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OXYGEN AGGREGATION IN SILICON — EPR AND ENDOR STUDIES*

(INVITED PAPER)

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The problem of thermal donors in silicon as part of the oxygen clustering scheme has been reviewed. Special emphasis has been given to the role of magnetic resonance techniques in unravelling the microscopic structure of thermal donor complexes. Recent results reporting on the structure of Si-NL10 and Si-NL8 centres as well as their relation to silicon thermal donors have been discussed.

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1. Introduction

A. General

Silicon is currently the basic material used by the electronic industry. Although GaAs is gaining more applications and might finally replace silicon this is not likely to happen before the end of this century. The dominant position of silicon is reflected also in the material research; at the moment about 90% of available funds is alotted to the studies of silicon and silicon based devices.

In view of the above our knowledge concerning oxygen, the basic silicon impurity, seems particularly limited. Unless special cleaning procedures are applied oxygen is always present in silicon in very high concentrations. It is introduced during pulling of silicon single crystals and stays after cooling in supersaturated solution. In Czochralski-grown silicon the oxygen concentration is as high as 10^{18} cm^{-3}. By zone refining oxygen contents can be lowered to about 10^{15} cm^{-3} which, however, strongly increases the price of the material. In the silicon lattice oxygen takes the puckered bonded interstitial position with the bond angle value estimated to be 150°–160°. The maximum solubility at the melting point

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is 2×10^{18} cm^{-3} and the diffusion constant is low, although higher than that of most of the acceptors. The actual concentration of interstitial oxygen in silicon is measured by infrared absorption at 9.1 μm; the absorption at 9.1 μm is proportional to the oxygen concentration, the proportionality factor is found to be between 2 and 3×10^{17} cm^{-2}.

In the situation when the temperature of the silicon crystal is high enough to permit significant migration the oxygen atoms will leave the supersaturated solution forming clusters of various size and structure. Upon prolonged annealing at elevated temperatures this will lead to the creation of extended oxygen precipitates of almost macroscopic scale.

Interstitial oxygen dispersed in the silicon lattice is not electrically active. Such behaviour is in contrast to other group VI dopants as sulphur and selenium, which act as double donors. However, both sulphur and selenium take not interstitial but substitutional positions and this alone can explain the difference.

Although interstitial oxygen itself is electrically neutral, the heat treatment of oxygen-rich silicon leads to formation of electrically active centres of donor character. These centres, generally termed "thermal donors" (TDs), are created in large concentrations (up to 10^{16} cm^{-3}) and therefore can fully control the electrical characteristics of the crystal. Since the temperature region of thermal donor generation — 400°C to 550°C — coincides with the temperatures used in silicon device manufacturing the whole problem is of basic importance to semiconductor technology. The technological driving force of the research in the field of thermal donors is based on the need to critically control the state of oxygen aggregation in silicon substrates so that the beneficial effect of the matrix hardening is preserved while the electrical effects of the oxygen aggregation are eliminated.

B. Thermal donors

Shallow donor centres formed in oxygen-rich silicon upon annealing have been thoroughly studied over the past thirty-five years. In spite of the continuous effort by both theory and experiment the issue of thermal donors has not been solved and presents itself as a major challenge in the field of the physics of silicon. The many experimental data gathered is not well correlated and frequently contradicting [1]. Nevertheless it is generally accepted that centres of donor character are formed as a result of oxygen clustering.

Many workers have attempted to elucidate the microscopic structure and growth mechanism for the defect. The early work focussed on the formation kinetics of the oxygen donor, that were determined through resistivity measurements. Kaiser et al. found an initial growth rate proportional to $[O]^4$ and a maximum concentration proportional to $[O]^3$. These findings led Kaiser et al. to propose an Si_nO_4 complex as a first model for TD [2]. Recently it has been found that the initial growth rate and maximum concentrations do not follow these power dependences, with the possible exception of boron doped material [3].

Information about the electronic structure of thermal donors was obtained from infrared measurements. From the infrared measurements of Wruck and Gaworzewski [4] it was concluded that upon thermal treatment of oxygen-rich silicon shallow double donors were formed. The spectra showed two series of absorption lines, one associated with the neutral charge state and one with the singly ionized charge state of the defect. Later studies [5] revealed that there were up to nine different double donors, all with slightly different ground-state energies. This could no longer be explained by the model of Kaiser et al.

