PHYSICAL REVIEW B VOLUME 35, NUMBER 8 15 MARCH 1987-I

EPR studies of heat-treatment centers in p-type silicon

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(Received 7 July 1986; revised manuscript received 12 November 1986)

The influence of acceptor doping (B,Al,Ga,In) on heat-treatment (HT) centers in oxygen-rich silicon was studied by means of EPR and resistivity measurements. EPR studies revealed that spectra Si-NL8 and Si-NL10 were practically the only ones which could be related to HT centers. They could be observed in all samples regardless of their acceptor doping. The creation of NL8 was found to depend on the initial acceptor concentration. For the aluminum-doped material the production of NL10 HT centers was particularly enhanced. No hyperfine structure of either NL8 or NL10 was found in EPR for specimens whose oxygen content was enriched to 46% in the ^{17}O isotope. Thermal donor (TD) concentrations, as found from the resistivity measurements, did not follow the relations predicted by the existing descriptions of TD formation. For all the studied samples concentrations of TD's and NL10 centers were of the same order of magnitude.

I. INTRODUCTION

It is well known that a large variety of heat-treatment (HT) centers ranging from point defects to large precipitates can be created in silicon upon annealing in different temperature ranges. The most-studied HT centers are probably the so-called "thermal donors," produced at ~450 °C annealing, that were discovered over 30 years ago, even before it was realized that oxygen was the main impurity present in crucible-grown silicon. Later studies revealed that interstitial oxygen was mobile at that temperature and could therefore form small aggregates upon annealing. Early investigations[1,2] suggested that a cluster of four oxygen atoms constituted these thermal donors (TD's), mainly on the basis of the experimental observation that the TD initial formation rate was proportional to the fourth power of the initial interstitial-oxygen concentration. Since that time many papers have appeared on the subject of oxygen aggregation, containing a large amount of experimental information[3,4] as well as theoretical studies;[5–7] those have recently been reviewed by Bourret.[8] The results obtained by different techniques are not well correlated, however, and no consensus has been reached on a theoretical model for TD's.

Among other techniques, magnetic resonance (EPR) has been applied in the studies of heat-treated (HT) silicon.[9–11] These studies revealed a variety of EPR centers, one of which, Si-NL8, has recently been identified with one of the energy levels attributed to TD.[12] The efficiency with which NL8 was produced increased with the boron concentration, which lead Muller *et al.* to the supposition that boron was incorporated in this center.[10] Their efforts to establish the presence of oxygen in these centers remained unsuccessful, but this may be attributed to the rather low concentration of ^{17}O ($\approx 2\%$) they could attain.

In the studies on oxygen aggregation it has become customary to distinguish two different types of donors: (1) the thermal donors, formed in the 450 °C region, and (2) the "new donors," formed at higher temperatures (650–750 °C). Infrared absorption studies[13] demonstrated that this distinction is only partially useful, since spectra produced at higher temperatures are in part the same as those formed in the 450 °C region, which could in principle be responsible for all of the donor formation at elevated temperature. Recent EPR studies on the defects produced on annealing in the 650–750 °C region by Wörner and Schirmer[14] revealed the formation of two EPR spectra distinctly different from those discovered by Muller, suggesting a different structure for the new donors.

The present study has a threefold aim: (1) to investigate the possible involvement of acceptor ions in the formation of the EPR active centers, (2) to establish the presence of oxygen in these centers, and (3) to investigate the difference in "thermal" and "new" donor structure. To achieve these goals EPR and resistivity measurements have been performed in parallel.

II. EXPERIMENTAL PROCEDURE

The materials used were purchased from Wacker Chemitronic, the starting parameters of which are given in Table I. The samples can be categorized as follows.

(1) Samples cut from high-quality crucible-grown Czochralski silicon (Cz-Si) (set I).

(2) Samples cut from float-zoned silicon (FZ-Si), that were diffused with oxygen under ultraclean circumstances (to be described below) to avoid undesired contaminations (set II).

(3) Same as (2), but the oxygen gas used was isotopically enriched in the (magnetic) ^{17}O isotope to 52.3% (set II′).

Each set consists of four samples of different acceptor doping; the samples are all characterized by approximately equal and low carbon contents—$[\mathrm{C}] \leq 5\times10^{15}$ cm^{-3}.[15] The oxygen concentration of sample set I was approximately twice as large as in sample sets II and II′, as determined by infrared absorption measurement with the new American Society for Testing and Materials (ASTM) calibration standard.

Oxygen diffusion of the FZ material was conducted in a commercial infrared oven (high density infrared quad-elliptical radiant chamber E4 manufactured by Research

TABLE I. Materials. The carbon concentration of all samples $[C] \leq 5\times10^{15}$ cm^{-3}.

