spite of $\langle 111 \rangle$ axiality of the ^{17}O hyperfine tensors, the oxygen atoms do not have to lay along $\langle 111 \rangle$ crystallographic directions.

In summary one has to conclude that although the NL8 and NL10 centers can have a different oxygen core structure, such a conclusion certainly cannot be reached on the basis of currently available results.

2. *Transformation mechanism*

Similarly as the core structure, the growth mechanism proposed for the two centers also provides, when superficially inspected, a distinction between NL8 and NL10. The most easily noticeable difference is the fact that while all the NL8 species are found to have orthorhombic C_{2v} symmetry, the actual symmetry of the NL10 centers lowers from orthorhombic to monoclinic upon growth. To discuss this issue one has to carefully examine the experimental evidence on which the two notions are based. Figure 3 presents the angular dependence of ENDOR transitions yielded by a single EPR orientation for the same ^{27}Al shell in two different species of the NL10 center; a splitting due to the lowering of the symmetry can clearly be seen. However, one should notice that, because of the very delocalized character of the center, the deviation of the hyperfine tensor $\overleftrightarrow{A}$ from purely orthorhombic symmetry towards monoclinic is very small.[12] Figure 4 presents the simulation of the same ENDOR transition as depicted in Fig. 3(b), but with the quadrupole interaction annuled. This serves to illustrate how the lowering of the symmetry would be visualized if the atomic site on which the interaction is probed would be occupied by a silicon and not the aluminum atom. As can be seen no splitting is distinguishable; it is well hidden in the width of the plotted line which is actually smaller than the experimental linewidth of the ENDOR transition [note the change of the frequency scale between Figs. 3(b) and 4]. One has then to conclude that the small admixture of the lower symmetry type for "later" NL10 species can solely be unraveled by the observation of its effect on the aluminum atoms whose higher nuclear spin value $I = \frac{5}{2}$ yields the quadrupole mo-

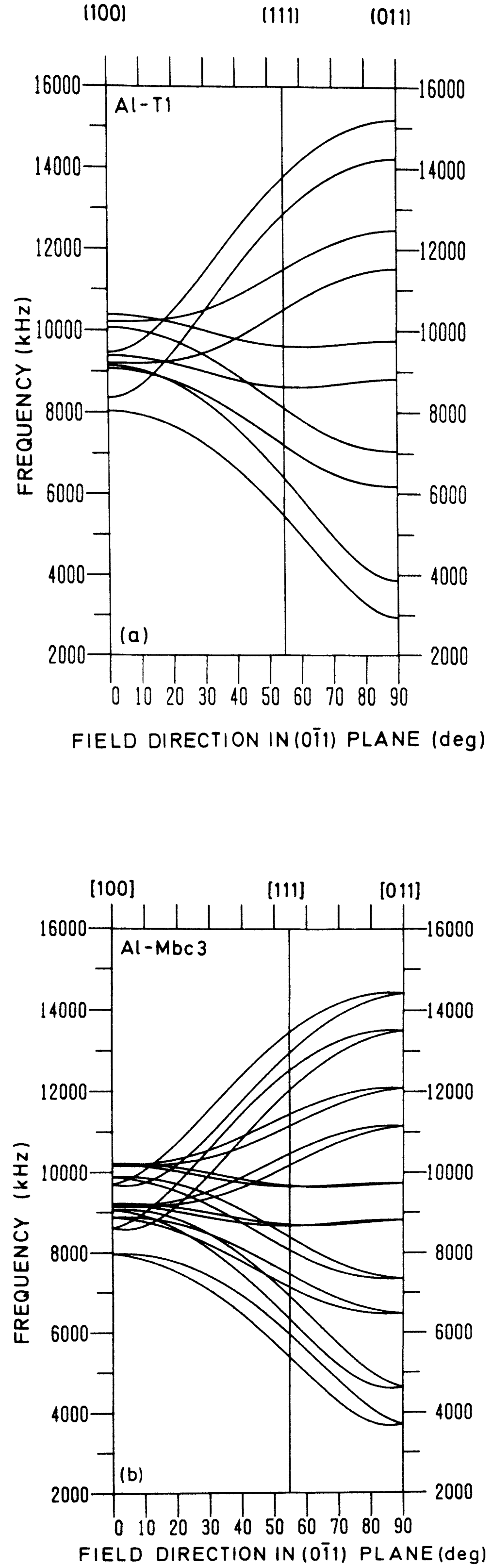

FIG. 3. The angular dependence of ENDOR frequency of the same shell of atoms for a single (and the same) EPR orientation of two different species of the Si-NL10 center of (a) orthorhombic and (b) monoclinic symmetry.

