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HEAT-TREATMENT CENTRES AND THERMAL DONORS IN SILICON

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ABSTRACT

The paper discusses the correlation of the EPR spectra with the silicon thermal donors. Recent ENDOR results and the emerging structural models for the prominent Si-NL8 and Si-NL10 centres are presented. Following the Si-NL10 model the identification of that centre as the overcharged TD^- acceptor-like state of the thermal donor is proposed and supported by experimental evidence.

INTRODUCTION

When oxygen-rich silicon is heat-treated in the 300-500 °C temperature range shallow double donor states are produced. Those are generally termed "thermal donors" and were subjected to intensive studies over the last 35 years. In spite of the experimental data gathered no structural model for the thermal donor could be established. This confusing situation is changing only recently as the detailed structural information becomes available from the electron nuclear double resonance (ENDOR) experiments.

Already at a relatively early stage of the thermal donor studies it was noted that the creation of the donor centres is accompanied by the simultaneous generation of several EPR spectra [1], predominantly of pointgroup 2mm (C_{2v}), or higher symmetry. Out of the nine different EPR spectra discovered at that moment two, namely Si-NL8 and Si-NL10, could later be attributed to the thermal donor centres on the basis of the production characteristics [2,3]. At the same time, in the infrared absorption experiment under uniaxial stress the Si-NL8 spectrum has directly been identified with the singly ionized TD^+ state of the thermal donor [4]. The origin of the other TD-related and generally more prominent Si-NL10 EPR spectrum remained unclear. In that situation, in order to unravel the structure of the thermal donors as well as to understand the identity of the Si-NL10 center, the ENDOR studies have been undertaken.

ENDOR STUDIES OF THE HEAT-TREATMENT CENTRES

The ENDOR study of the heat-treatment centers was possible only after the successful diffusion of the 17-oxygen isotope into silicon crystals [2]. For the Si-NL10 centre already the preliminary ENDOR experiment was very successful, establishing unambiguously for the first time the direct involvement of oxygen in the structure of the thermal donor centre [5]. Following that, full ENDOR analysis of the hyperfine (and quadrupole) interactions with the 29-silicon, 27-aluminium and 17-oxygen nuclei has been performed [6]. As a result the

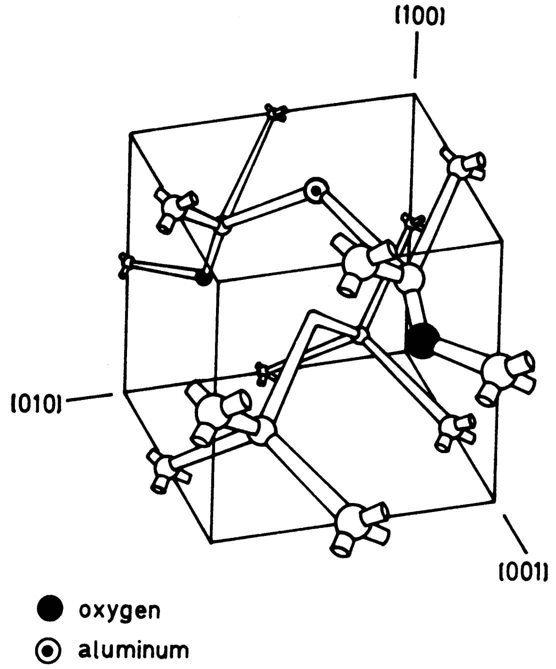

Figure 1. Structural model for the Si-NL10 centre.

detailed microscopic model of the Si-NL10 centre could be proposed - figure 1. According to that model the Si-NL10 EPR spectrum is generated by a series of very similar oxygen aggregates. A smallest species involves 2 oxygen atoms which take the usual puckered bond-centered interstitial position in the silicon chain in one of the {011} planes of the crystal. To release the stress accumulated by oxygen clustering the vacancy is created in the centre of the defect. For the aluminium doped silicon, due to substantial oxygen - aluminium afinity, the aggregation will take place in the direct vicinity of the aluminium atoms. In such case aluminium interstitials will be formed as a result of heat treatment and oxygen aggregation process. Upon prolonged heat treatment the Si-NL10 centre will grow by further addition of the oxygen atoms along the [0$\bar{1}$1] oriented silicon chain. The structure created in this way will be planar in one of the mirror planes of the defect. The symmetry, which for the smallest possible species (the Si-NL10 core) is orthorhombic will be lowered to monoclinic for later species. Different species of the Si-NL10 centre are characterized by slightly different g-values; the varying concentration of various species with heat-treatment time is then responsible for the observed semicontinuous shifting of the experimentally determined overall g-value of the superimposed, inhomogeneously broadened EPR spectrum.