Sample	Growth	Type	Resistivity (Ω cm)	Impurity	Dopant concentration (cm^{-3})	Oxygen concentration (cm^{-3})
			Set I			
Cz-Si:B	Cz	*p*	1.3	B	1.3×10^{16}	1.3×10^{18}
Cz-Si:Al	Cz	*p*	3–5	Al	4.0×10^{15}	1.3×10^{18}
Cz-Si:Ga	Cz	*p*	2	Ga	2.0×10^{15}	1.3×10^{18}
Cz-Si:In	Cz	*p*	7–11	In	4.5×10^{14}	1.3×10^{18}
			Set II			
FZ-Si:B	FZ	*p*	0.3	B	2.7×10^{16}	7×10^{17}
FZ-Si:Al	FZ	*p*	0.8	Al	9.0×10^{15}	7×10^{17}
FZ-Si:Ga	FZ	*p*	1.5	Ga	3.6×10^{15}	7×10^{17}
FZ-Si:In	FZ	*p*	10	In	7.0×10^{14}	7×10^{17}
			Set II′			
IE-FZ-Si:B	FZ	*p*	0.3	B	2.7×10^{16}	7×10^{17}[a]
IE-FZ-Si:Al	FZ	*p*	0.8	Al	9.0×10^{15}	7×10^{17}[a]
IE-FZ-Si:Ga	FZ	*p*	1.5	Ga	3.6×10^{15}	7×10^{17}[a]
IE-FZ-Si:In	FZ	*p*	10	In	7.0×10^{14}	7×10^{17}[a]

[a] Isotopically enriched to 46% ^{17}O.

Inc.) equipped with four 2-kW halogen lamps and four water-cooled elliptic aluminum mirrors. The samples for the diffusion were carefully aligned along the coinciding secondary foci of the mirrors. The samples were closed in a high-purity synthetic quartz ampoule filled with oxygen gas. Within the ampoule silicon supports were provided so that the samples could be placed along the axis while avoiding direct contact with the quartz. Such arrangement allowed the temperature of the ampoule to stay relatively low while the temperature of the samples was close to that of the melting point of silicon (1380–1400 °C). A temperature difference of some 300 °C between sample and quartz wall could be achieved if the ampoule diameter was chosen properly. The combined oxidation and diffusion process was continued for 10 days. The samples of one set were diffused simultaneously in order to attain identical oxygen concentration. After the diffusion the samples were rapidly cooled in a procedure similar to that described by Muller.[11] This diffusion procedure was superior to the conventional procedure in two aspects.

(1) The process was clean. The EPR spectrum of the "as-diffused" samples showed no traces of any (paramagnetic) impurities in contrast to earlier experiments (diffusion process conducted in conventional ovens) in which always traces of rapidly diffusing transition-metal species were found.

(2) There was only little exchange of oxygen atoms between the gas in the ampoule and the quartz as proved by checking the isotope composition of the restant gas; the ^{17}O concentration had dropped from 52% to some 40% after 10 days of combined oxidation and diffusion. This could not be achieved in the earlier experiments[11] and was of crucial importance for the diffusion of samples of set II′.

The samples of set I were carefully chosen for maximum and equal oxygen concentration and underwent a similar quenching procedure as the samples of sets II and II′ to ensure equivalent starting conditions. Heat treatments at $T = 470\,^{\circ}\mathrm{C}$ were carried out under argon atmosphere in subsequent steps, in between which resistivity and EPR measurements were performed. In order to ensure equal HT conditions the four samples of each set were heat treated simultaneously. Heat treatments in the higher temperature range with intermittent EPR and resistivity measurements were performed similarly on the following samples: (a) Samples of set II, that had undergone extensive HT at 470 °C, were subjected to a subsequent anneal at 550 °C for various times, and (b) Cz-Si samples, that were given a two-hour anneal at 650 °C, followed by a two-hour anneal at 750 °C.

Sample resistivity was monitored by conventional four-point-probe technique. EPR measurements were performed with a superheterodyne spectrometer operating at 23 GHz and tuned to dispersion; the signal was phase sensitive detected at 83-Hz magnetic field modulation. The magnetic field could be rotated in the $(0\bar{1}1)$ plane of the silicon samples. The measurements were performed in the temperature region between 1.5 and 15 K. The experimental arrangement permitted *in situ* white-light illumination.

