

High-field EPR spectroscopy of thermal donors in silicon

T. Gregorkiewicz^a, W. Knap^b, H.H.P.Th. Bekman^a, L.C. Brunel^b, C.A.J. Ammerlaan^a
and G. Martinez^b

^a*Van der Waals–Zeeman Laboratorium, Universiteit van Amsterdam, Valckenierstraat 65, NL-1018 XE Amsterdam, The Netherlands*

^b*Service National des Champs Intenses – CNRS, 25, avenue des Martyrs, F-38042 Grenoble Cedex, France*

Si-NL10 thermal donors were investigated by high-field electron paramagnetic resonance in an experimental set-up consisting of a pumped far-infrared laser operating in the 350 GHz frequency range and a superconducting coil. The experiment was conducted at a magnetic field of about 12 T. Under these conditions the first direct experimental evidence for the multispecies character of the Si-NL10 thermal donor centres has been obtained.

1. Introduction

1.1. Thermal donor centres in silicon

Thermal donors are among the most studied systems relevant to the materials science of silicon. In the early 1950s it was noticed that when oxygen-rich silicon is exposed to isothermal annealing in the 450°C temperature range, electrically active centres of shallow donor character are created. These are usually termed thermal donors (TDs); due to their high abundance they appear to be of considerable significance for device manufacturing. These practical considerations stimulated research in the TD field. However, the TD issue turned out to be particularly complex and in spite of intensive studies no single undisputed thermal donor model has so far been proposed. Nevertheless, some important information on the TD structure has been obtained. The two most significant findings are:

1. participation of oxygen atoms in TD formation, and
2. multispecies character.

The second point is especially intriguing; infrared absorption spectroscopy revealed the existence of a series of up to 11 very similar but clearly different shallow (double) donor centres.

This characteristic feature, which is uncommon for defect centres in semiconductors, has recently received support from photoluminescence studies of TD-bound excitations. Also in this case a series of luminescence lines of very similar energy could be observed.

1.2. Magnetic resonance studies of thermal donors

Magnetic resonance studies with their unique ability to reveal the details of the microscopic structure of paramagnetic centres have been applied to TDs in silicon. Here two electron paramagnetic resonance (EPR) spectra, namely Si-NL8 and Si-NL10, were found to be TD-related [1, 2]. The Si-NL8 spectrum was shown to originate from the singly ionized TD⁺ state of the thermal donor [3], while the origin of the Si-NL10 paramagnetic centre is still under discussion [4]. In the case of EPR, the multispecies character of TDs could not be observed while it was suspected to give rise to the so-called “g-shifting” effect, i.e. the quasi-continuous transformation of both spectra upon prolonged annealing time. In figs. 1(a) and (b) the “g-shifting” effect is illustrated for the Si-NL8 and Si-NL10 spectra, respectively. As can be seen, the effect manifests itself as a subsequent de-

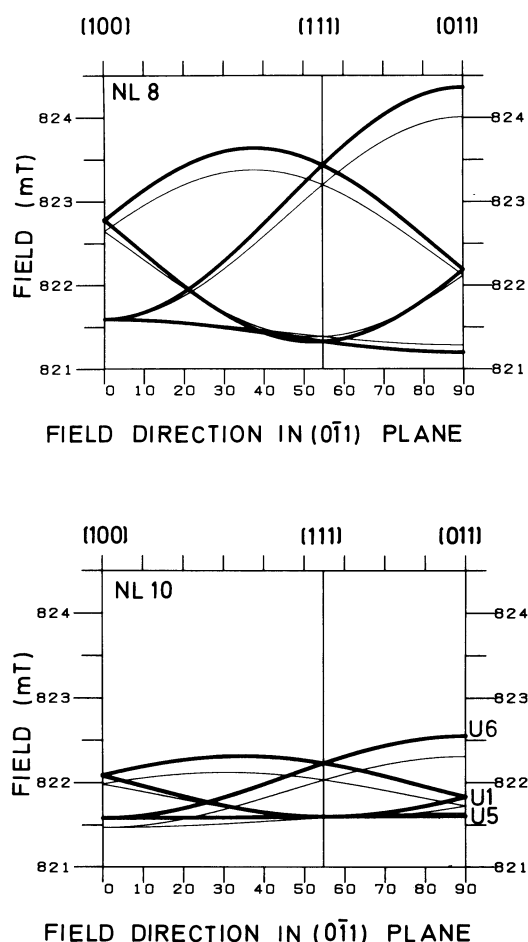


Fig. 1. g -shifting effect as observed by standard EPR technique (23 GHz) for (a) Si-NL8 and (b) Si-NL10 TD-related spectra. The thick and thin lines correspond to annealing at 470°C for 10 and 100 h, respectively. For the Si-NL10 spectrum the U1, U5, and U6 high symmetry points are marked.

