

EPR SPECTRA OF HEAT-TREATMENT CENTERS IN OXYGEN-RICH SILICON

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After heat-treatment of oxygen-rich silicon at 410-550 °C ten different EPR spectra were observed. Nine of these are new spectra, seven of them reveal 2mm symmetry for the corresponding heat-treatment center, thereby reducing considerably the number of possible atomic configurations. In some cases the number of paramagnetic centers could account for the observed changes in carrier concentration.

1. Introduction

During nearly 25 years the effects of heat-treatment on oxygen-rich silicon, especially between 400 and 600 °C, have been investigated. From electrical resistivity, Hall effect, and infrared absorption measurements it was concluded that oxygen clusters are formed, some of which can act as donors<sup>1</sup>. Carbon and the acceptor elements turned out to play an important role in these processes<sup>2,3</sup>. The infrared measurements demonstrated that several different types of centers are involved<sup>2</sup>. However, detailed atomic models for the heat-treatment centers still have not been established. Although electron paramagnetic resonance (EPR) can give detailed information on a microscopic scale<sup>4</sup>, this technique was applied to the study of heat-treatment centers only in a few cases<sup>5,6,7</sup>.

2. Experimental

2.1. Samples

To investigate the effects of heat-treatment four silicon single-crystalline ingots were used. Their properties are summarized in table 1. One type of silicon contained oxygen because it was quartz crucible (Q.C.) grown. The other three materials were floating-zone (F.Z.) silicon with an

originally low ( $<10^{15}$  atoms/cm<sup>3</sup>) oxygen content. In samples from these materials, having dimensions of 25x2x2 mm<sup>3</sup>, oxygen was introduced by diffusion at 1370-1390 °C in an alumina furnace for about ten days. This resulted in a nearly uniform distribution of oxygen. The procedure for the introduction of oxygen was similar to that of Abou-el-Fotouh *et al*<sup>8</sup>. The concentration of isolated interstitial oxygen was determined from the intensity of the associated 9 μm infrared band<sup>9</sup>.

Some samples were diffused with oxygen isotopically enriched in <sup>17</sup>O to 10%. The actual percentage of <sup>17</sup>O in these samples was determined in a control measurement from the intensity of the <sup>17</sup>O hyperfine lines in the EPR spectrum Si-SL1, produced by electron irradiation<sup>10</sup>. Apparently due to contamination during the diffusion process with natural oxygen with an abundance of 0.037% <sup>17</sup>O the samples contained only 2.2% of the magnetic isotope.

As a consequence of the long treatment at a high temperature the samples inevitably are contaminated with some fast diffusing elements like iron, manganese, and chromium. To eliminate the disturbing EPR spectra associated with these impurities and to obtain a standardized starting situation preceding the heat-treatment cycle all samples were again heated at 1390 °C for 15 minutes. This was followed by slow cooling at the entrance of the furnace during two minutes just

Table 1. Properties of the samples.

Ingot number	Growth	Type	Resistivity Ohm.cm	Dopant Imp.	C	O	<sup>17</sup> O	
					Conc. 10 <sup>14</sup> at.cm <sup>-3</sup>	Conc. 10 <sup>15</sup> at.cm <sup>-3</sup>	Conc. 10 <sup>17</sup> at.cm <sup>-3</sup>	Conc. %
1	QC	p	1.1	B	140	6	9	0.037
2a	FZ	p	0.9	B	170	?	17	0.037
b							13	2.2
3	FZ	p	800	B P	0.7 0.5	?	15	0.037
4	FZ	n	0.34	P	220	?	12	2.2

until below red heat and a subsequent quench to room temperature in water.

Heat-treatments were carried out under nitrogen ambient in a quartz tube during 1 to 300 hours at  $410 \pm 3$  °C and at  $550 \pm 3$  °C after a preceding heat-treatment at 450 °C during 100 to 300 hours. Changes in the electrical resistivity were determined by four-point probe measurements at room temperature. The Fermi level usually rises with increasing heat-treatment time and p-type samples convert to n-type as verified by measuring the thermo-voltage using a hot-point probe. From the resistivity and conductivity type the number of produced donor-electrons was calculated.

## 2.2. Electron Paramagnetic Resonance Technique.

The EPR measurements were performed with a K-band (23 GHz) superheterodyne spectrometer. Spectra were observed in the dispersion mode and audio-frequency modulation of the magnetic field was employed. Samples could be illuminated before or during EPR measurements through a quartz lightpipe. Centers originally unobservable in EPR are sometimes converted to a paramagnetic charge state using light of appropriate wavelengths.