III. EXPERIMENTAL RESULTS

No new EPR spectra were discovered in the present studies. Generally speaking, two types of $2mm$ symmetry spectra have been observed, which will hereafter be referred to as NL8 and NL10 families in accordance with the nomenclature adopted by Muller *et al.*[9] Figure 1 presents an exemplary EPR spectrum for the sample Cz-Si:Al given 470 °C/40 h HT; as can be seen Si-NL8 and

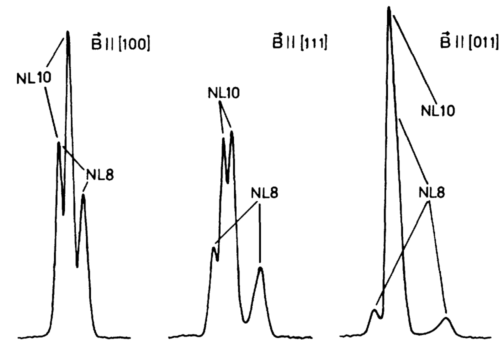

FIG. 1. EPR spectrum of the sample Cz-Si:Al after 470 °C/40 h HT, showing simultaneous presence of Si-NL8 and Si-NL10 spectra.

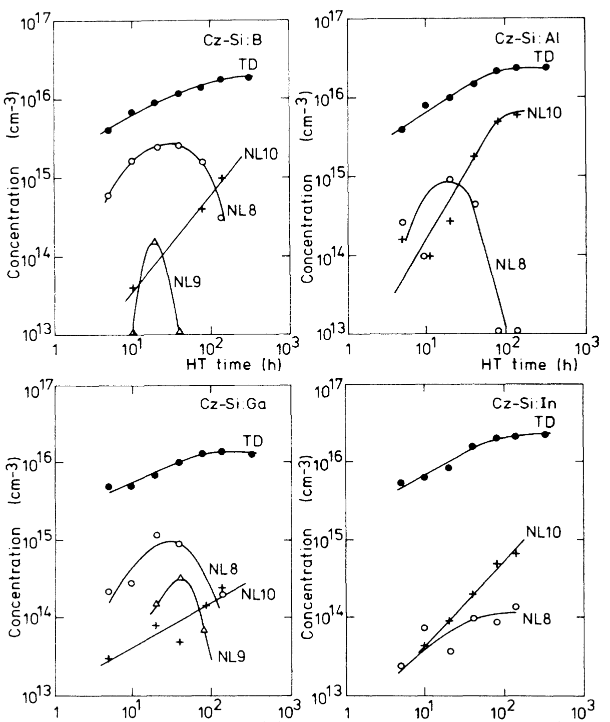

FIG. 2. Concentration of heat-treatment centers for crucible-grown silicon samples (set I) as a function of annealing time. ○, NL8; △, NL9; +, NL10; ●, thermal donors (TD's) as calculated from room-temperature resistivity measurements under the assumption that each TD supplies one electron.

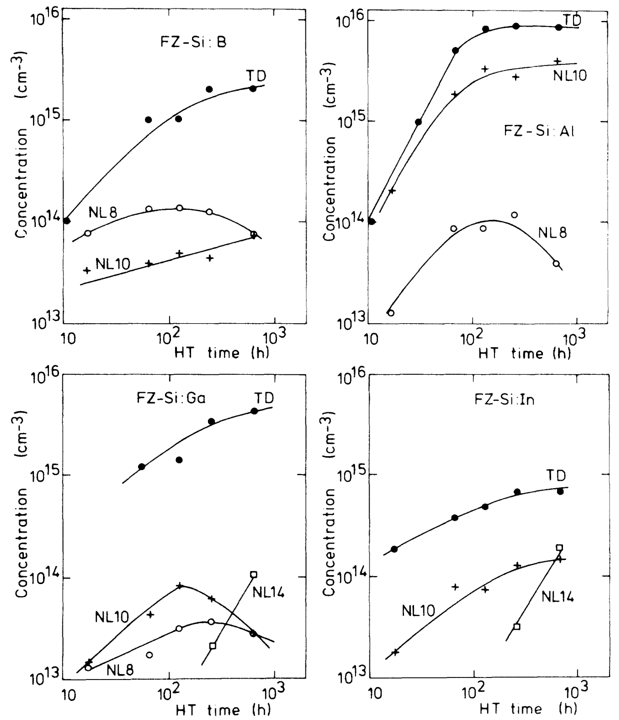

FIG. 3. Concentration of heat-treatment centers for float-zone oxygen-doped silicon samples (set II) as a function annealing time. ○, NL8; +, NL10; □, NL14; ●, thermal donors as calculated from room-temperature resistivity measurements under the assumption that each TD supplies one electron.

Si-NL10 spectra can be resolved. In Figs. 2 and 3 the intensities of the NL8 and NL10 spectra as a function of anneal time at 470° C are given for sample sets I and II, respectively. The concentration of EPR centers has been estimated by comparison with the reference signal of a standard phosphorus-doped silicon sample. Although phosphorus is also a shallow donor and the concentration of phosphorus in the reference sample was chosen to be comparable to the concentrations of HT centers it should be clearly stated that the absolute values given in Figs. 2 and 3 are only accurate within an order of magnitude. However, the relative changes are far more reliable as the comparison is then made between data obtained for (basically) the same sample, and the same center under the same passage conditions. In these figures the concentrations of TD's are also included. These were calculated from room-temperature resistivity measurements under the assumption that each TD supplied one electron. Both spectra were appearing practically in all the investigated samples with the exception of FZ-Si:In in which NL8 could not be produced even after relatively long annealing times. In addition to NL8 and NL10, traces of a resonance spectrum, possibly NL9, could be seen for some annealing stages of Cz-Si:Ga and Cz-Si:B materials. Its intensity was always low and the spectrum was hardly resolved. For longer annealing times the NL14 spectrum could be observed on several occasions, but its intensity was also low.