crease of the anisotropy of the spectra upon prolonged annealing. In terms of g -value analysis this implies considerable lowering of the value of the off-diagonal element g_{yz} of the (orthorhombic I) g tensor for both spectra as well as gradual equalization of both diagonal elements. In the case of the Si-NL10 centre, the idea of the direct relation between the “ g -shifting” and the multispecies character of TDs was further supported by indirect evidence obtained by the advanced field-stepped electron nuclear double resonance (FStENDOR) technique [5]. The FStENDOR

results indicated that indeed the EPR line width was inhomogeneously broadened, containing several components which then could be related to the individual TD species. In fig. 2 the results as obtained by the powerful FStENDOR technique are shown; as can be noted for a Cz-Si:Al sample annealed for 48 h at 470°C, the presence of up to 8 subcomponents was unraveled in the superimposed overall EPR line [5]. Each subcomponent would then correspond to an individual TD species and the (time) varying ratio of the concentration of various species would provide a natural explanation of the “ g -shifting” phenomenon. The FStENDOR experiment was capable of providing the indicative positions – in terms of effective g -value parameters – for the individual EPR lines and the separation between them. However, due to the physical background of this technique, no accurate information as to the magnitude of the subcomponents could be given thus severely restricting the applicability of the concept. The direct EPR experiment does not possess this handicap since, under certain conditions, the intensity of the resonance line is directly proportional to the concentration of paramagnetic centres. However, the EPR experiments performed at the microwave bands of 9 and 23 GHz fail to resolve these subcomponents.

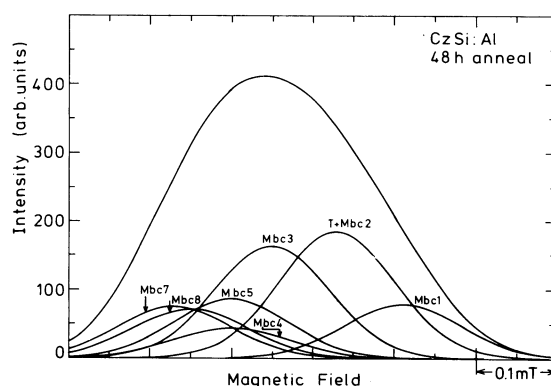


Fig. 2. Multispecies character of the Si-NL10 thermal donor as unraveled by the FStENDOR technique for an Al-doped Cz-Si sample following 470°C/48 h annealing. As can be seen, at least seven different components contributing to the overall EPR line could be traced.

2. High-field experiment

2.1. Experimental details

In view of the above consideration an EPR experiment in high magnetic field has been prepared with the idea of combining the semi-quantitative (relative information only) character of the classical low frequency EPR technique with enhanced resolving power as provided by high magnetic field measurements. The experimental set-up, the details of which can be found elsewhere [6], consisted of an optically pumped far-infrared (CO_2) laser as a stable 350 GHz source and a high homogeneity superconducting coil capable of providing magnetic fields in the 12 T range necessary to observe the expected EPR signals with $g \approx 2$.

Since the high field (HF) EPR experiment was to be conducted without a microwave cavity and would comprise direct measurement of the magneto-absorption, a relatively high concentration of paramagnetic centres in the studied sample was required to compensate for the loss of sensitivity. To achieve that situation a sample of Cz-Si:Al silicon was prepared by annealing for 200 h at 470°C [2].

2.2. Results

Prior to the high field experiment the sample was first measured by conventional low frequency (23 GHz) EPR; a strong Si-NL10 spectrum could be detected showing no dependence of its intensity on (white light) illumination. This spectrum with the magnetic field along the [0 1 1] crystallographic direction is depicted in fig. 3(a). As can be seen it is in full agreement with the angular dependence presented in fig. 1(b) with no splitting visible even at the U6 point where the g -shifting phenomenon manifests itself best. The ENDOR spectrum has also been measured and is depicted in fig. 3(b) as recorded for the U6 high symmetry point of the EPR line. The individual resonances – marked T, Mbc3, Mbc4, Mbc5 and Mbc7 – belong to different Si-NL10 species. From the FStENDOR measurement the effective g values of EPR corresponding to these