To obtain a high accuracy for the g-values and to determine spin concentrations a reference sample was used. This consisted of a cube, with an edge of 1.6 mm, of n-type 8.2 Ohm.cm silicon containing  $2 \times 10^{12}$  phosphorus atoms. Postulating  $g = 1.99850^6$  as an exact g-value for the center of the two phosphorus EPR lines and using the hyperfine splitting of 117.53 MHz<sup>6</sup> most g-values could be determined with an accuracy of  $\pm 0.00004$ . By comparing the intensities of the observed spectra with the reference spectrum rough estimates of the numbers of unpaired spins in the heat-treatment centers could be made. In view of the different passage conditions and line shapes errors of a factor five are possible.

## 3. Results

Following various heat-treatments altogether ten different EPR spectra were observed. One of these spectra, labelled Si-G15, was already known from EPR studies on irradiated silicon. The spectrum is ascribed to a carbon-oxygen pair in a

divacancy<sup>11</sup>. The remaining nine spectra were never reported before and we therefore label them Si-NL8, NL9, NL10, NL13, NL14, NL15, NL16, NL17, and NL18, extending the labelling system generally adopted for irradiation defects in silicon, so as to include heat-treatment centers<sup>12</sup>. Their g-values, symmetry properties, and some other relevant resonance data are presented in table 2.

Among the new spectra many nearly equal g-values occur. It was possible to distinguish between these spectra as they exhibit a different behaviour as a function of heat treatment and EPR conditions. In particular the g-tensors of NL10, NL13, and NL17 show very small differences. All three spectra appear in the same sample, but fortunately they occur successively upon prolonged heat-treatment. In our opinion these spectra are just significantly different. If in a spectrum no angular dependence could be observed, even with the high resolution of the K-band spectrometer, we called it isotropic.

Spectrum G15 has a g-tensor reflecting 2/m or m symmetry. While NL15 and NL18 are isotropic, the other seven new spectra show an angular dependence of the g-values corresponding to point-group 2mm symmetry. So the associated heat-treatment centers must have two mutually perpendicular {011} planes of reflection. Five of these spectra, i.e. NL8, NL10, NL13, NL16, and NL17 have g-tensors which in addition exhibit approximate <011> axial symmetry. In the silicon lattice no atomic arrangement is possible with this axial symmetry. It may however be an indication that the unpaired electrons of the corresponding centers are principally accommodated in combinations of atomic p-orbitals having their lobes in the correct directions. In figure 1 an example is given of the angular dependence of the g-values both for a g-tensor with and without <011> axial symmetry. The pattern formed by the g-values when the magnetic field direction is varied in the (011) plane reflects the 2mm center symmetry<sup>13</sup>.

From figure 1 it appears that the g-values of NL8 are quite similar to the values as reported by Graff *et al*<sup>7</sup>. However, while these authors attribute their resonances to a center with <111> axial symmetry, we definitely established a different symmetry for the center corresponding to spectrum NL8.

Table 2. Principal values  $g_1$ ,  $g_2$ , and  $g_3$  of the new EPR spectra. The accuracy is  $\pm 0.00004$  except for NL16 where it is  $\pm 0.00001$ . Angle  $\theta$  is between the direction of the  $g_1$ -axis and the [011] direction. Typical full linewidth at half maximum is denoted by  $\Delta B$ . Temperature range for observation is given in the last column.

Spectrum	$g_1$	$g_2$	$g_3$	$\theta$	Point-group	System	$\Delta B$ (mT)	T (K)
NL 8	1.99323	2.00091	1.99991	0	2mm	Rhombic I	0.43	4.2-77
NL 9	1.99758	1.99847	1.99917	0	2mm	Rhombic I	0.3	2 -10
NL10	1.99747	1.99957	1.99959	0	2mm	Rhombic I	0.2	4.2-40
NL13	1.99770	1.99949	1.99974	0	2mm	Rhombic I	0.16	2 -40
NL14	1.99880	1.99919	1.99966	0	2mm	Rhombic I	0.16	2 - 6
NL15	1.99926	isotropic			23,43m	Cubic	0.22	2 -20
NL16	1.9949	1.9995	1.9995	0	2mm	Rhombic I	0.6	4.2-20
NL17	1.99799	1.99946	1.99982	0	2mm	Rhombic I	0.2	2 -40
NL18	1.99944	isotropic			23,43m	Cubic	0.2	2 -10