Important structural information on TDs was obtained from magnetic resonance (EPR) measurements [6, 7]. These studies revealed a variety of EPR centres, predominantly of 2 mm point-group symmetry, which could be related with thermal donor centres. One of these centres Si-NL8 could be related to the shallow double donors as found in infrared absorption [8]. The Si-NL8 spectrum was found to arise from the singly ionized state of the double donor. It was not clear from these measurements whether Si-NL8 was connected to one of the nine donors or to all of them. The identification of Si-NL8 with the infrared double donors was possible due to the infrared and DLTS studies on TDs under uniaxial stress [9–12]. The infrared studies revealed that the ground-state wavefunction of the TD in its neutral and singly ionized charge state is effective-mass like [13]. The ground-state is constructed from a single pair of conduction band valleys. Additional small splittings due to deviations from the effective-mass theory, show that the wavefunction of the TD is distorted by an extended "central cell" potential with 2 mm symmetry (consistent with the pointgroup symmetry of the Si-NL8 EPR spectrum).

The new experimental data stimulated theoretical workers to propose a number of alternative models (YLID [14], OBS [15], Si_I [16]). Among them the OBS-model was the most promising. According to the OBS-model the electrical activity appears with clusters containing five or more oxygen atoms, and arises from a divalent silicon atom at the centre of the cluster. The donor activity of a cluster is terminated upon the ejection of this central silicon atom in order to bring about stress relaxation. A large number of electrically active donor species was predicted, differing in the number of oxygen atoms incorporated in each species. The OBS-model is an example of an inner-outer well potential, the divalent silicon is the inner well, and the two nearest oxygen neighbours act as barrier. The majority of the donor wavefunction lies in the inner well, tunnels through the barrier and then decays much more slowly in the outer well as a normal shallow state would. The donor state is primarily localised on the $p\pi$ orbital of the divalent silicon. Calculations by Robertson et al. [17] predicted an anisotropic hyperfine interaction with the central ^{29}Si atom, largest in the $[\bar{1}10]$ direction, to be of about 80 MHz for the smallest thermal donor containing five oxygens. However, such interaction has not been confirmed in the experiment thus directly contradicting the OBS model.

2. *Magnetic resonance studies of thermal donors*

A. Electron paramagnetic resonance

As already mentioned the early EPR study by Muller et al. [6, 7] revealed a variety of heat treatment centres of (predominantly) 2 mm (C_{2v}) symmetry labeled through NL8 to NL18. This pioneering work was later followed by more systematic studies [3, 18] in which, among others, the idea of possible dopant involvement in the structure of the thermal donor has been traced. The EPR investigations were performed on both Czochralski-grown Cz-Si and float-zoned FZ-Si diffused with natural and isotopically enriched oxygen. Since the majority of the existing experimental data concerned only boron doped silicon (with the important exception of the work by Fuller et al. [19]) it was important to study the influence of other dopants. Following that objective, samples doped with aluminium, indium, gallium and phosphorus were investigated in addition to boron doped material. A new, ultraclean diffusion technique was developed by means of which high concentrations of the ^{17}O magnetic oxygen isotope could be introduced into silicon.

In the studies two different 2 mm symmetry spectra were seen: Si-NL8 and Si-NL10 as labeled when first reported by Muller et al. [6] for heat-treated boron doped Cz-Si. The EPR results were similar for Czochralski-grown and FZ oxygen doped silicon regardless of the dopant present in the sample. This is illustrated in Fig. 1 and Fig. 2 where the concentration of EPR centres is presented as a function of heat treatment duration respectively for Czochralski-grown and FZ, oxygen diffused silicon. Also the concentration of thermal donors is shown as calculated from room temperature resistivity measurements under the assumption that each TD supplied one electron to the conduction band. The relative concen-