Also the Si-NL8 centre has been studied by the ENDOR technique [7] with the aim to determine the thermal donor core. Until now the results of the ^{29}Si ENDOR as well as some preliminary data from the ^{17}O ENDOR have been published. Following the results of the study the once prominent OSB and Ylid thermal donor models could be rejected. The ^{17}O ENDOR confirmed the involvement of oxygen in the structure of thermal donors and resulted in a tentative model of the thermal donor core consisting of 4 oxygen atoms in a vacancy.

MUTUAL RELATION BETWEEN THE Si-NL8 AND NL10 CENTRES AND THERMAL DONORS

As pointed out in the preceding paragraph the currently proposed models for the Si-NL8 and Si-NL10 centres differ in the structure of their core. However otherwise the two centres appear remarkably alike. Let us now summarize the characteristic features which the two centres have in common:

1. production;
   both centres are generated in oxygen-rich silicon by the same heat treatment regardless of the doping impurity. The generation of the Si-NL8 and Si-NL10 EPR spectra always coincides with simultaneous formation of thermal donors. Also the liquidation of the heat-treatment centres and thermal donors is evidently correlated.
2. g-values;
   both spectra have g-values which fall in the common category of shallow defects.
3. g-shifting phenomenon;
   both spectra exhibit a rather unique feature of the semicontinuous, gradual change of their g-values as a function of the heat-treatment duration.
4. oxygen incorporation and structure;
   both centres are beyond any doubt identified as gradually growing oxygen aggregates of the same symmetry. Both develop a series of (otherwise) very similar species by subsequent addition of oxygen atoms along an <011> crystallographic direction.
5. ground state;
   both centres have an A_1-ground state.
6. spin function distribution;
   both centres have very similar ^{29}Si ENDOR data with bigger delocalization for the Si-NL10 centre.

As can be concluded from the above list the two centres are almost identical. In view of the well-established identification of the Si-NL8 centre as TD^+ its similarity to the Si-NL10 centre and consequently the close correlation of the Si-NL10 centres with the thermal donors appears extremely intriguing. The Si-NL8 and NL10 centres are so similar that it seems useful to point out their differences. The most important of them are:

1. g-values;
   the anisotropy of the Si-NL10 spectrum is substantially smaller than that of Si-NL8.
2. production;
   in p-type silicon Si-NL8 spectrum is generated first and is then followed by the creation of the Si-NL10 centre (in usually higher concentrations). In n-type Czochralski silicon only the Si-NL10 spectrum can be observed.

In view of the above two possible interpretations of the origin of the Si-NL10 EPR spectrum seem possible. According to the first one the Si-NL10 centre would be an oxygen aggregate very similar to the thermal donor but of more shallow character. However this seemingly plausible idea has to be rejected on basis

of several independent and direct arguments. Firstly, the proposed centre, being on one side significantly different from the "standard" thermal donor, should arise, grow and decompose in parallel to it. At the same time the new centre is identified as an oxygen aggregate of 2mm (C_{2v}) symmetry in complete analogy to the thermal donor. This requires two closely parallel clustering mechanisms which, however, lead to significantly different results. Such a possibility seems very improbable. Secondly, it is difficult to propose which structural component could possibly discriminate the two different thermal donor types. The last, but probably the most convincing argument is provided by the fact that should the different thermal donor exist, be it of double or single character, in view of the large concentrations of the Si-NL10 centres its (ladder of) energy levels would have been seen in the infrared absorption. That however is clearly not the case; the only series of energy levels ever observed (in significant concentrations) in heat-treated silicon belongs to the "standard" thermal donors.
The suggested generation of a vacancy on the twofold axis of the Si-NL10 centre offers yet another interpretation of the Si-NL10 spectrum. In close analogy to the vacancy centre in silicon one can expect that also the vacancy-based cluster could have several states within the silicon energy band gap. The Si-NL10 EPR spectrum could then be identified with the overcharged, acceptor-like TD^- state of the thermal donor.