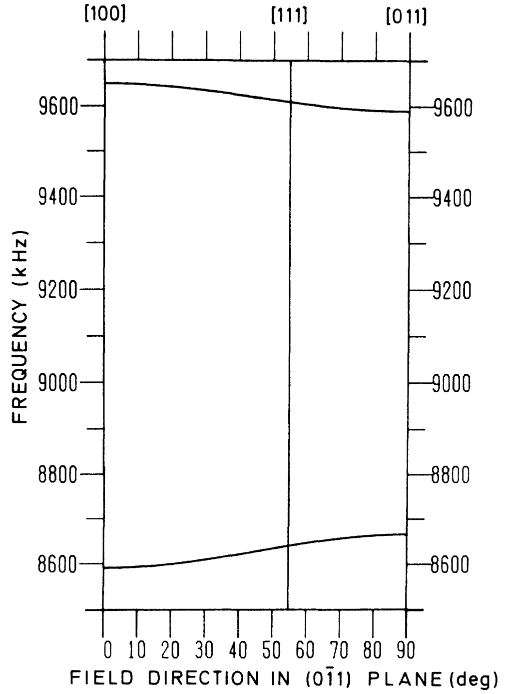

FIG. 4. A simulation of the same ENDOR dependence as in Fig. 3(b), but with annuled quadrupole interaction. This simulation corresponds to the situation in which a silicon atom is substituted for an aluminum.

ment which serves to "magnify" the splitting. The presence of the lower symmetry component is revealed neither in the ^{29}Si ($I=\frac{1}{2}$, $Q=0$) ENDOR experiment nor in the ^{17}O study as no oxygen atom is found on the twofold symmetry axis of the defect. In view of the above it is clear that in case of the NL8 study a symmetry lowering of a magnitude comparable to that of the NL10 centers could never have been revealed as only silicon and oxygen interactions were investigated. Therefore, the argument of the symmetry difference between the NL8 and NL10 centers cannot be sustained.

3. *Different structural component*

Finally a possibility has to be considered that the NL8 and NL10 centers are basically identical with the difference resulting from the presence of a single, different structural component. It is indeed plausible that while the oxygen structure of the two centers is the same, both in the core and in the development mechanism, incorporation of a strange atom (atoms) differentiates them. Since the results of ^{29}Si ENDOR are remarkably similar, the possibilities here are not too numerous. The aluminum atom appears then as a most natural candidate; its incorporation in (at least some) NL10 species has been determined in the ENDOR experiment, while no trace of aluminum has been found for the NL8.[17] Additionally the incorporation of an aluminum atom, possibly instead of a silicon atom, could convert a double donor into a single one in agreement with the previous deliberation. However, the same experiment[21] clearly shows that aluminum incorporation in the NL10 centers, although certainly possible, is not absolutely necessary for their creation; for the NL10 centers generated in boron-doped (and also phosphorus-doped) Czochralski silicon, no aluminum (or other acceptor) ENDOR could be detected. It has further been shown that NL10 centers can be generated with concentrations by far exceeding those of the available aluminum doping level.[22] Therefore, although there exist at least two different types of NL10 centers, i.e., with and without aluminum, the influence of that on the properties of the center is not of primary importance (almost the *same* EPR spectrum) and certainly cannot be responsible for the NL8-NL10 difference. Once aluminum is eliminated as an eventual candidate to distinguish between NL8 and NL10 centers (and not only between some variations within the family of NL10 centers) then still carbon participation could be considered.[22] That possibility however is rather unlikely; by substituting silicon with carbon, the center would probably stay a double donor and that is contradicted by the observation conditions for the NL10 center. On the other hand, a retarding action that the presence of carbon exhibits on the generation of TD's is well established.[23] Finally, one has to note that, adding up to the list of aluminum and carbon, the differentiation between NL8 and NL10 centers due to incorporation of some "exotic" component like nitrogen etc., although it cannot be absolutely excluded, also appears very improbable in view of the wide abundance of both centers in a vast variety of silicon materials.