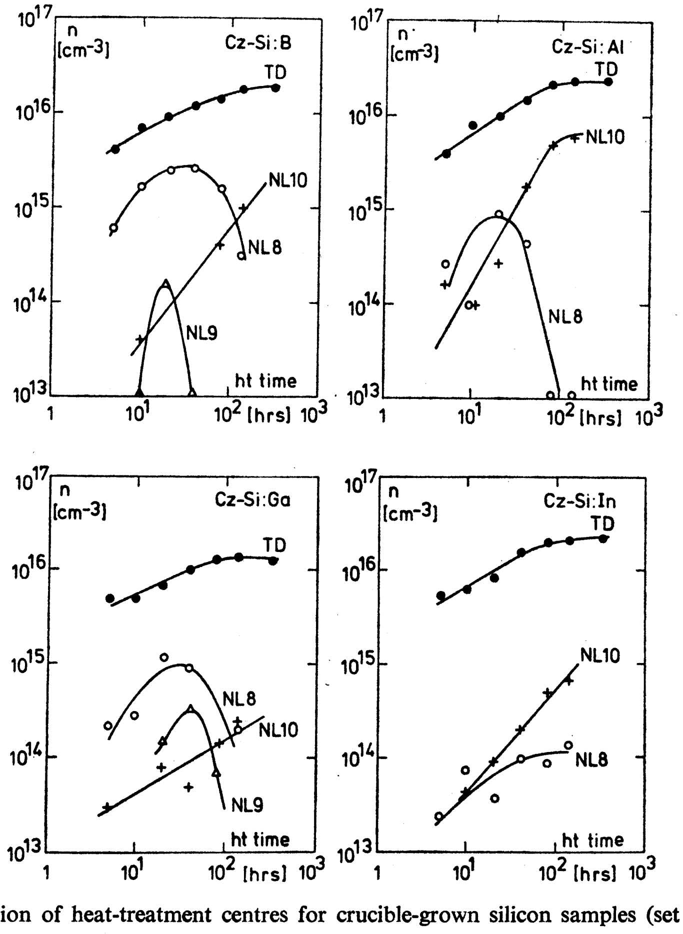

Fig. 1. Concentration of heat-treatment centres for crucible-grown silicon samples (set I) as a function of annealing time. ○ — NL8, △ — NL9, + — NL10, ● — thermal donors TD as calculated from room temperature resistivity measurements under assumption that each TD supplies one electron

trations of the EPR centres ruled out the possibility of relating Si-NL8 to residual boron concentrations. The Si-NL8 spectrum could not be observed in phosphorus doped silicon, which can possibly be understood as Si-NL8 is related to the singly ionized state of the TD; in phosphorus doped material the Fermi level is close to the phosphorus donor level and TDs are in the neutral, nonparamagnetic state. The studies have shown that the production of the Si-NL8 spectrum was favored in boron doped material. The Si-NL10 spectrum which could be observed for all the investigated samples attained the highest concentration for aluminium doping. Following the results of the studies any hypothesis of direct acceptor involvement in the structure of heat-treatment centres became doubtful. However, the incorporation of the dopant could not be ruled out completely. If the dopant takes a position where the spin density is low for symmetry reasons, this leads to undetectable changes in the EPR-spectrum. A different dopant would then produce the same EPR--spectrum.

Another characteristic feature of the Si-NL8 spectrum, the shifting of its *g*-values