Muller *et al.* discovered in their EPR study of TD's,[10] that the NL8 spectrum was changing its g values with increased annealing time, while preserving its $2mm$ symmetry. The most pronounced shifting upon prolonged HT was exhibited by the off-diagonal element g_{yz} of the Cartesian g tensor. This latter shift may conveniently be expressed as the decrease of the separation in magnetic field ΔB ($\propto g_{yz}$) of the two EPR resonances observed with the magnetic field **B** parallel to the [111] direction. These two resonance lines have the same intensity and are well resolved even for spectra with relatively small anisotropy as for instance NL10. In Fig. 4 this separation ΔB for NL8 (obtained from the spectra of white-light-illuminated samples and scaled to microwave frequency 23 GHz) as a function of annealing time is given for sample sets I and II. A continuous change of ΔB with HT time may be noticed for all samples, while the data obtained from sample set I clearly fall on a different line than the data from sample set II. It is obvious that the Cz-Si samples are in a later stage of the g-shifting process than the FZ samples at equal HT times, i.e., for FZ material the ΔB value corresponding to that of the NL8 spectrum as originally published by Muller *et al.*[9] could be observed after approximately 200 h annealing time, while for Cz material this already occurred after 10 h. Apart from this effect another remarkable phenomenon could be observed. Figure 5 presents a comparison of data obtained for the same sample with and without illumination. The effect of switching off the light on the observed ΔB value is comparable to that of about 100 h annealing. No clear influence of the acceptor on the transformation process can be seen, although some influence of acceptor doping might be concluded from the spectra taken without illumination.

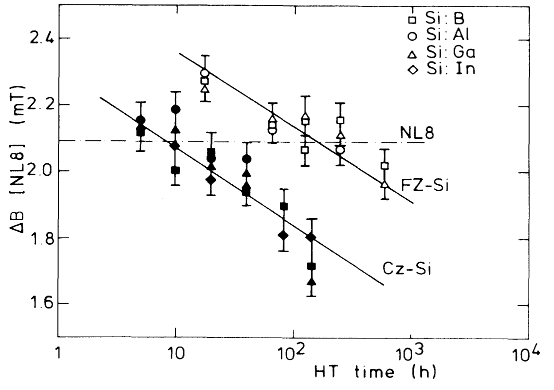

FIG. 4. The annealing time dependence of g shifting for the spectrum NL8 as observed under (white light) illumination. Solid symbols, crucible-grown silicon samples (set I): $[O_i]=1.3\times10^{18}$ cm^{-3}; open symbols, FZ oxygen-doped silicon samples (set II): $[O_i]=7\times10^{17}$ cm^{-3}. ΔB values are scaled to a 23-GHz microwave frequency.

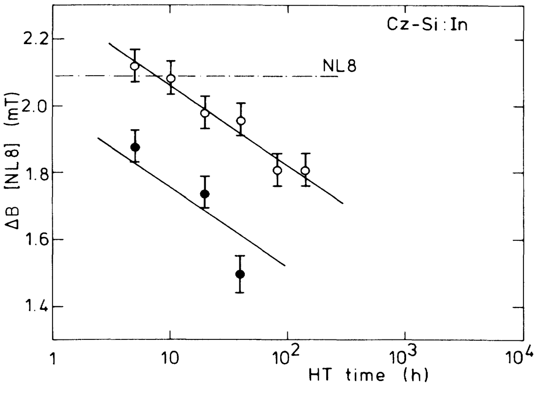

FIG. 5. The effect of (white light) illumination on g shifting of the spectrum NL8 for the crucible-grown indium-doped sample. Open symbols, with illumination; solid symbols, without illumination. ΔB values are scaled to a 23-GHz microwave frequency.

Spectrum NL10 undergoes a similar transformation as NL8, i.e., the observed spectra also become less anisotropic with increasing annealing time. Figure 6 presents the ΔB dependence on HT time for sample sets I and II. In this figure the ΔB values for spectra NL10, NL13, and NL17,[9] that all have similar g-value patterns, are also indicated. The earlier supposition,[10,11] that these three spectra probably correspond to different stages of the same center and should therefore not be distinguished as arising from different defects is herewith confirmed. In the following we will therefore no longer make this distinction and refer to these spectra as NL10. Another similarity to the case of NL8 is the same forward shift on the time scale of the g-value transformation process in going from the FZ samples to the Cz samples. In contrast to the case of NL8 a clear influence of acceptor dopant is observed.