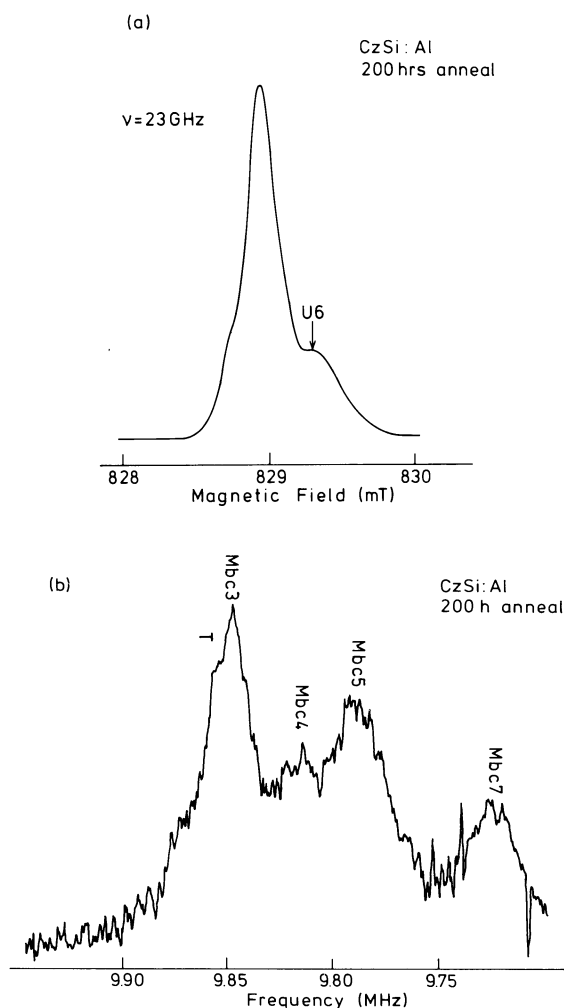


Fig. 3. Si-NL10 EPR (a) and ENDOR (b) spectra of a Cz-Si:Al sample annealed at 470°C for 200 h obtained for 23 GHz microwave frequency. Magnetic field is along the [0 1 1] crystallographic direction. The same sample was used for the HF-EPR experiment (see fig. 4). The ENDOR spectrum was measured at the U6 high symmetry point. The individual resonance lines are marked according to their different species of origin.

species could be determined. These are collected in table 1.

The high field EPR experiment conducted in the 349 GHz/12 T range was very successful. Ultrahigh resolution has been achieved allowing, for the first time, the observation of EPR spectra related to the individual TDs and thus confirming the multispecies character of the Si-NL10

Table 1

Comparison of results obtained by FStENDOR measurements conducted at 23 GHz and by the HF-EPR technique at 349 GHz. The effective g values for the U6 high-symmetry point $g_{\text{eff}}(\text{U6})$ in both cases are given. In addition, for all the observed Si-NL10 thermal donor species, complete g -tensors, as determined on the basis of HF-EPR measurements, are also presented. For both kinds of measurements the error in g value determination can be estimated as 10^{-4} .

Si-NL10 species	FStENDOR (23 GHz) $g_{\text{eff}}(\text{U6})$	HF-EPR (349 GHz)			
		$g_{\text{eff}}(\text{U6})$	g_{xx}	g_{zz}	g_{yz}
Al-T	1.99767	1.99765	1.99978	1.99853	0.00088
Al-Mbc3	1.99785	1.99779	1.99978	1.99860	0.00081
Al-Mbc4	—	1.99793	1.99978	1.99867	0.00074
Al-Mbc5	1.99810	1.99797	1.99978	1.99869	0.00072
Al-Mbc7	1.99833	1.99813	1.99978	1.99877	0.00064

thermal donor. Figure 4 presents the Si-NL10 spectrum as measured at 349 GHz with the magnetic field parallel to $[011]$. In the figure the actual scans with three different (magnetic field) modulation amplitudes are presented. For direct correlation with standard EPR, the spectra should be compared with that shown in fig. 3(a). A substantial increase of the resolution can be

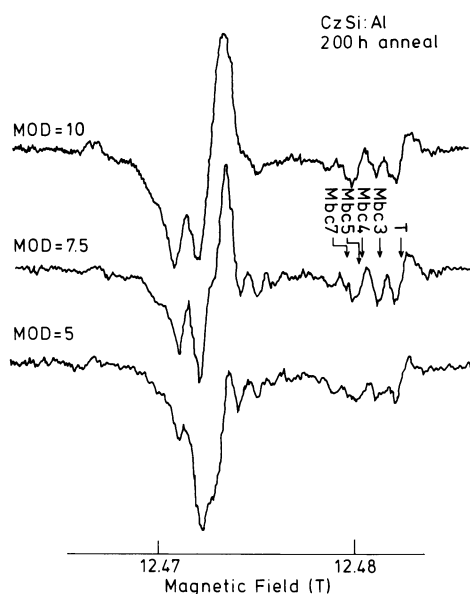


Fig. 4. HF-EPR spectrum of a Cz-Si:Al sample heat-treated for 200 h at 470°C. The frequency is 349 GHz and the magnetic field (along the $[011]$ crystallographic direction) is in the 12 T range. The well-resolved EPR lines corresponding to individual Si-NL10 species are indicated. Three spectra as obtained for three different field modulation values are shown.

