

An EPR observation of changes in heat-treatment centres in oxygen-rich silicon

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Abstract. Upon heat treatment at about 450°C in boron-doped silicon two strong EPR spectra are observed. One of these spectra cannot be described by a constant g tensor. The principal g -values vary nearly logarithmically with heat-treatment time. A discussion is given on the kinds of change of the corresponding centre that may be responsible for the observed phenomenon.

1. Introduction

For 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 has been concluded that oxygen clusters are formed, some of which can act as donors (Kaiser *et al* 1958). Carbon and the acceptor elements play an important role in these processes (Bean and Newman 1972, Fuller *et al* 1960). The infrared measurements demonstrate that several different types of centres are involved (Bean and Newman 1972). However, detailed atomic models for the heat-treatment centres have still not been established. To obtain detailed information on a microscopic scale, electron paramagnetic resonance (EPR) has been applied to study heat-treatment centres (Muller *et al* 1978). In that study nine new EPR spectra labelled NL8–NL10 and NL13–NL18 have been reported. These were all due to $S = 1/2$ centres. The principal g -values are given in table 1. None of the EPR spectra from (multiple-)oxygen–(multiple-)vacancy centres (Lee and Corbett 1976) have been observed, ruling out the possibility that these centres act as the donor centres in heat-treated silicon, as suggested by Helmreich and Sirtl (1977). The present work is a continuation of our earlier study in which a more complete list of references has also been given.

2. Experiment

Oxygen-containing samples were obtained in two different ways. Part of the samples was cut from a crucible-grown rod (supplied by Wacker). The others were cut from floating-zone ingots and, after cutting, oxygen was introduced by diffusion at 1370–1390°C for about ten days. To eliminate disturbing EPR spectra of isolated iron, chromium and other fast-diffusing elements, a not-too-fast standardised quenching procedure was used. A detailed description of the sample production has been given in Muller *et al* (1978).

The properties of the samples which were used for the present study are summarised in table 2. All samples were p-type boron-doped. Samples A were crucible-grown (CG),

Table 1. The principal values g_1 , g_2 and g_3 of the EPR spectra observed after heat treatment (Muller *et al* 1978). The g_1 and g_2 axes are in a $\langle 011 \rangle$ direction.

Spectrum	g_1	g_2	g_3
NL8	1.99323	2.00091	1.99991
NL9	1.99758	1.99847	1.99917
NL10	1.99747	1.99957	1.99959
NL13	1.99770	1.99949	1.99974
NL14	1.99880	1.99919	1.99966
NL15	1.99926	isotropic	
NL16	1.9949	1.9995	1.9995
NL17	1.99799	1.99946	1.99982
NL18	1.99944	isotropic	

Table 2. Properties of the samples.

Material	Resistivity (Ω cm)	Boron concentration (cm^{-3})	Carbon concentration (cm^{-3})
A	1.1	1.4×10^{16}	6.0×10^{15}
B	0.89	1.7×10^{16}	2.6×10^{16}
C	0.34	6.5×10^{16}	3.0×10^{16}
D	0.1	4.5×10^{17}	?

the others were cut from float-zoned (FZ) material and then diffused with oxygen. Determination of the oxygen content in the latter small samples using room-temperature infrared measurements is too inaccurate to be more than a rough indication.

The EPR experiments have been performed as described in Muller *et al* (1978). For the present study, the spectrometer was better adapted for routine illumination of the samples with infrared light.

3. Results

Before heat treatment at 450°C an EPR spectrum, NL10, is already present in all samples. It is moderately strong in the originally FZ samples, both after slow or fast cooling. In very low intensity, this spectrum is also present in completely untreated CG material. Upon 450°C heat treatment of boron-doped samples, two strong EPR spectra, NL8 and NL9, appear. After long heat-treatment times (40–100 h), the number of observed paramagnetic centres, as determined from comparison with a reference sample, was about 10^{16}cm^{-3} . This is almost sufficient to account for the observed resistivity changes (Muller *et al* 1978). Spectra NL8 and NL9 are therefore possibly associated with the major donor centres in boron-doped silicon. For a definitive identification it is desirable to measure the growth of these spectra for short heat-treatment times of only a few hours to establish a correspondence with the known donor production rate (Kaiser *et al* 1958). Unfortunately the spectra are not observed in such cases, as the centres are in a non-paramagnetic state. By illumination with light from a quartz lamp during EPR, however,

NL8 could be made visible in such short-treated samples. We did not achieve our original purpose to measure the intensity of NL8 as a function of heat-treatment time, as we did not then have an accurate method to calibrate the amount of light. Variations of the light intensity cause variations in the intensity of NL8 and moreover the intensity of the phosphorus reference signal depends on the presence of light.