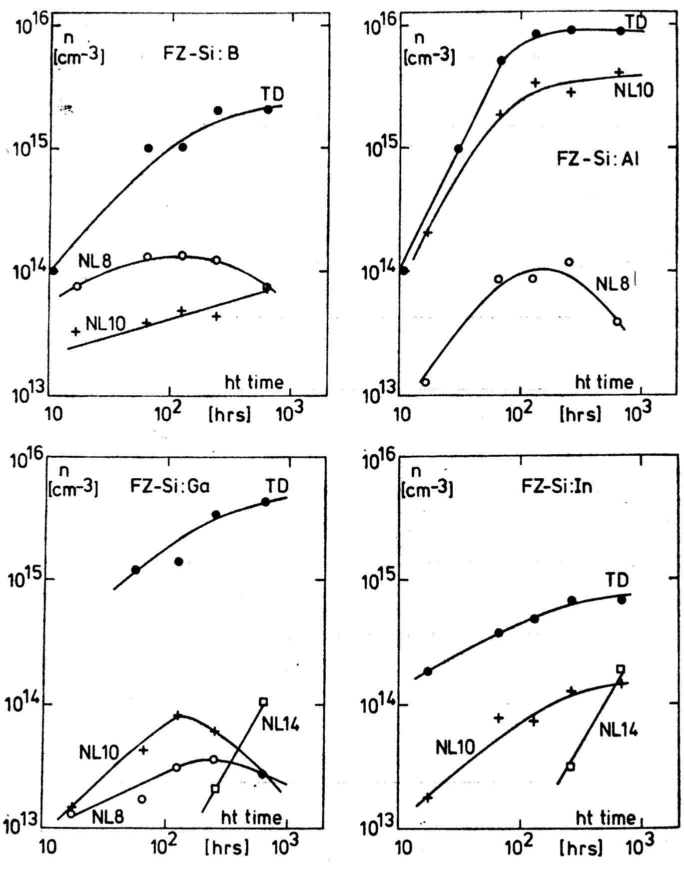

Fig. 2. Concentration of heat-treatment centres for float-zone oxygen doped silicon samples (set II) as a function of annealing time. ○ — NL8, + — NL10, □ — NL14, ● — thermal donors TD as calculated from room temperature resistivity measurements under assumption that each TD supplies one electron

with increased annealing time while preserving the 2 mm symmetry, was confirmed. The studies have further revealed that the Cz-Si samples, which had higher oxygen concentration, were always in a later stage of the g-shifting process than the FZ oxygen doped material.

A similar transformation process was discovered for the Si-NL10 spectrum. It is illustrated in Fig. 3 where the separation ΔB of the two resonances observed with the magnetic field B parallel to the [111] direction is plotted against the annealing time. This separation ΔB is proportional to the component g_{yz} of the g tensor. It was found that the EPR spectra Si-NL10, Si-NL13 and Si-NL17 reported earlier by Muller et al. [6] correspond to different transformation stages of the same centre. Also, as in the case of the Si-NL8, the same forward shift on the time scale of the g-value transformation for higher oxygen contents could be noted (Fig. 3).

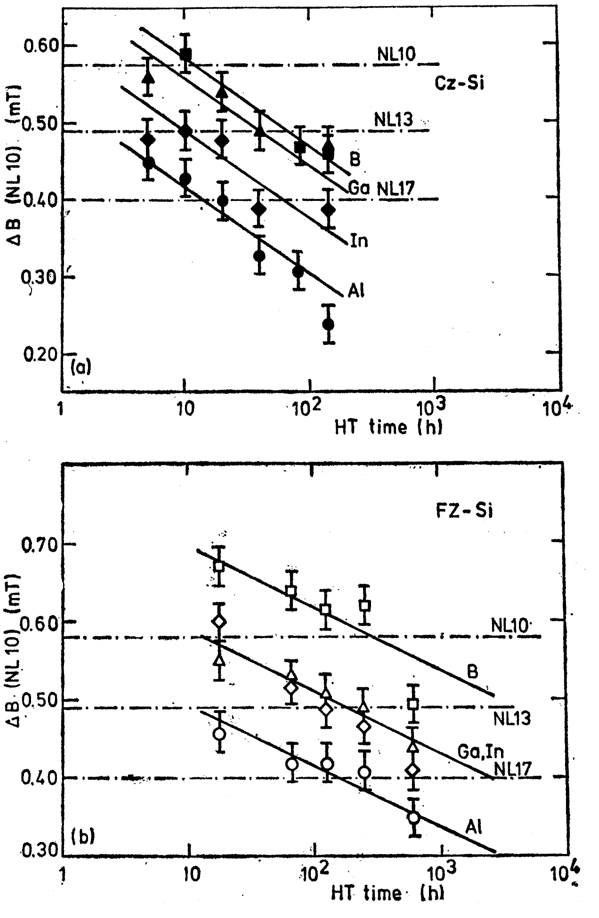

Fig. 3. The annealing time dependence of g-value shifting for the Si-NL10 spectrum as observed under (white light) illumination for (a) Czochralski-grown and (b) FZ oxygen-diffused samples. The transformation of the spectrum is expressed as the time dependent change of the separation ΔB between the two resonances observed with external magnetic field $B \parallel [111]$. ΔB values are scaled to 23 GHz microwave frequency

For all the studied samples, as far as the available concentrations were concerned, the Si-NL10 centre presented the more likely candidate to account for the resistivity changes (as measured at room temperature by four point probe). Since at the same time Si-NL8, and not the Si-NL10 centre, had been correlated to the shallow double donor levels as found in infrared, further studies on microscopic structure, mutual relation and identity of both Si-NL8 and Si-NL10 centres seemed necessary.