Concluding the exploration of consequences of relating the Si-NL10 EPR spectrum to a donor center different from the NL8 TD's, one should remark that in such case the infrared (ir) absorption investigation would be expected to reveal a prominent (high concentration of NL10 centers) series of excitations which could be related to those centers. Until now no such series has been detected. The only other ir series found in heat-treated oxygen-rich silicon belongs to so-called shallow thermal donors (STD's).[24] These centers seem, however, to be produced by very short annealing times and in relatively low concentration. Very recently a rather similar series of ir absorption levels has been detected in heavily aluminum-doped heat-treated Czochralski silicon.[25] However, these donor levels appear to be uniquely related to the presence of aluminum, and therefore their correlation with NL10 centers is unlikely. Also, EPR studies of heavily aluminum-doped material do not indicate any enhancement of the NL10 center generation further undermining the possibility of such correlation.[26]

C. Possible identification of NL10 centers with NL8 TD's

In view of the above-mentioned considerations it appears that the currently available experimental information does not support the identification of all the NL10 centers as being structurally different from TD's (with an obvious exception of those containing aluminum atoms, whose presence however does not appear crucial for generation of the NL10 center nor for its properties). In that situation the possibility of relating both NL10 and NL8 spectra to basically the same center has to be explored. Many of the striking similarities of the two centers have already been mentioned. Generally one could conclude that if it were not for the slightly more delocalized character of NL10, the ENDOR data for both centers appear almost identical. This is especially apparent when ^{29}Si data are compared; both sets of data are practically identical taking into account the difference in total electron localization. Another important notion is that the quadrupole interaction measured from the ^{17}O ENDOR is practically identical for both centers. Since the quadrupole interaction of that magnitude can only arise from bonding *p* electrons, this observation indicates that the oxygen atoms participating in the structure of both centers are involved in a very similar bonding arrangement.

If it is assumed that the structures of the NL10 and NL8 centers are the same and therefore identical with TD's, then the possibilities for the identification of the NL10 spectrum appear rather limited. Here they will be discussed in order of decreasing probability.

1. *Different charge state*

Quite recently the interpretation of the NL10 spectrum as generated by an overcharged $(\mathrm{TD})^-$ state of the thermal-donor center was suggested.[10] It has been put forward on the basis of the experimental conditions in which the NL10 centers can be observed; namely it has been noticed that while in *p*-type material (white light) illumination was necessary for the generation of NL10 spectrum, no such illumination was needed in the case when the starting material for the heat treatment was clearly *n* type (phosphorus doped). Moreover, in Czochralski silicon doped with phosphorus at $\sim 10^{15}$ cm^{-3} level a drop of phosphorus EPR signal of the magnitude comparable to that of the simultaneously generated NL10 signal was observed upon heat treatment. This notion could easily be explained by the assumption of a $(\mathrm{TD})^-$ level positioned below or in close vicinity of the 45-meV phosphorus ionization level. The $(\mathrm{TD})^-$ state could then be populated at the expense of the phosphorus donor level.

The identification of the NL10 center with $(\mathrm{TD})^-$, although very plausible, faces two major problems. Firstly, the position of the associated energy level has to be contained within the relatively narrow region of the silicon band gap, i.e., between ~ 60 and 45 meV [$(\mathrm{TD})^0/(\mathrm{TD})^+$ and phosphorus ionization levels, respectively]. Such a region appears very small, especially when compared to the situation of the phosphorus overcharged state *p*. Secondly, recent experiments[26] show that in originally *p*-type aluminum-doped Czochralski silicon, which has been converted to *n* type after annealing, the NL10 spectrum can be also observed without illumination. Since no (significant) amounts of phosphorus doping can be present in such material, the experiment would then require an alternative source of donor electrons to populate the $(\mathrm{TD})^-$ level. Similar requirement would also follow from the observation that in slightly phosphorus-doped samples NL10 signals exceeding the doping level can be generated.[17]

