Inst. Phys. Conf. Ser. No 95: Chapter 3
Paper presented at Int. Conf. Shallow Impurities in Semiconductors, Linköping, Sweden, 1988

The structure of the NL10 thermal donor in silicon

C.A.J. Ammerlaan, T. Gregorkiewicz and H.H.P.Th. Bekman

Natuurkundig Laboratorium der Universiteit van Amsterdam
Valckenierstraat 65, 1018 XE Amsterdam, The Netherlands

ABSTRACT: The Si-NL10 is a prominent thermal-donor-related EPR spectrum. Electron nuclear double resonance measurements on ^{29}Si nuclei show that the defect centre generating this spectrum has very shallow, delocalised character. At the same time it is found that the spectrum is inhomogeneously broadened as a superposition of a series of very similar components. It is concluded that the spectrum originates from a series of similar centres which are subsequently generated during the heat treatment at about 450 °C. The exhaustive study unravels the electronic and microscopic structure of these centres.

1. INTRODUCTION

Already more than 3 decades ago it was discovered that the heat treatment of oxygen-rich silicon at about 450 °C leads to the formation of shallow donor states, called thermal donors - Fuller et al. (1954), Fuller and Logan (1957), Kaiser et al. (1958). The first publication on thermal donors appeared in 1954 and since then a vast amount of data was gathered on the subject - for a recent review see e.g. Bourret (1985). It is nowadays established that upon heat treatment in the 300-500 °C temperature region a series of very similar shallow double donor centres is created - Wruck and Gaworzewski (1979). They can be observed by standard infrared absorption techniques and up to 9 different species have been reported - Pajot et al. (1983).

Among other experimental techniques also electron paramagnetic resonance has been used in the thermal donor studies. It has been noted that the formation of thermal donors (as monitored in infrared) is accompanied by the simultaneous generation of several electron paramagnetic resonance (EPR) spectra of predominantly 2mm point group symmetry - Muller et al. (1978), (1979). Further studies showed, on the basis of the production characteristics, that the Si-NL8 and Si-NL10 spectra were practically the only ones which could be related to the thermal donor centres as observed in infrared - Gregorkiewicz et al. (1987), Bekman et al. (1987). For one of these - the Si-NL8 spectrum - a direct identification with the singly ionised state of the infrared double donors was made - Lee et al. (1985). Following that a further studies of the Si-NL8 center by the electron nuclear double resonance (ENDOR) technique were undertaken - Michel et al. (1986). At the same time the origin of the other thermal-donor-related and usually the more prominent Si-NL10 centre remained unclear and required further investigation. Consequently the ENDOR study of the

Si-NL10 centre has been performed - Gregorkiewicz et al. (1988).

2. EPR STUDIES OF THE Si-NL8 AND Si-NL10 CENTRES

2.1 Symmetry

The paramagnetic centre is characterised by the g-factor which is a basic spin-Hamiltonian parameter and therefore acts as a characteristic identification mark discriminating various EPR spectra. The symmetry of the centre is reflected directly by the symmetry of its g-tensor. The g-values for the Si-NL8 and Si-NL10 spectra in their early and late transformation stages are presented in Table 1.

Table 1. Principal g-tensor values for the Si-NL8 and Si-NL10 EPR spectra in early and late transformation stages (10 and 200 h heat-treatment time, respectively).

Spectrum	transformation stage	g_1 ∥[011]	g_2 ∥[0$\bar{1}$1]	g_3 ∥[100]
Si-NL8	early	1.9926	2.0012	1.9999
	late	1.9938	2.0008	1.9999
Si-NL10	early	1.9975	1.9996	1.9996
	late	1.9980	1.9995	1.9998

For both Si-NL8 and Si-NL10 TD-related EPR spectra the symmetry was found to be orthorhombic, point group 2mm. This means that the defects generating those spectra must have two nonequivalent symmetry planes. This information is of basic importance for the modeling of the thermal donor core structure; following this result the most prominent OSB and Ylid models could be constructed. One should however note here that the conclusion concerning the symmetry of the centre is valid only within the resolution of the EPR experiment; it can never be excluded that lower symmetry interactions exist but are small for some reasons and therefore remain hidden within the resonance linewidth or lead to its inhomogeneous broadening.