Here especially the incorporation of oxygen presented an intriguing question. The oxygen diffused samples with enriched concentration of the ^{17}O isotope were first carefully examined in the EPR-measurements for any ^{17}O hyperfine structure. No such structure was observed. However an ENDOR attempt that followed was successful. In the preliminary ENDOR measurements oxygen involvement has been conclusively confirmed first for Si-NL10 [20] and a year later also for the Si-NL8 centre [21]. Further, more detailed ENDOR studies followed and at the moment extensive ENDOR data are available for both centres.

B. ENDOR study of the Si-NL10 centre

a. Experimental details

The sample used for the ENDOR measurements [22] was commercial (Wacker Chemitronic) aluminium doped FZ silicon with resistivity $\varrho = \sim 2\ \Omega\text{cm}$, aluminium concentration $[\text{Al}] = 9 \times 10^{15}\ \text{cm}^{-3}$ and carbon concentration $[\text{C}] \lesseqgtr 5 \times 10^{15}\ \text{cm}^{-3}$. The sample was further diffused with isotopically enriched oxygen to a total concentration of $4 \times 10^{17}\ \text{cm}^{-3}$ while the concentration of the ^{17}O magnetic isotope was $1.2 \times 10^{17}\ \text{cm}^{-3}$. After the diffusion process the sample was heated up to 1380°C and then rapidly quenched in order to disperse the oxygen. This was followed by a heat-treatment for 200 hrs at 470°C. After 200 hrs the sample was on the brink of p to n-type conversion. The EPR-spectrum showed a strong Si-NL10 signal with a concentration of EPR-active centres of $\sim 10^{16}\ \text{cm}^{-3}$. Some additional measurements were performed also on commercial aluminium doped Czochralski grown silicon.

The measurements were performed with a superheterodyne spectrometer operating at 23 GHz and adjusted to detect the dispersion part of the EPR signal. The magnetic field, modulated at a frequency of 83 Hz, could be rotated in the $(0\bar{1}1)$-plane of the sample. A cylindrical TE_{011}-mode silver coated epibond cavity was used. In the thin silver layer on the cylindrical side wall of the cavity a spiral groove was cut which could serve as an ENDOR-coil. For ENDOR-measurements the radio frequency was square-wave modulated at 3.3 Hz to allow double phase-sensitive detection of the signal. The sample was held at 4.2 K. The ENDOR-measurements were performed under white light illumination. Light from a halogen source was transmitted to the sample by a quartz rod.

b. Results and conclusions

Three independent ENDOR experiments have been performed on the Si-NL10 centre in the same sample: ^{17}O ENDOR, ^{27}Al ENDOR and Field Stepped ENDOR (FStENDOR) allowing to establish the mutual correlation between the results of the first two.

The oxygen ENDOR study revealed that the Si-NL10 centre is an oxygen aggregate.

During 450°C annealing several different species develop by subsequent addition of oxygen atoms (one at the time) along the $[0\bar{1}1]$ crystallographic direction in the (011) plane. The experimental data show that the oxygen atoms incorporated in the centre occupy their "normal" puckered bonded-centred interstitial position with a bond angle of $\sim 114°$.

The ^{27}Al ENDOR study showed that a single aluminium atom was present in the centre regardless of its growth stage. The position of the aluminium was argued to be rather tetrahedral interstitial than substitutional, but the experiment cannot provide a decisive answer here. The conclusion of the aluminium involvement in the Si-NL10 centre was unexpected and difficult to reconcile with the fact that the Si-NL10 spectrum is not characteristic for aluminium doped silicon and can be observed in any heat-treated oxygen-rich silicon regardless of its doping. It has been proposed that aluminium is not really necessary for the formation of the Si-NL10 centre. Due to its affinity to oxygen it takes, when present, an active part in the oxygen aggregation. In that case the aluminium atom provides a very convenient means of probing into the aggregation mechanism.

Additional valuable information was obtained from a FStENDOR experiment. Here is the summary of the most important results which finally allowed to construct for the first time ever the experimentally derived microscopic model of the silicon heat-treatment centre:

— different Si-NL10 species have slightly different EPR spectra thus providing a natural explanation for the so called "*g*-shifting effect",

— the basic Si: Al-NL10 species present in the sample consists of a single aluminium and two oxygen atoms. The centre has 2 mm symmetry with the aluminium atom located on the twofold axis of the defect. The microscopic model of the smallest possible Si-NL10 centre species is depicted in Fig. 4,

— the later developing species have no longer exactly 2 mm type symmetry, although the deviation towards the lowei m-type symmetry is very small and as such not resolved in the EPR experiment. The second species of the defect incorporates again only one aluminium atom and (most probably) three oxygen atoms. All later species also incorporate a single aluminium atom and a subsequently growing number of oxygens,

— in case of relatively high oxygen contents also centres similar to the two discussed above but (most probably) with the silicon and not the aluminium atom moving away to create a vacancy may be formed.