The samples of set II', designated IE-FZ-Si (isotope-enriched FZ silicon), which were diffused with oxygen to

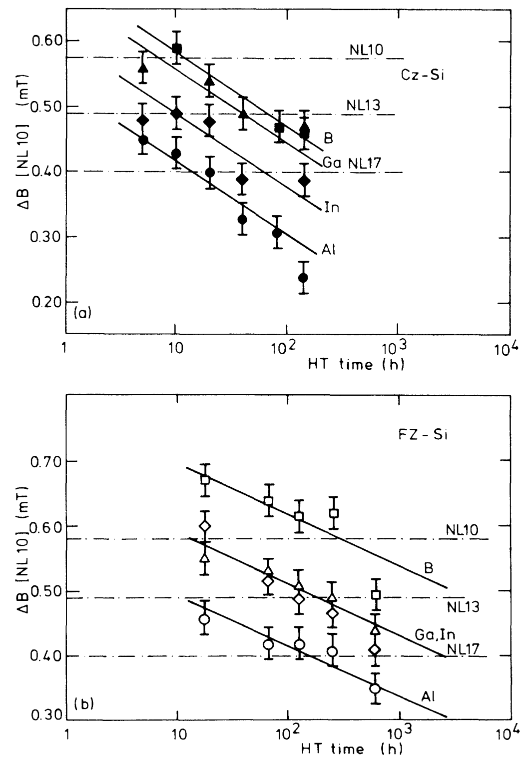

FIG. 6. The annealing time dependence of g shifting for the NL10 spectrum as measured under (white light) illumination for (a) crucible-grown silicon samples (set I) (closed symbols), and (b) FZ oxygen-doped silicon samples (set II) (open symbols). ΔB values are scaled to a 23-GHz microwave frequency. ΔB values for NL10, NL13, and NL17 are taken from Ref. 9. □, Si:B; ○, Si:Al; △, Si:Ga; ◇, Si:In.

a total concentration of $\sim 7\times 10^{17}$ cm^{-3} contained oxygen isotopes in the following ratio (as measured by infrared absorption on samples cooled to 4.2 K):

$$^{16}\mathrm{O}:^{17}\mathrm{O}:^{18}\mathrm{O}=0.39:0.46:0.15\ .$$

In spite of the high concentration of $I=\frac{5}{2}$ ^{17}O nuclei no hyperfine structure has been observed for either NL8 or NL10. The situation was similar to that described in detail in Ref. 9 where only 2% ^{17}O enriched samples were used.

After the prolonged HT at 450 °C the samples of set II were annealed for various time durations at 550 °C. The results can be summarized as follows.

(1) No new EPR spectra were observed; the only EPR spectrum found was that of NL10.

(2) The concentration of both TD's (as found from the resistivity measurements) and the NL10 centers decreased upon annealing at 550 °C. The only and remarkable exception here was the aluminum-doped FZ-Si:Al sample for which TD concentration remained almost constant and the NL10 intensity even increased.

Additionally, some crucible-grown material samples were studied following 2 h successive heat treatments at 650 °C and 750 °C. Also here only NL10 was observed in contrast to recent results of Wörner and Schirmer.[14] Moreover, the concentration of NL10 centers could be well correlated to the number of donors created by this heat treatment.

IV. DISCUSSION

A. Resistivity measurements

The experimental values of maximum TD concentration and formation rate as obtained from the resistivity measurements are presented in Table II. It can clearly be noticed from the second and the third columns of this table that the experimental values do not follow the well-known power dependences on initial interstitial-oxygen concentration: maximum concentration $N_{\max}\sim[\mathrm{O}_i]^3$, initial formation rate $R\sim[\mathrm{O}_i]^4$ as given by the Kaiser, Frisch, and Reiss (KFR) model,[2] with the possible exception of the boron-doped material for which the eventual agreement is poor. Samples with identical oxygen (and carbon) concentration are capable of developing different TD concentrations under identical HT conditions. These results therefore give clear experimental evidence that TD formation is not only a function of the initial oxygen concentration and the annealing conditions. In view of this discrepancy with the predictions of Kaiser *et al.*,[2] it seems therefore natural to employ the only existing TD formation description which takes into consideration more parameters than $[\mathrm{O}_i]$ and the formation temperature T, namely the carrier concentration n. This formalism has been developed by Wada,[16] who gives the following expression for the equilibrium TD concentration:

$$n_{\mathrm{eq}}(\mathrm{TD})=(a/b)[\mathrm{O}_i]^3 n^{-2}\ , \tag{1}$$

where $[\mathrm{O}_i]$ is the initial interstitial-oxygen concentration, n is the carrier concentration at 470 °C, a and b are parameters ($a/b=5.5\times 10^{-6}$). The results of this computation are collected in the last two columns of Table II, which also incorporates carrier concentration values n calculated for all the studied samples at the experimental TD formation temperature (470 °C).