2.2 Shallow character

The shallow character of the centre can already be deduced from its g-tensor value. Although the g-tensor of the defect is an important EPR parameter unfortunately its theoretical interpretation presents a very complicated problem. Even for relatively simple cases as the shallow donor and acceptor impurities, whose wave functions are known in sufficient detail no satisfactory calculations of g-values are available. For the more complicated systems of lattice defects in silicon, generally of deep level character, at most qualitative considerations can be given. On the other hand, Lee and Corbett (1973) proposed an empirical classification of g-values, which was further extended by Sieverts (1983). In this classification scheme 4 different types of defects are distinguished:

type A: vacancy-type defects with one dangling bond or two parallel dangling bonds,
type B: vacancy-type defects with two or more dangling bonds under tetrahedral angles,
type C: interstitialcies,
type D: impurities on substitutional and interstitial sites.

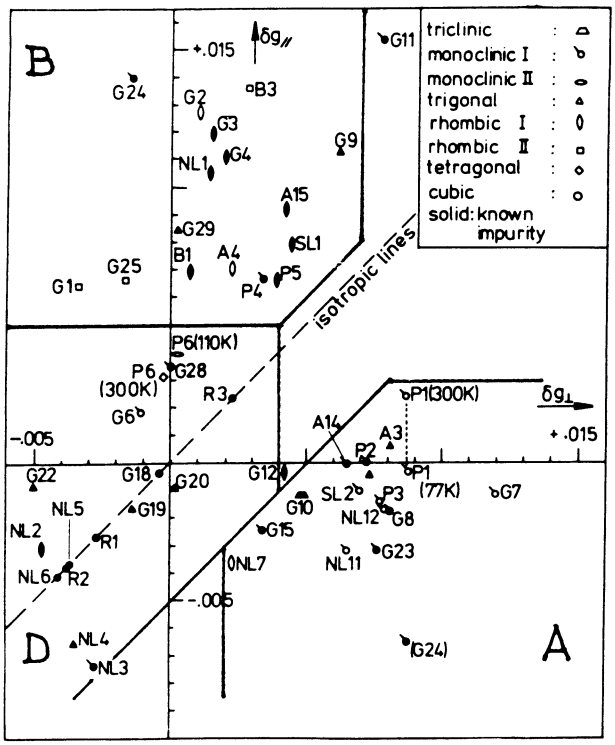

Figure 1. Plot of δg-values ($\delta g = g-2.0023$) of EPR spectra from A) defects with one or two parallel broken bonds, B) defects with two or more broken bonds under tetrahedral angles, C) interstitial-type defects, and D) substitutional and interstitial impurities and their complexes (closed symbols - known impurity) - Sieverts (1983).

In the proposed scheme g-values of defect centres are represented in a 2-dimensional plot of reduced g-values. The reduced g-values are constructed from the principal g-values by assuming them to be axially symmetric. Then the most deviating g-value is defined as the parallel value $g_{\parallel}$ and the average of the other two principal g-values is the perpendicular value $g_{\perp}$. If then $g_{\parallel}$ is plotted against $g_{\perp}$ different types of defects will group in different sections of the diagram as depicted in Fig.1. In Fig.2 the small section of the diagram grouping shallow defects and impurities of type D (the "Dutch corner") is shown. As can be seen the

heat-treatment centres Si-NL8 and Si-NL10-13-17 (presently identified to be one centre) both have their g-values in this particular region. The identification of the Si-NL8 spectrum as originating from the singly ionised TD^+ state of the thermal donor directly confirms the shallow character of the centre. Thus the conclusion that also the Si-NL10 spectrum originates from a loosely bound electron is supported.

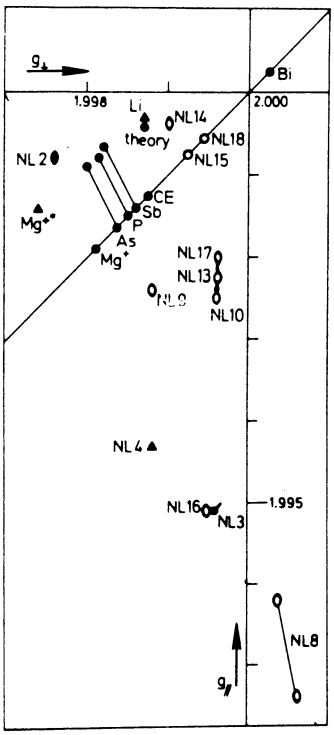

Figure 2. The "Dutch corner" - plot of shallow, effective-mass donor defects - Sieverts (1983).