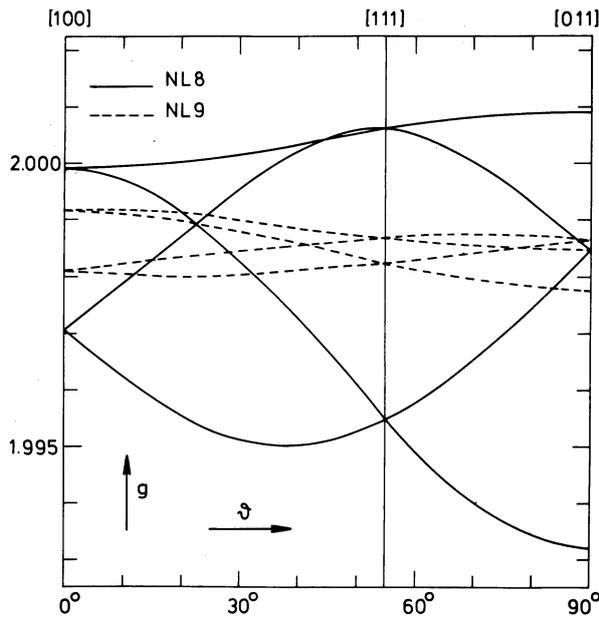


Figure 1. g-values of the EPR spectra NL8 and NL9 for directions  $\theta$  of the magnetic field in the (011) plane.

Table 3 summarizes the appearance of the EPR spectra in the four materials as specified in table 1. Also given are the heat-treatment temperatures by which the spectra were produced and estimates, within the factor five mentioned, of the maximum concentrations of spins which were produced.

Table 3. Production of the EPR spectra.

§ Heat-treatment at 550°C occurred only after preceding long treatment at 450°C.  
 §§ NL10 was already present after slow or fast cooling from 1390°C.

Spectrum	Ingot	Maximum concentration (cm <sup>-3</sup> )	Temperature for production (°C)
G15	1,2	2x10 <sup>13</sup>	410,450
NL 8	1,2	8x10 <sup>15</sup>	410,450
NL 9	1,2	10 <sup>16</sup>	410,450
NL10	3	4x10 <sup>14</sup>	§§
NL13	2,3,4	8x10 <sup>14</sup>	450,550 <sup>§</sup>
NL14	2	2x10 <sup>14</sup>	550 <sup>§</sup>
NL15	3	2x10 <sup>14</sup>	450
NL16	2	3x10 <sup>13</sup>	550 <sup>§</sup>
NL17	3	10 <sup>15</sup>	450
NL18	3	5x10 <sup>14</sup>	450

In all four types of silicon about 3x10<sup>16</sup> donors per cm<sup>-3</sup> were formed by heat-treatments of approximately 100 hours. It is assumed that the change of resistivity is only due to singly ionized donors. From the data in table 3 it can be concluded that only in the type 1 and 2 samples the numbers of paramagnetic centers derived from the spectra NL8 and NL9 have this order of magnitude. These spectra are possibly associated with the major donor center(s) in

boron doped silicon. The correlation between the growth of spectra NL8 and NL9 and the formation of donors is illustrated in figure 2. The sudden appearance of the spectra is presumably due to the rise of the Fermi level converting the centers to the paramagnetic charge state. This is supported by the fact that after 10 hours heat-treatment NL9 can only be observed with illumination.

Attempting to confirm the presence of oxygen in the heat-treatment centers <sup>17</sup>O was diffused into some samples. The presence of <sup>17</sup>O nuclei with a nuclear spin I = 5/2 can cause hyperfine splittings in the EPR spectra. For an enrichment to 2.2% <sup>17</sup>O the hyperfine lines should be about 270 times smaller than the main EPR line corresponding to non-magnetic oxygen, assuming that