2. *Bound exciton system*

The idea of an exciton bound to the TD center is, in some way, similar to the overcharged state as described in the previous paragraph. The proposed model of such system is in full analogy to that proposed by Wagner *et al.*[27] for the center giving rise to the prominent photoluminescence line at 0.7672 eV ("*P* line") which is characteristic for heat-treated Czochralski silicon. It assumes that the TD core strongly binds a hole by a short-range potential whose orbital momentum is quenched by the local strain field of the defect. The resulting hole with spin $\frac{1}{2}$ represents an ionized pseudodonor which can bind an electron in its long-range Coulomb potential. In EPR such a system should produce two spectra. One of them would be generated by a deeply bound hole, and its *g* value and observation conditions are difficult to predict; the other one should be effective-mass-donor-like with the *g* value close to that of the free electron and that one would correspond to NL10. In that sense, the center would be paramagnetic in its zero charge state in agreement with the observation conditions for the NL10. Extending the analogy between the *P* line in luminescence and the Si-NL10 EPR center further, it would be tempting to identify the two centers with each other. Such possibility certainly cannot be excluded, but appears not very likely when production characteristics of both centers are compared.[28] Moreover, recent findings concerning the *P*-line luminescence[29] suggest the presence of a carbon atom (atoms) in the relevant center as the isotope shift in ^{13}C doped material has been found. Should 0.7672-eV luminescence and NL10 EPR spectrum be related to the same center, an ENDOR experiment would reveal hyperfine interactions with carbon nuclei. In such a case the presence of a carbon atom in the NL10 center would provide a clear structural distinction from TD's. Although that issue certainly requires further investigations, it should nevertheless be noted that at the moment no hyperfine interactions with carbon atoms have been reported either for NL8 or for the NL10 centers in spite of the completed extensive ENDOR studies.

3. *Higher spin state*

Although the NL10 spectrum can be well described with spin $S=\frac{1}{2}$, the higher $S=1$ spin value cannot be excluded. The necessary requirement in that case would be that the zero-field splitting is sufficiently small to be contained within the linewidth. Since thermal donors constitute a heliumlike series, then extending the analogy further to parahelium and orthohelium the existence of an $S=1$ state may be speculated upon and has actually been postulated to interpret the ir absorption data of thermal donors in germanium.[30] This somewhat unlikely possibility may receive unexpected support from recent EPR investigations of TD centers in germanium[31] which show that one of the two TD related EPR spectra[32] is better described with $S=1$ spin value. One should also note here that for chalcogen double donors in silicon, spin triplet states have already been reported.[33] It is, however, only fair to mention that the $S=1$ value for the NL10 center appears very improbable in view of the ENDOR results.

4. *Different structural configuration*

The first two of the TD species have been found to exhibit bistable behavior.[34] This means that when the Fermi level of the sample is in appropriate position, then, depending upon the experimental conditions, TD can exist in two different structural configurations; in one of them, it is the usual shallow double donor giving rise in its singly ionized state to the NL8 EPR spectrum. The other configuration would have a deep center character. Although the deep configuration of TD shows some indication of being a negative correlation energy center,[35] it cannot be at the present stage excluded that it could also exist in a paramagnetic state which could then be correlated to the NL10 spectrum. However, although the whole issue is rather new and lacks more complete investigations it appears that the observation conditions of the NL10 center do not coincide with the conditions for which the bistable behavior occurs. In view of that the eventual identification of the NL10 center as the paramagnetic state of the deeper (usually referred to as *X*) configuration of TD seems rather improbable and is listed here for the sake of completeness.

V. CONCLUSIONS

A detailed examination of the available ENDOR results for the two TD-related NL8 and NL10 EPR centers clearly shows that experimental evidence supporting the apparent differences between the microscopic structural models proposed for both centers is superficial. Participation of aluminum atoms in some of the centers of the NL10 family, which is not observed for the NL8 centers provides some distinction, but cannot be responsible for the NL8-NL10 difference, as frequently suggested to be the case. The structural properties as revealed in experiment appear remarkably similar for both centers and no clear general difference can be pointed out. Therefore, on the basis of properly interpreted experimental findings, an identical structural arrangement for those centers cannot be excluded and is indeed supported by substantial evidence. In this perspective plausible identifications of the NL10 center as different charge state, bound-exciton, or higher spin states of silicon thermal donor are discussed. It is argued that both Si-NL8 and Si-NL10 EPR spectra are related to the same ir identified series of TD's.

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