2.3 g-shifting effect

The most peculiar feature of the two TD-related EPR spectra is the gradual, semicontinuous change of their g-tensor values upon duration of the heat-treatment time. Such a feature is rather unique and the fact that it is being found for both centres indicates close similarities of their structure. The shifting of the g-values can be explained either by subtle changes within the centre itself or by gradual changes of the environment - e.g. stress accumulation or release connected with oxygen aggregation in the direct vicinity of the paramagnetic centre. The EPR studies could not discriminate between those two drastically different possibilities which, at the time that the g-shifting phenomenon was first noticed, seemed equally probable. Such a distinction was only possible in the electron nuclear double resonance studies that followed.

3. ENDOR STUDY OF THE Si-NL10 CENTRE

For the Si-NL10 centre whose origin was particularly intriguing an extensive ENDOR study has been performed. This included analysis of the hyperfine interactions with ^{29}Si, ^{17}O and ^{27}Al nuclei. As a result both the microscopic - Gregorkiewicz et al. (1988) - and the electronic - Bekman et al. (1988) - structure of the Si-NL10 centre has been unraveled. It was confirmed that, as already indicated in EPR by the g-shifting phenomenon, the Si-NL10 spectrum originates from a series of gradually developing, very similar centres.

3.1 Shallow defect character

Figs. 3a and 3b show the angular dependence of the $\overleftrightarrow{A}$-tensor as determined from a ^{29}Si ENDOR experiment for two shells within one species of the Si-NL10 centre. The tensors are of orthorhombic and triclinic symmetry, respectively.

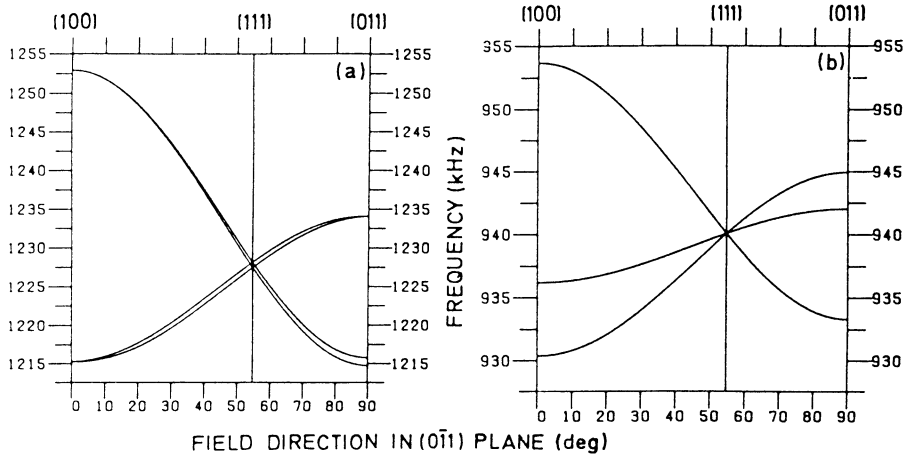

Figure 3. Computer simulations of the angular dependences of two silicon hyperfine tensors of the Si-NL10 spectrum of (a) orthorhombic (tensor T2) and (b) triclinic symmetry (tensor G2). Microwave frequency 23 GHz.

The experimental ENDOR data are usually analysed employing the linear combination of atomic orbitals (LCAO). In the LCAO analysis the wave function at the ligands is approximated by a linear combination of 3s and 3p silicon atomic orbitals, centred on that ligand. The LCAO treatment works well for deep, localised defects. A deep defect produces a ground-state wave function with big gradients over the ligand atoms. For a deep defect the wave function can quite often be approximated by almost one sp^3-hybridised orbital. This results in a hyperfine tensor which is approximately axial along a <111> bonding direction. For an electron in an orbital pointing in any of the four <111> directions a sp^3- hybridised orbital with s-character α^2 = 25%, p-character β^2 = 75% and α^2/β^2 = 0.33 is expected.