Before discussing the results given in Table II the applicability of formula (1) and therefore of the whole TD formation kinetics as proposed by Wada[16] for our measurements should be considered. In general, our samples which differ in their initial acceptor concentration but have equal initial oxygen contents should provide a good test for that kinetics. However, for the Cz-Si samples the approach of Wada cannot be applied, due to high oxygen concentration of these samples. As can be seen from Table II, TD concentrations produced in those samples are comparable to the intrinsic electron concentration n_i for silicon at the TD formation temperature ($n_i=1.24\times 10^{16}$ cm^{-3} for $T=470$ °C) thus conflicting the condition $n_{\mathrm{TD}}<n_i$ assumed by Wada. For FZ oxygen-doped material (samples designated FZ-Si) all the necessary conditions are fulfilled. Here FZ-Si:In and FZ-Si:Ga fall into the "lightly doped materials" category with

TABLE II. TD formation. The experimental values have been calculated under the assumption that every TD supplies one electron and no other processes are involved. Theoretical values are obtained in Wada's formalism, in which we used the following numerical values: $n_i=1.24\times 10^{16}$ cm^{-3}, $D=8.65\times 10^{-19}$ cm^2/s, $a/b=5.5\times 10^{-6}$, $a=2.75\times 10^{-10}$.

	TD experimental		Carrier	TD calculated	
Sample	Maximum concentration (cm^{-3})	Initial formation rate (s^{-1})	concentration n (cm^{-3})	Maximum concentration (cm^{-3})	Initial formation rate (s^{-1})
Cz-Si:B	2.6×10^{16}	1.1×10^{11}			
Cz-Si:Al	2.4×10^{16}	1.5×10^{11}			
Cz-Si:Ga	1.5×10^{16}	1.1×10^{11}			
Cz-Si:In	2.1×10^{16}	1.4×10^{11}			
FZ-Si:B	2.0×10^{15}	4.4×10^{9}	4.83×10^{15}	8.09×10^{16}	2.45×10^{12}
FZ-Si:Al	9.0×10^{15}	4.7×10^{10}	8.69×10^{15}	2.50×10^{16}	7.56×10^{11}
FZ-Si:Ga	4.5×10^{15}	3.1×10^{9}	1.07×10^{16}	1.65×10^{16}	4.99×10^{11}
FZ-Si:In	7.0×10^{14}	3.1×10^{9}	1.21×10^{16}	1.29×10^{16}	3.90×10^{11}

$N_a < n_i$ while FZ-Si:Al and Fz-Si:B are "heavily doped" in that classification[16] and should therefore exhibit enhanced TD formation. There is no numerical agreement between experimental values and those predicted by formula (1), however. This result indicates at least that the a/b parameter introduced by Wada does not have universal character and should be adjusted separately for different acceptors. Additional discrepancy is found for materials FZ-Si:Al and FZ-Si:B; according to Wada a significant increase of TD equilibrium concentration (and formation rate) should be observed for FZ-Si:B in comparison to FZ-Si:Al. The experiment indicates, however, the contrary: a remarkable decrease of both values for FZ-Si:B sample in comparison to FZ-Si:Al (in the case of the formation rate the effect is even an order of magnitude).

From Tables I and II one can also notice that the early observation by Fuller *et al.*[17] that equilibrium TD concentrations coincide with initial acceptor concentrations, although true for FZ-Si:Al, FZ-Si:Ga, and FZ-Si:In, is not followed for all our samples.

B. EPR measurements

The spectra NL8 and NL10 were first reported by Muller *et al.* for heat-treated, oxygen-rich silicon doped with boron.[9] They observed that the NL8 intensity was growing upon increased boron concentration and thus boron involvement in the center was tentatively assumed.[10] The present results show that NL8 (and NL10) can be observed regardless of the actual acceptor present in the sample. The relative intensities of the spectra rule out the possibility of relating NL8 to residual concentrations of boron in those materials intentionally doped with other acceptors. This observation makes any hypothesis of direct acceptor involvement in the structure of HT centers rather doubtful. Incorporation of the acceptor in the HT center cannot be ruled out completely on the basis of this experimental fact alone, however, as the acceptor might take a position where the spin density is low for symmetry reasons, which could lead to undetectable changes in g values in going from one acceptor to the other and absence of any acceptor hyperfine structure in the EPR spectrum. The conclusion that the actual acceptor is not of basic importance for the formation of these centers is, however, further supported by recent evidence that these centers are also produced in n-type material[18] and by photoluminescence studies on heat-treated crucible-grown silicon doped with various acceptors[19] where practically no influence of the acceptor doping on photoluminescence spectra attributed to HT centers has been found.