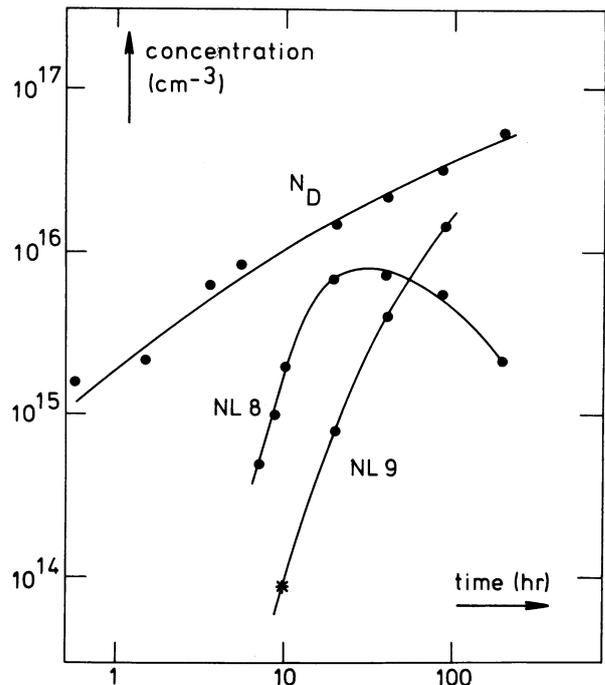


Figure 2. The production of donors  $N_D$  and paramagnetic centers from the EPR spectra NL8 and NL9 in samples of type 2 as a function of time of heat-treatment at 450°C. p- to n-type conversion occurs after about 14 hours.  
 \* After 10 hours spectrum NL9 could only be observed under illumination.

one equivalent oxygen atom is present in the centers. In figure 3 it is illustrated that for NL8 the <sup>17</sup>O hyperfine interaction could not be observed. No other hyperfine satellites, for instance from <sup>29</sup>Si, <sup>13</sup>C, <sup>10</sup>B, <sup>11</sup>B, or <sup>53</sup>Cr, are visible as well. From the observed linewidth and -shape upper limits for the hyperfine constants for each of these nuclei can easily be found. NL9 did not show any hyperfine interactions with <sup>17</sup>O or other nuclei either. The other new EPR spectra were measured with a smaller signal to noise ratio. For them only hyperfine interactions with the more abundant isotopes might be expected to be visible. No hyperfine lines were observed.

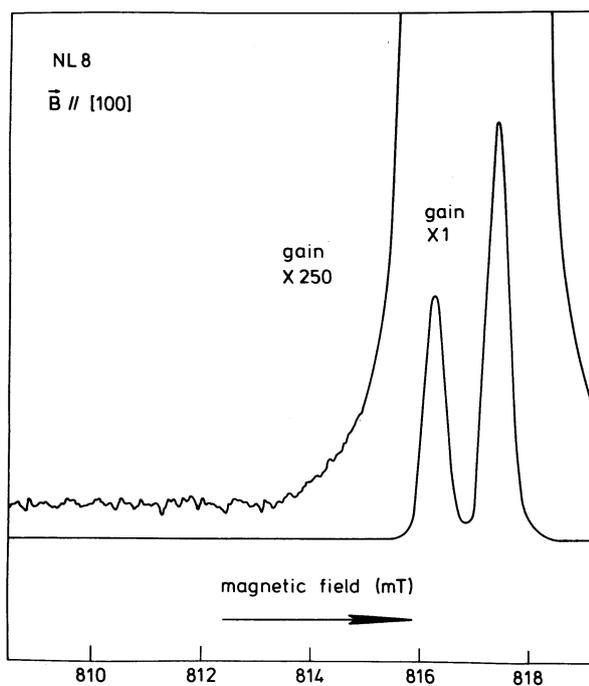


Figure 3. The EPR spectrum NL8 for  $B // [100]$  in sample type 2b, measured at 20 K.

The absence of any resolved hyperfine structure, even with  $^{29}\text{Si}$ , implies a very low probability density of the paramagnetic electron at all nuclei involved. This may be due

to symmetry, the electron wavefunction may have a widely spread character, or the electron is primarily accommodated in non-s-type atomic orbitals.

Preliminary ENDOR experiments on spectrum NL8 showed some  $^{29}\text{Si}$  hyperfine interactions of about 2.4 MHz. Spectra NL8 and NL9 were studied under  $[0\bar{1}1]$  uniaxial stress. Application of a stress of  $2.2 \text{ kg/mm}^2$  between 20 and 300 K did not induce any changes in the spectra.

#### 4. Conclusions

The EPR results have shown the production of several centers by heat-treatment of oxygen-rich silicon. However it may not be excluded that distinct spectra arise from different charge states of the same center.

From the observed g-tensors a pointgroup symmetry  $2mm$  is determined for most centers. In addition the g-tensors of some of them indicate a  $\langle 011 \rangle$  axial symmetry for the wavefunction of the center. Moreover this wavefunction will be either very delocalized or strongly p-type.

Unfortunately the presence of oxygen in any of these centers could not yet be established by EPR.

The spectra NL8 and NL9, which occur with the highest intensities, are tentatively identified with the donor center(s). As these spectra only appear in low resistivity boron doped silicon, boron is probably involved in their formation.

At present not enough information is available to suggest detailed atomic models for the various centers.

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