Table 2a. Hyperfine parameters in kHz for some typical <111>-axial silicon hyperfine tensors of two characteristic deep defects V^- and VV^- after Sprenger et al. (1987) and Sieverts et al. (1978).

centre	tensor	a	b	c	a/b	α^2/β^2	η^2(%)
Si:V^-	G1	13366.0	2039.3	64.4	6.55	0.16	2.08
	G26	239.3	36.7	4.0	6.53	0.16	0.04
	Mad1	355845.6	22303.4	1262.9	15.95	0.40	27.28
	Mad17	203.7	23.1	1.5	8.80	0.22	0.02
Si:VV^-	G1	31470	2230	460	14.11	0.35	2.97
	G20	297	59	3	5.03	0.13	0.07
	M1	195200	23300	100	8.38	0.21	27.71
	M12	701	97	2	7.23	0.18	0.11

Table 2b. Hyperfine parameters in kHz for some typical silicon hyperfine tensors of two characteristic shallow defects phosphorus and arsenic on substitutional positions - after Hale and Mieher (1969).

centre	tensor	a	b	c	a/b	α^2/β^2	η^2(%)
Si:P	B	4508	70.6	18.6	63.9	1.58	0.160
	C	3298	5.0	0.0	659.6	16.7	0.076
	I	1370	21.4	2.2	64.0	1.59	0.049
	R	758	18.4	7.6	41.2	1.02	0.033
Si:As	B	6000	105.2	22.2	57.0	1.42	0.223
	C	4074	5.8	0.0	702.4	17.5	0.094
	I	1436	23.1	1.3	62.2	1.55	0.051
	R	856	23.1	10.7	37.1	0.92	0.039

Table 2c. Hyperfine parameters in kHz for two prominent silicon interactions for the Si-NL8 - after Michel et al. (1986), and the Si-NL10 spectrum. Only one species is concerned.

centre	tensor	a	b	c	a/b	α^2/β^2	η^2(%)
Si-NL8	1	9890	70	-30	141.3	3.5	0.277
	2a	8530	60	-30	142.2	3.5	0.221
Si-NL10	T2	2455.6	25.1	1.0	97.8	2.4	0.08
	G2	1880.3	13.6	8.3	137.8	3.3	0.05

For a shallow defect all four sp^3-hybridised bonds contribute. If the four sp^3-bonds are equally occupied the hyperfine tensor is isotropic and in the LCAO analysis we will find only an s-contribution. For a shallow defect we will observe therefore mainly the s-part of the wave function, i.e. $\alpha^2 > 25\%$, or $\alpha^2/\beta^2 \gg 0.33$, and most of the p contribution,

expressed by β^2, cancels. This results in the underestimation of the localisation η^2, $\eta_{total}{}^2 \ll 100\%$. Therefore, a shallow defect is characterised by:

1) $\alpha^2/\beta^2 \gg 0.33$

2) $\eta_{total}{}^2 \ll 100\%$

The first criterion can be replaced by a/b >> 13 (where a and b are the reduced hyperfine parameters), which makes a comparison with literature values easier. The above criteria are shown in tables 2a,2b and 3 for a few tensors of two typical deep centres - V^- and VV^- - and two typical shallow donor centres - P and As. In tables 2c and 3 the corresponding values are shown for the heat-treatment centres Si-NL8 and Si-NL10.

Table 3. Total localisation values $\eta_{total}{}^2$ as obtained by LCAO analysis for several defects in silicon.

	V^-	VV^-	P	As	Si-NL8	Si-NL10
$\eta_{total}{}^2$ (%)	114.76	118.90	14.58	18.86	5.64	0.36

For deep centres with missing or dangling bonds the LCAO analysis is successful. The total localisation adds up to values close to 100%. Sometimes localisations over 100% are found, which is due to effects not accounted for in the LCAO treatment, e.g. core polarisation. However for the shallow donors, like P, As, or Sb, the LCAO analysis turns out to be less applicable. In our experiment the biggest hyperfine interaction is found to have an isotropic part a = 2.51 MHz. This corresponds to a localisation of 0.07%. In this way the LCAO analysis shows that both heat-treatment centres fall into the category of shallow defects. A comparison of the Si-NL10 data with the silicon ENDOR results for the Si-NL8 spectrum obtained by Michel et al. (1986) shows that the wave function of the Si-NL10 defect is probably more shallow. For Si-NL8 the biggest hyperfine interaction gives a localisation of 0.277%.

3.2. Symmetry of ground-state wave function

Wave functions of shallow centres can be described with the effective mass theory - Kohn and Luttinger (1955). The wave function of an electron in its ground state can be approximately represented by a linear combination of six wave functions corresponding to the six minima of the conduction band which for silicon lie along the <100> directions. Table 4 gives the combinations of one-minimum wave functions which are allowed in the case of orthorhombic symmetry. The wave functions of types A_2, B_1 and B_2 are zero on one or two of the mirror planes. The probability density of the electron on atoms which are situated in those "forbidden" mirror planes would not only be low because of the widely spread character of the shallow donor wave function, but even zero by symmetry.