Table III summarizes results of the EPR measurements for various materials, giving maximum concentrations and initial formation rates for both NL8 and NL10. In spite of what was stated above these results do indicate an influence of the initial acceptor concentration on the creation of NL8 centers. This is clearly demonstrated in Fig. 7, where NL8 maximum intensity and formation rate are plotted against the initial acceptor concentrations. The experimental points in both cases fall clearly on two lines, depending on the initial oxygen concentration of the material. One should note here that a similar result regarding NL8 intensity dependence on boron concentration was obtained by Muller *et al.*[10] for samples with different boron concentrations, i.e., for one and the same acceptor doping. The straight lines in Fig. 7 represent least-squares fits to the linear dependence on the acceptor concentration. By comparing the fits obtained for the different initial oxygen concentrations the following dependence could be derived for both the maximum concentration NL8 and its initial formation rate:

$$A = \text{const} \times N_a [\mathrm{O}_i]^n \,, \tag{2}$$

where N_a is the initial acceptor concentration, $[\mathrm{O}_i]$ is the initial interstitial-oxygen concentration, and n is a parameter.

The following values for the exponent n have been determined: for maximum concentration $N_{\max}(\mathrm{NL8})$, $n = 5.0 \pm 0.1$; for initial formation rate $R(\mathrm{NL8})$, $n = 6.1 \pm 0.1$.

By applying these formulas, the experimental points of Muller[11] which are also shown in Fig. 7 can be reproduced with good accuracy.

It should be noted here that the dependence of the intensity of EPR spectrum NL8 on the initial acceptor concentration cannot possibly be understood as a Fermi-level effect. In such a case an increased acceptor concentration should pull the Fermi level down, thus making A of Eq. (2) inversely related to the acceptor concentration in con-

TABLE III. Summary of EPR results.

	NL8		NL10	
Sample	Maximum concentration (cm^{-3})	Initial formation rate (s^{-1})	Maximum concentration (cm^{-3})	Initial formation rate (s^{-1})
Cz-Si:B	2.8×10^{15}	4.4×10^{10}	1.0×10^{15}	6.1×10^{8}
Cz-Si:Al	9.5×10^{14}	1.4×10^{10}	6.0×10^{15}	5.5×10^{9}
Cz-Si:Ga	3.5×10^{14}	7.2×10^{9}	8.0×10^{13}	1.1×10^{10}
Cz-Si:In	1.4×10^{14}	1.2×10^{9}	7.0×10^{14}	1.2×10^{9}
FZ-Si:B	1.4×10^{14}	1.2×10^{9}	5.0×10^{13}	3.6×10^{8}
FZ-Si:Al	1.2×10^{14}	3.4×10^{8}	4.5×10^{15}	3.9×10^{9}
FZ-Si:Ga	3.5×10^{13}	1.4×10^{8}	8.5×10^{13}	1.8×10^{8}
FZ-Si:In			1.5×10^{14}	2.8×10^{8}

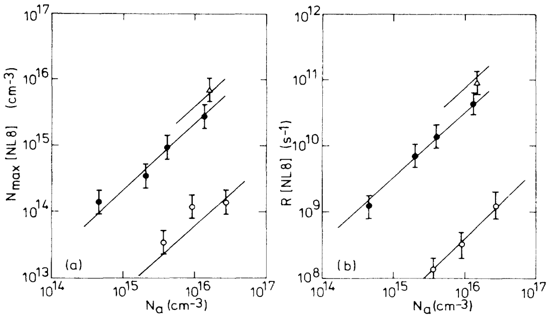

FIG. 7. The dependence of maximum concentration (a) and initial formation rate (b) for the spectrum NL8 on the initial acceptor concentration. ●, crucible-grown samples (set I) $[O_i]=1.3\times10^{18}$ cm^{-3}; ○, FZ oxygen-doped samples (set II) $[O_i]=7\times10^{17}$ cm^{-3}; △, as calculated from Ref. 11: $[O_i]=1.5\times10^{18}$ cm^{-3}.

trast to experiment. Lower intensity of the EPR signal should then be expected for higher acceptor concentrations. It must therefore be concluded that the acceptor plays an, admittedly mysterious, role in the formation of NL8. This acceptor concentration dependence of NL8 is not reproduced for TD's, thus excluding NL8 as the dominant thermal donor in our samples.

As far as the available concentrations are concerned, the NL10 centers present the more likely candidates to account for the resistivity changes (Figs. 2 and 3) in all samples. To conclude anything about the dopant dependence for the formation of these centers is, however, even more difficult than for the NL8 HT centers. By inspecting the results of Table III, two observations can be made.

(1) Increased oxygen concentration results in higher maximum concentration and a higher (initial) formation rate of NL10.