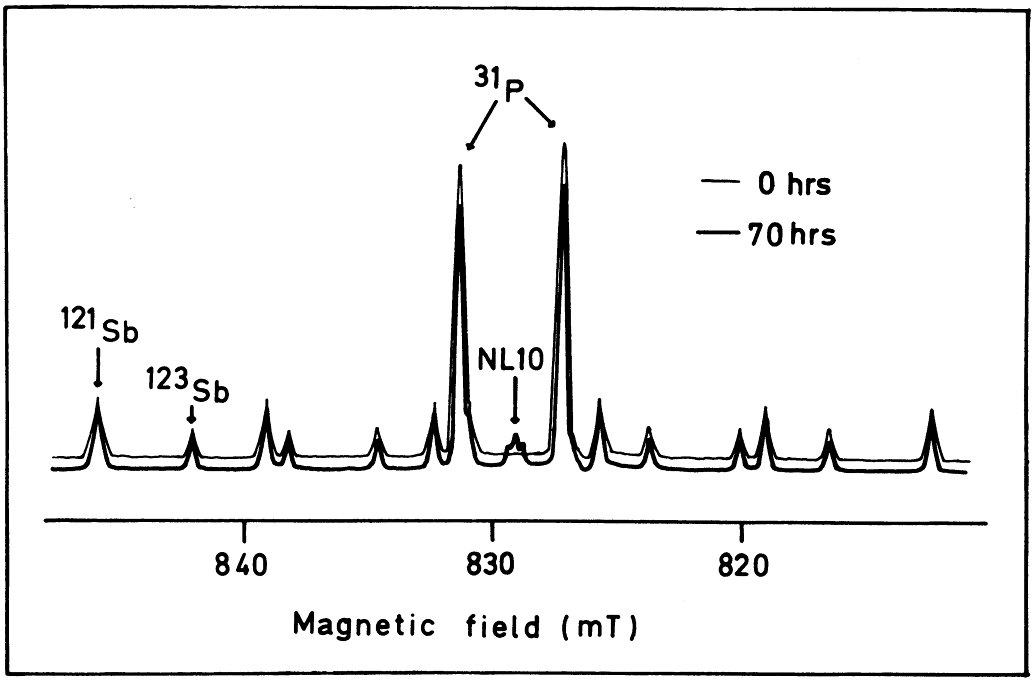

Figure 2. EPR spectrum of the n-type, Czochralski-grown silicon sample before - thin line - and after - thick line - 70 h heat-treatment. The EPR signal of the standard antimony doped silicon sample is also shown.

ACCEPTOR CHARACTER OF THE Si-NL10 CENTRE

Following the idea to identify the Si-NL10 EPR spectrum with the overcharged TD^- state of the thermal donor the acceptor character of the Si-NL10 centre has further been investigated [8]. The idea of the experiment stemmed from the observation that while in p-type material the Si-NL10 signal was strongly growing upon illumination almost no such effect existed in case of the phosphorus doped n-type silicon. The effect could possibly be explained assuming that while in p-type material light was necessary to provide electrons to populate the TD^- level, in n-type silicon that level could be populated at the expense of the phosphorus donor.

In the experiment a phosphorus doped Czochralski silicon sample was used. The intensity of the phosphorus and the Si-NL10 EPR signal was carefully monitored against the annealing time. An antimony doped silicon sample was used as a standard for the determination of the relative concentrations of the EPR centres. The result of the experiment is depicted in figure 2. As can be seen, after 70 hours of heat treatment at 470 °C a relatively strong Si-NL10 signal was produced. At the same time a clear decrease of the phosphorus signal intensity could be observed, the size of it being similar to that of the created NL10 signal. Such effect can only be understood if acceptor centres were created in the energy gap. This result provides a very strong indication of the acceptor character of the Si-NL10 centre giving thus major support for the identification of the centre as the overcharged state TD^- of the thermal donor.

ACKNOWLEDGMENT

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