Another unusual phenomenon was observed however. Determination of the g tensor of an obvious NL8 spectrum yielded a tensor which was clearly different from the tensor

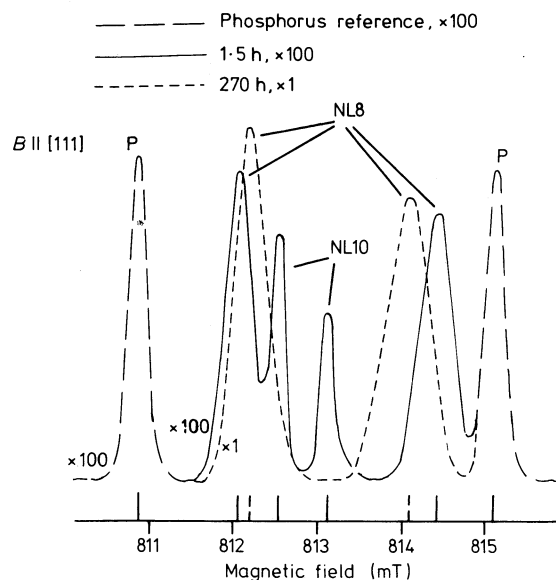


Figure 1. EPR spectra of NL8 after 1.5 and 270 h heat treatment at 450°C. Microwave frequency, 23 GHz; sample temperature, 8 K. NL8 can easily be observed in the temperature range 6–30 K without change in g -values.

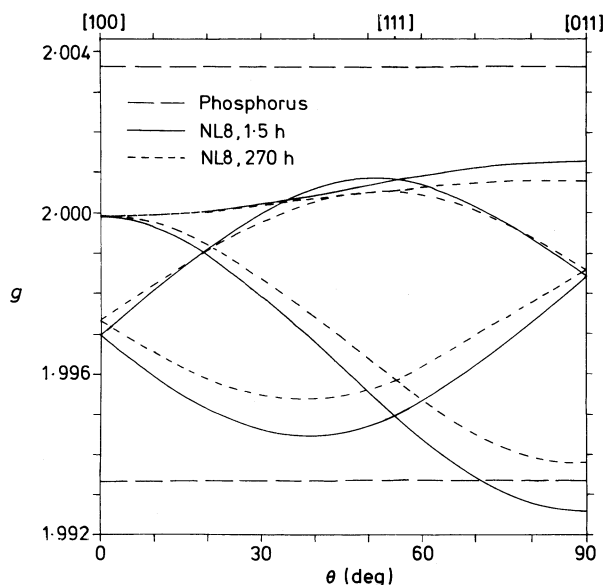


Figure 2. The g -value pattern of NL8 for magnetic field directions in the (011) plane, after 1.5 and 270 h. These patterns were derived from the principal g -values, which were determined by a least-squares fit to results for the [100], [111] and [011] directions.

determined after long heat-treatment time (figures 1 and 2). Using the two EPR lines of a phosphorus-doped sample not only as an intensity calibration but also as an accurate relative field calibration, as described in Muller *et al* (1978), we made a study of the changes of the g tensor.

In the simple spin Hamiltonian $H = \mu_B \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S}$ of an $S = 1/2$ centre like NL8, a g tensor reflecting 2 mm point group symmetry can be written as

$$\mathbf{g} = \begin{pmatrix} g_{xx} & 0 & 0 \\ 0 & g_{yy} & g_{yz} \\ 0 & g_{yz} & g_{yy} \end{pmatrix}.$$

The principal g -values are $g_1 = g_{yy} - g_{yz}$, $g_2 = g_{yy} + g_{yz}$ and $g_3 = g_{xx}$. In figures 3(a), (b) and (c) it can be seen how g_{xx} , g_{yy} and g_{yz} behave as a function of heat-treatment time for samples with different boron concentrations and for different heat-treatment temperatures. The errors in the determination of the individual g -values are about ± 0.0001 , but larger for both short and long heat-treatment times, due to obscuring other spectra (NL10, NL9 etc).

We see that g_{xx} does not depend on the heat-treatment time, but g_{yy} and g_{yz} have a nearly logarithmical time dependence. Neither the boron nor the carbon concentration seems to have any influence on the change of the g -value. Whether the small difference between samples of type A and B must be attributed to a difference in oxygen content is not clear.

Heat treatment at 480°C causes faster changes, while changes by 510°C treatment are not faster than at 480°C. The errors at this temperature are larger, however, as NL8 is fairly weak and obscured by other spectra like NL10, NL13 and NL17.

A further phenomenon is the asymmetric EPR lineshape which is observed after long heat treatment for those lines which are shifted most. This asymmetry can be slightly observed in figure 1 for the EPR line which is found at 814 mT. It is more pronounced however in spectra for the [011] direction, not shown here.

4. Discussion

For the formation of the NL8 centres, boron turns out to be essential. A higher boron content also produces more NL8. Therefore, the NL8 centre presumably contains a boron atom. This boron atom seems to convert to a donor after capturing some oxygen atoms.

The process of adding more oxygen atoms is unlikely to account for the observed changes in the g tensor. Such discrete changes in the number of oxygen atoms cannot be expected to cause the nearly continuous small changes which were observed. It is, moreover, unlikely that the symmetry of the centre can be conserved in that way. It is more probable that the observed effect is caused by changes in the structure of centres with a constant number of oxygen atoms.