(2) Aluminum-doped material is especially favorable for the creation of NL10 HT centers. The actual enhancement of NL10 concentration in the presence of aluminum as compared to other acceptors is more pronounced for the material with lower oxygen concentration.

The latter observation could be consistent with the data of Fuller *et al.*, who found enhanced TD formation in Al-doped silicon crystals.[17] A similar observation has recently been published by Jie *et al.*[20] Additional evidence of exceptional features for Al-doped silicon is provided by its behavior for higher annealing temperatures and will be discussed later. The actual reason for the strong influence of the aluminum doping can only be speculated upon as long as the structure of the NL10 center remains unknown.

Experimentally it is found that an increased oxygen concentration results in a shift of the *g*-value transformation process forward on the time scale for both NL8 and NL10. Such behavior can be understood if one assumes that the spectra change due to oxygen aggregation (either directly by incorporating more oxygen atoms or indirectly by lattice strain release). If two samples with different oxygen concentration undergo the same HT, the one with the highest initial oxygen concentration will always be in a later stage of the oxygen clustering process. The effect of light on NL8 is particularly interesting as it shows that HT centers giving rise to NL8 do not only transform with HT time (or slightly different species develop gradually upon prolonged HT), but could already be present in variety in the sample even after relatively short annealing times. In the case of NL10 there is a clear dependence of ΔB on the acceptor; if the actual value is considered as an indication for the stage of the oxygen clustering process, then it could be concluded that the oxygen aggregation proceeds most rapidly for aluminum-doped material. This conclusion is in agreement with the already mentioned observation by Fuller *et al.*,[17] as well as with our own data on both TD concentration and HT center EPR intensity in aluminum-doped samples. The reason for this enhanced donor production and production rate in Al-doped material remains unclear, however.

The absence of ^{17}O hyperfine interaction in the EPR spectra of sample set II′ can only be understood if either no oxygen is involved in the center (which is in contrast to the rest of the experimental evidence) or the actual electron density on oxygen nuclei is low due to symmetry reasons or delocalization of the electron wave function. Alternatively it is possible that, when the EPR spectra are thought to arise as the average of several centers, the observation of hyperfine structure is obstructed by severe line broadening due to strongly varying hyperfine interactions. It is clear that it will be necessary to apply the far larger resolving power of electron-nuclear double resonance (ENDOR) to this system in order to settle this matter.

The results of our experiments in the new-donor formation temperature range show that, as far as the EPR studies are considered, there can hardly be any distinction between these HT centers and those formed in the 450 °C range. This conclusion, which is in agreement with Ref. 13, is further supported by our recent studies on *n*-type crucible-grown silicon[18] in which both NL8 and NL10 were observed after 650 °C temperature heat treatments. It should also be noted here that the concentrations of the NL10 centers and new donors created in our samples could be correlated.

V. CONCLUSIONS

The presented resistivity measurements on heat-treated oxygen-doped samples can neither be described by the kinetics theory of Kaiser, Frisch, and Reiss nor by that of Wada. EPR spectra NL8 and NL10 are the dominating spectra observed in 470 °C heat-treated oxygen-rich silicon and are produced irrespective of the actual acceptor present. Direct incorporation of the acceptor ion in these centers is therefore unlikely. Indirect involvement of the acceptor in their production is, however, indicated by the following experimental results:

(1) Maximum concentration and formation rate of NL8 depend on the initial acceptor concentration.

(2) Production of NL10 is enhanced in Al-doped FZ-Si,

parallel to an enhancement in TD production.

(3) The g shift of NL10 with increasing HT time is dependent on the acceptor present.

The spectra NL10, NL13, and NL17 of Muller *et al.* were found to be subsequent stages of the same defect. For all studied materials the NL10 spectrum intensity could be correlated to TD concentrations, which indicates that the defect giving rise to NL10 is the dominant TD in the final stage of the heat treatment. Although no ^{17}O hyperfine structure of NL8 and NL10 was observed in samples whose oxygen content was enriched to 46% in this isotope, it cannot be concluded that oxygen is not involved in these centers in view of the enhanced production of these centers with increasing oxygen concentration (and their absence in heat-treated oxygen-lean samples); it probably takes a position where the unpaired spin density is low. Further evidence of oxygen involvement in these centers is provided by the influence of the oxygen concentration on the g-value transformation process with HT time. Heat treatment in the 650—750 °C region only produced NL10; the structure of the EPR active centers formed in this temperature range is therefore similar to the structure of those formed in the 450 °C region.

ACKNOWLEDGMENTS

The authors are grateful to H. Schlatter for suggesting the application of the infrared elliptical oven for the oxygen diffusion as well as for his valuable assistance throughout the whole sample preparation process. This work has been supported by the Netherlands Foundation for Fundamental Research on Matter (FOM).

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