On the basis of the discussion two possible identifications of the Si-NL10 centre were proposed. According to one of them Si-NL10 centre is an oxygen heat-treatment aggregate, growing in parallel to TDs and with very similar structure. However the incorporation of an acceptor would probably make it a shallow single donor instead of a double donor. An alternative explanation identifies Si-NL10 as an acceptor TD^- state of the silicon thermal donor. This attractive possibility which has recently been further supported by confirmation of the acceptor character of the Si-NL10 centre [23] allows to understand the majority of experimental data. However in such case the core of the TD would involve a vacancy which by itself has a deep centre character. Although one can expect that the presence of oxygen atoms in direct vicinity of the vacancy would most certainly influence its electrical properties this possibility would have to be confirmed by theoretical calculations.

Recently also the ^{29}Si ENDOR experiment on the Si-NL10 centre has been performed

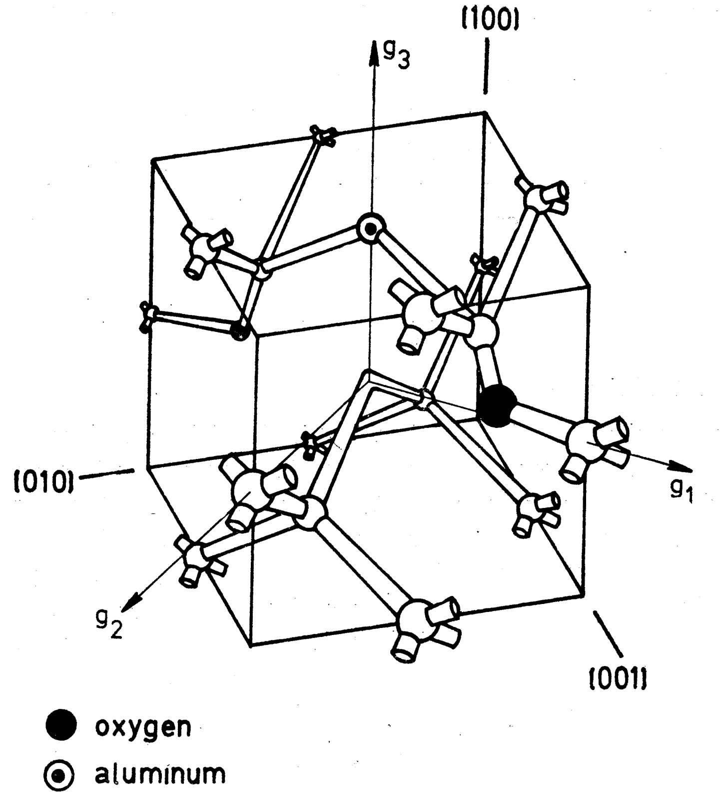

Fig. 4. Structural model for the smallest species of the Si-NL10 centre with the possible incorporation of the aluminium atom shown in here on tetrahedral interstitial position

[24]. The results which will be published shortly fully confirm the extremely shallow character of the centre. On the other hand the revealed interactions with silicon nuclei have very similar character to those published before for Si-NL8 centre. This supplies a substantial support for the correlation of the Si-NL10 centre with TD^-.

C. ENDOR study of the Si-NL8 centre

Also the Si-NL8 centre has been investigated with the ENDOR technique. The ENDOR data on the Si-NL8 had been awaited with much interest due to the established relation of this centre to silicon thermal donors.

a. ^{29}Si ENDOR of the Si-NL8 centre

The experiment [25] has been performed on commercial Czochralski grown boron doped silicon with initial oxygen concentration above 10^{18} cm^{-3}. The X microwave band of $\sim$9 GHz was used. Due to higher anisotropy of the Si-NL8 centre (in comparison to that of the Si-NL10) the lower EPR resolution of X-band did not present a major setback. However one has to note that the reported linewidth of the ENDOR resonances was bigger than in the previously described Si-NL10 ENDOR experiment thus severly limiting the resolving power.