It is believed that a superposition of the EPR spectra from centres which are in different stages of their structure change give rise to the observation of an average g tensor. The formation kinetics of the centres and their successive structure changes have to account for two observed phenomena: firstly, the logarithmic time dependence of the g -values, and secondly the asymmetry of the EPR lines after long heat treatment.

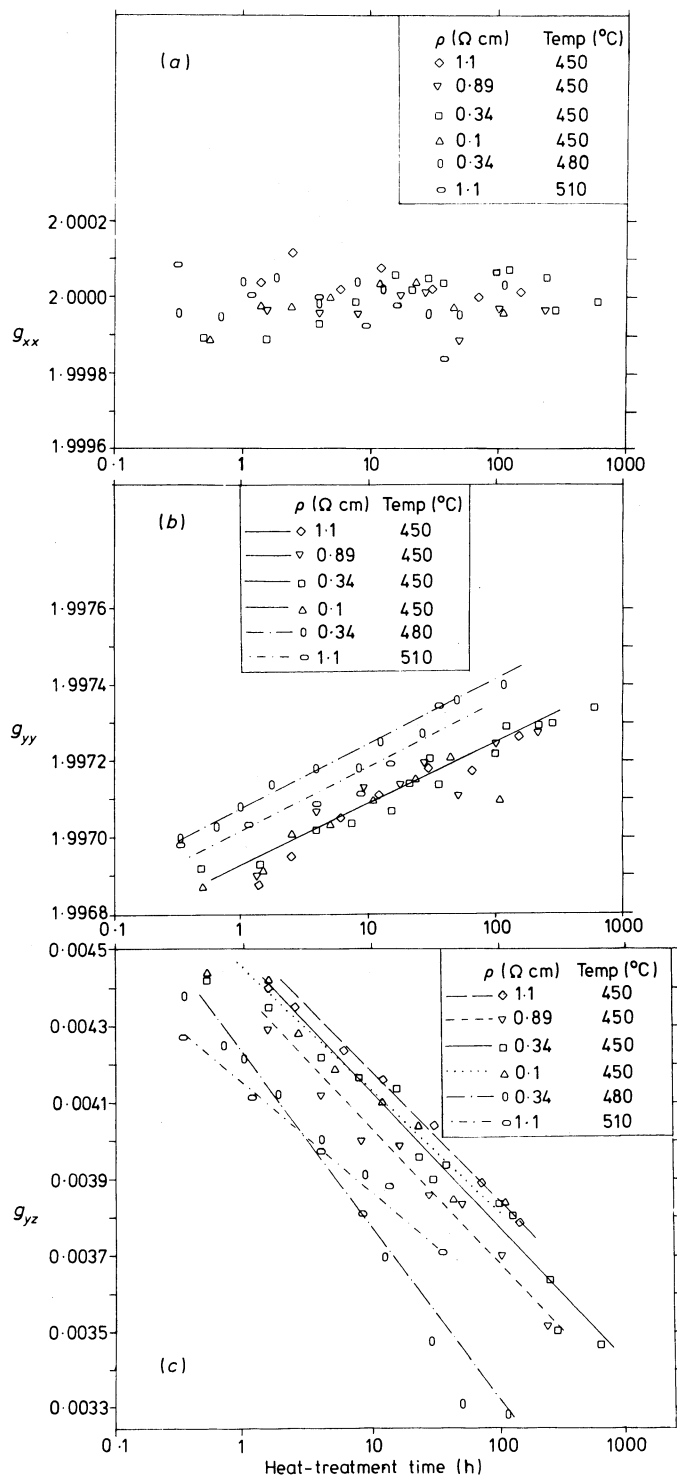


Figure 3. (a) g_{xx} , (b) g_{yy} and (c) g_{yz} as a function of heat-treatment time for samples with different boron concentrations and for different heat-treatment temperatures.

At this moment a quantitative model cannot yet be presented in this way. A different explanation for the changes of the g tensor can be sought in the interaction of NL8 centres among themselves or with other centres which are present and are produced by heat treatment. The absence of any hyperfine interaction which is observable in EPR can be caused by a very unlocalised wavefunction of the unpaired electron, as discussed in Muller *et al* (1978). A wavefunction which is so far extended can easily give rise to interactions with other centres. EPR measurements when the position of the Fermi level was such that in equilibrium only a small fraction of the NL8 centres were in their paramagnetic state, did not exhibit any difference in g -value with or without infrared illumination. This is an indication that the changes in g -value cannot be caused by interactions between the NL8 centres themselves, by means of their paramagnetic electrons. Although interaction with other centres may present a possible explanation, no model which accounts for the g -value changes and the asymmetric line shapes could yet be conceived in this way.

Although spectrum NL16 is somewhat similar to NL8, no continuous change from NL8 to NL16 could be observed, so it is likely that they are due to different centres. On the other hand, another group of very similar spectra, NL10, NL13 and NL17, has been observed. It is possible that these spectra do not originate from essentially different centres, but arise from a centre with varying g -values, as for spectrum NL8.

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