concluded with the individual species clearly separated in the U6 high symmetry point. This made it possible to determine the individual effective g values. In table 1 these values are compared with analogous values obtained from earlier FStENDOR investigations. A remarkable agreement can be concluded.

Upon closer inspection of fig. 4 some further details are revealed, namely the U5 point appears to be identical for all the spectra while (for the lowest value of the modulation current) the U1 point shows a similar splitting to that of U6 but of smaller magnitude. In the case of the orthorhombic-I symmetry, the g -tensor has three independent components: g_{xx} , g_{zz} and the off-diagonal element g_{yz} . For the measurement in the $[011]$ direction ($\mathbf{B} \parallel [011]$), the effective g values are easily connected with g -tensor elements. Namely for U1, $g_{\text{eff}} = 1/2(g_{xx} + g_{zz})$, for U5, $g_{\text{eff}} = g_{zz} + g_{yz}$, and for U6, $g_{\text{eff}} = g_{zz} - g_{yz}$. Since the biggest splitting between the species is observed at the U6 point, this could imply that the g -tensors of the individual species differ most in their off-diagonal element g_{yz} . In earlier investigations of the g -shifting effect this was indeed shown to be the case [7]. It has further been found that g_{xx} was (within experimental error) constant while the other diagonal element g_{zz} also exhibited a linear shift with annealing time. The g_{zz} shift was somewhat smaller than that of g_{yz} and opposite in sign. As a result, the effective position of the U5 point remains almost constant upon annealing (see fig. 1(b)).

Taking into account the above information

one can use the spectra depicted in fig. 4 to determine complete g -tensors for individual Si-NL10 thermal donor species. The procedure is based on the following assumptions:

1. all the Si-NL10 species are of orthorhombic-I symmetry,
2. the position of the U5 high-symmetry point is the same for all individual EPR spectra, and
3. the g_{xx} diagonal element is identical for all species.

Following the above assumptions complete g -tensors can be calculated. The results are included in table 1.

3. Conclusions

The multispecies character of the Si-NL10 thermal donor centres in silicon has been confirmed by direct experimental evidence. Excellent agreement of the individual effective g -values obtained by both experimental techniques has been found. For the first time the EPR spectra of the individual Si-NL10 thermal donor species could be identified and their g -tensors determined. Future experiments will aim at confirmation of the spectroscopic description of subsequently formed TD species with particular emphasis on the precise determination of their symmetry type and generation kinetics. The experiment clearly demonstrates the new possibilities

offered by the HF-EPR technique in the highly demanding field of TD research.

Acknowledgement

This project has been partially sponsored by the Netherlands Foundation for Fundamental Research on Matter [Stichting voor Fundamenteel Onderzoek der Materie (FOM)].

References

- [1] S.H. Muller, M. Sprenger, E.G. Sieverts and C.A.J. Ammerlaan, *Solid State Commun.* 25 (1978) 987.
- [2] T. Gregorkiewicz, D.A. van Wezep, H.H.P.Th. Bekman and C.A.J. Ammerlaan, *Phys. Rev. B* 35 (1987) 3810.
- [3] K.M. Lee, J.M. Trombetta and G.D. Watkins, in: *Microscopic Identification of Electronic Defects in Semiconductors*, eds. N.M. Johnson, S.G. Bishop and G.D. Watkins (MRS, Pittsburgh, 1985) p. 263.
- [4] T. Gregorkiewicz, H.H.P.Th. Bekman and C.A.J. Ammerlaan, *Phys. Rev. B* 41 (1990) 12628.
- [5] T. Gregorkiewicz, H.H.P.Th. Bekman and C.A.J. Ammerlaan, to be published.
- [6] F. Muller, M.A. Hopkins, N. Coron, M. Grynberg, L.C. Brunel and G. Martinez, *Rev. Sci. Instrum.* 60 (1989) 3681.
- [7] S.H. Muller, E.G. Sieverts and C.A.J. Ammerlaan, in: *Defects and Radiation Effects in Semiconductors 1978* (Inst. of Physics, Bristol, 1979), p. 297.