The ^{29}Si ENDOR experiment confirmed the relatively shallow character of the thermal donor. The most significant result was the lack of the big hyperfine interaction of 80 MHz. Such interaction was predicted by at that time commonly accepted OBS model for the central interstitial silicon atom positioned on the 2-fold symmetry axis of the thermal donor. The experiment also confirmed the 2 mm symmetry of thermal donor species. However that particular conclusion has to be viewed with special care; a very small deviation from the 2 mm symmetry type of the magnitude similar to that found for the Si-NL10 centre would in this case be far beyond the available resolution.

b. ^{17}O ENDOR of the Si-NL8 centre

Very recently also ^{17}O ENDOR data for the Si-NL8 centre became available [21]. In the experiment which was again conducted under the same conditions as ^{29}Si ENDOR a boron doped FZ silicon sample was used. The sample was further diffused with isotopically enriched oxygen in the oxidation/diffusion procedure similar to that used before for the sample of the Si-NL10 study. On the basis of the interpretation of the experimental results the model of the silicon thermal donor as depicted in Fig. 5 has been proposed. As can be seen from the figure the proposed model involves 4 oxygen atoms and a vacancy in the

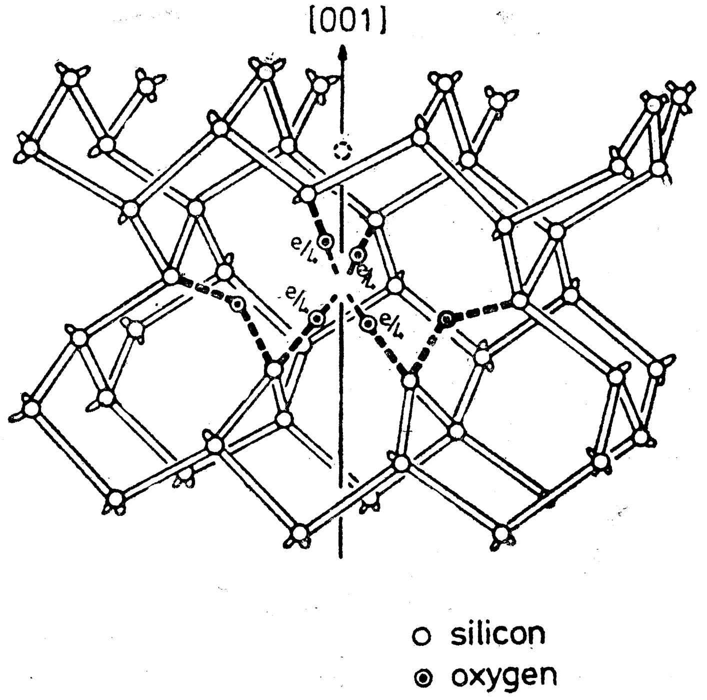

Fig. 5. Structural model for the thermal donor species TD2 as developed by Michel et al. [21] on the basis of ^{17}O ENDOR data

core of the thermal donor. Simultaneous addition of two oxygen atoms along the [011] crystallographic direction on both sides of the core is suggested as the thermal donor growing mechanism.

While comparing the model for the Si-NL8 centre with the one discussed before for the Si-NL10 one cannot escape the conclusion that experimental evidence supporting it is by far insufficient. Here especially the growth mechanism of the thermal donor is weakly founded; it finds absolutely no evidence in the ^{17}O hyperfine interactions and is deduced entirely from the overall 2 mm character of the defect. In view of the already mentioned resolution considerations this growth mechanism, which is otherwise very difficult to accept from purely conceptional point of view, has to be treated yet as one more suggestion and not as the experimental conclusion. Also the evidence on which the model of the thermal donor core (which in contrast to the Si-NL10 involves 4 and not 2 oxygen atoms) is based appears fragile and remains to be further verified.

3. Conclusions

On the basis of the experimental information reviewed here and concerning heat-treatment centres in silicon one is tempted to conclude that the problem of the thermal donors, one of the longest unravelled puzzles of silicon, will very soon find its final solution. And although several surprises might still be awaiting, there is such a wealth of information available at the moment that, when finally sorted out, it must result in a clear and consistent physical picture of the phenomenon.

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