The biggest hyperfine interaction found in the present ENDOR experiment has 2mm symmetry indicating that none of the two mirrorplanes is symmetry forbidden. Therefore the ground state wave function of the Si-NL10 defect

has A_1 symmetry. As can be seen from Table 4, three combinations of the six conduction band minima are then possible.

All the hyperfine interactions determined for the Si-NL10 centre in the ^{29}Si ENDOR experiment have an approximate [100] axial character, with the two-fold axis along [100]. The axial direction of the tensors coincides therefore with the two-fold axis of the defect. However this feature of the ground state wave function offers no extra information to discriminate between the three available A_1 states; all three of them allow the [100]-axiality.

Table 4. Symmetry-allowed combinations of wave functions of conduction band minima in 2mm point group symmetry. The two-fold axis is along x.

wave function symmetry	coefficients for conduction band valleys					
	x	-x	y	-y	z	-z
A_1	0	0	1	1	1	1
A_1	0	1	0	0	0	0
A_1	1	0	0	0	0	0
A_2	0	0	1	1	-1	-1
B_1	0	0	1	-1	-1	1
B_2	0	0	1	-1	1	-1

The results of the ^{29}Si-ENDOR study of the Si-NL8 centre by Michel et al. (1986) appear very similar. The biggest localisation is observed for atoms on the two-fold axis, while most of the tensors show near [100] axiality. Therefore the ground state wave function of the Si-NL8 defect also has A_1 symmetry. In case of the Si-NL8 defect additional information is available from infrared (IR) measurements under uniaxial stress. Stavola and Lee (1986) concluded from the stress response of the IR that the ground state of the thermal donor (the Si-NL8 spectrum is related to TD^+) is constructed from a single pair of conduction band valleys along the two-fold axis. From the wave functions consistent with the 2mm symmetry of the defect only two of the A_1 symmetry type can be constructed in this way. In case of the Si-NL10 centre, despite its large concentrations, no identification with levels has been made in IR. Therefore no additional information is available about the ground state wave function and three A_1-symmetry combinations are possible.

3.3 Microscopic structure

The microscopic atomic structure of the Si-NL10 centre has been established by detailed analysis of the hyperfine interactions with ^{17}O and ^{27}Al nuclei supplemented by the field-stepped-ENDOR experiments. It was further confirmed by the ^{29}Si ENDOR study.

From the ^{17}O ENDOR measurements up to eight oxygen shells could be distinguished. All of them were of the same mirror plane symmetry type proving that the oxygen structure of the centre is planar with all the oxygen atoms lying in one of the mirror planes. The localisation of the defect electron on oxygen nuclei was found to be very low. The quadrupole interactions were almost identical for all the shells and indicated that

the oxygen atoms were in the usual puckered bonded interstitial position.

^{27}Al ENDOR showed that although aluminium was not really necessary for the creation of the Si-NL10 centres it participated, when present, actively in the oxygen aggregation process leading to the significant enhancement in the generation rate and concentration of the Si-NL10 centres. In such case, for the early stage of the Si-NL10 formation process

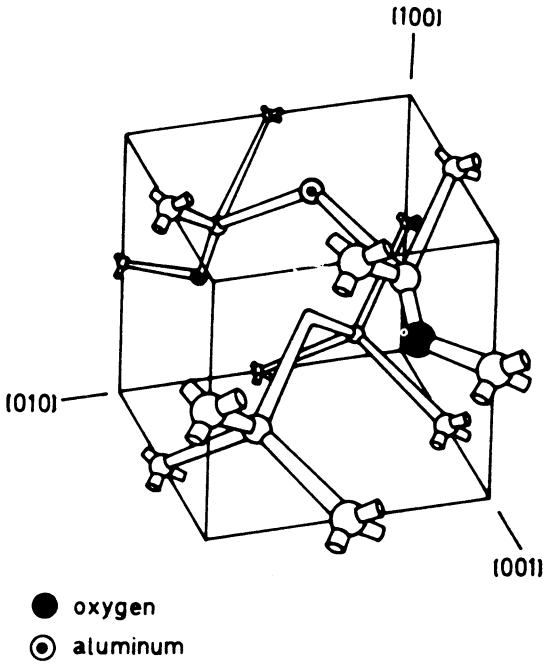

Figure 4. Structural model for the Si-NL10 centre.

the aluminium atom takes a position on the two-fold axis of the defect. The field-stepped-ENDOR technique uses the high resolution of nuclear resonance to unravel unresolved structure of the EPR signal. Applied in the current study it showed that the Si-NL10 EPR spectrum originated from a series of gradually developing similar centres, each characterised by its own spectrum with slightly different g-values. Field-stepped-ENDOR allowed also mutual correlation of the hyperfine interactions originating from different kinds of magnetic nuclei thus establishing the number of oxygen atoms participating at various stages of the transformation of the Si-NL10 centre. The smallest possible Si-NL10 species was found to incorporate 2 oxygen atoms; in the growth process a **single** oxygen atom (at a time) is added along the [0$\bar{1}$1] directed silicon chain. The structure of the centre remains planar while its overall symmetry is lowered upon growth from orthorhombic for the smallest species to monoclinic for the later ones. The structural model of the Si-NL10 centre as emerging from the ENDOR study by Gregorkiewicz et al. (1988) is depicted in Fig.4. As can be seen from the figure it is postulated that a vacancy is created in the core of the defect in order to release the stress accumulated by the

oxygen clustering. On the basis of the measurements no conclusion could be reached concerning the position of the aluminium atom on the two-fold axis nor its possible bonding to the lattice.

ACKNOWLEDGMENT

This work received support from the Netherlands Foundation for Fundamental Research on Matter (FOM).

REFERENCES

Bekman H H P Th, Gregorkiewicz T, van Wezep D A and Ammerlaan C A J 1987 J. Appl. Phys. **62** 4404
Bekman H H P Th, Gregorkiewicz T and Ammerlaan C A J 1988 to be published
Bourret A 1985 Proc. Thirteenth International Conference on Defects in Semiconductors, Coronado, California, 1984, ed. by L C Kimerling and J M Parsey, Jr. (The Metallurgical Society of AIME, Warrendale, Pennsylvania) p 129
Fuller C S, Ditzenberger J A, Hannay N B and Buehler E 1954 Phys. Rev. **96** 833
Fuller C S and Logan R A 1957 J. Appl. Phys. **28** 1427
Gregorkiewicz T, van Wezep D A, Bekman H H P Th and Ammerlaan C A J 1987 Phys. Rev. B **35** 3810
Gregorkiewicz T, Bekman H H P Th and Ammerlaan C A J 1988 Phys. Rev. B **38** 3998
Hale E B and Mieher R L 1969 Phys. Rev. **184** 739
Kaiser W, Frisch H L and Reiss H 1958 Phys. Rev. **112** 1546
Kohn W and Luttinger J M 1955 Phys. Rev. **98** 915
Lee K M, Trombetta J M and Watkins G D 1985 Microscopic Identification of Electronic Defects in Semiconductors, ed. by N M Johnson, S G Bishop and G D Watkins (Materials Research Society, Pittsburgh, Pennsylvania) p 263
Lee Y H and Corbett J W 1973 Phys. Rev. B **8** 2810
Michel J, Niklas J R, Spaeth J-M and Weinert C 1986 Phys. Rev. Lett. **57** 611
Muller S H, Sprenger M, Sieverts E G and Ammerlaan C A J 1978 Solid State Commun. **25** 987
Muller S H, Sieverts E G and Ammerlaan C A J 1979 Defects and Radiation Effects in Semiconductors 1978 (Inst. Phys., Bristol) p 297
Pajot B, Compain H, Lerouille J and Clerjaud B 1983 Physica **117B** & **118B** 110
Sieverts E G, Muller S H and Ammerlaan C A J 1978 Phys. Rev. B **18** 6834
Sieverts E G 1983 Phys. Status Solidi (b) **120** 11
Sprenger M, Muller S H, Sieverts E G and Ammerlaan C A J 1987 Phys. Rev. B **35** 1566
Stavola M and Lee K M 1986 Oxygen, Carbon, Hydrogen and Nitrogen in Crystalline Silicon, ed. by J C Mikkelsen, Jr., S J Pearton, J W Corbett and S J Pennycook (Materials Research Society, Pittsburgh, Pennsylvania) p 95
Wruck D and Gaworzewski P 1979 Phys. Status Solidi (a) **56** 557