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ELECTRON PARAMAGNETIC RESONANCE STUDY OF THE NL51 SPECTRUM IN HYDROGEN-IMPLANTED SILICON

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High-resistivity silicon samples have been implanted with hydrogen and deuterium (dose $5 \times 10^{15}\,cm^{-2}$). After a short heat treatment at low temperatures (20 min at 380–540°C) several electron paramagnetic resonance (EPR) spectra could be detected upon illumination. The most prominent ones were Si-B3 which is ascribed to a well-known radiation defect, i.e., the split self-interstitial, and a new spectrum, labeled Si-NL51. On the basis of its angular dependence as well as the production and observation conditions the Si-NL51 centre is proposed to arise from the $S = 1$ excited neutral charge state of a $\langle 1\,0\,0\rangle$-oriented complex, with tetragonal g tensor ($g_{\|} = 2.00707$, $g_{\perp} = 2.00069$) and crystal field interaction ($D = 19\,MHz$).

1. INTRODUCTION

MANY YEARS of research in the field of radiation effects in silicon have resulted in the discovery and identification of a variety of centres, including vacancies, self-interstitials and complexes of these primary defects. One of the most prominent and easy to produce radiation defects is Si-B3 [1, 2], which is well established to be originating from a self-interstitial complex oriented along the $\langle 1\,0\,0\rangle$ crystallographic direction, resulting in an electron paramagnetic resonance (EPR) spectrum with fairly uncommon (tetragonal) magnetic field angular dependence. In our current study of defects created by hydrogen implantation of silicon we encountered a defect which seems to be related to Si-B3, in the sense that it has the same symmetry and similar, though not identical, formation kinetics.

2. EXPERIMENTAL DETAILS

As starting material for the experiments high-purity, high-resistivity (6 kΩ cm), silicon was used. The material was submitted to proton or deuteron beam implantation with a starting energy of about 30 MeV (H) and 25 MeV (D) per nucleon. In between the cyclotron source and the target an aluminium absorber of 3.9 or 1.6 mm thickness was placed. The ion current of circa $0.5\,\mu A\,cm^{-2}$ yielded a dose of circa $1 \times 10^{15}\,cm^{-2}$. The implantation was repeated with different absorber thicknesses in order to produce a homogeneous distribution of hydrogen and the defects. The total dose was then estimated to be $5 \times 10^{15}\,cm^{-2}$ in the 1 mm thick sample [3]. During implantation the sample was kept at a temperature of approximately 300 K.

After the implantation, the samples were given short (20 min) anneal stages at comparatively low temperatures (380–540°C) in air, without any form of quenching afterwards. To remove surface defects, the samples were etched in a solution of HF and HNO_3 in a ratio of 1 : 3.

The measurements were performed on two superheterodyne EPR spectrometers, one with an operating frequency of 9.2 GHz (X band) [4] and one with 23.3 GHz (K band). Both have low-frequency field modulation and were tuned for dispersion. The sample was kept at low temperatures in TE_{011}

Table 1. Quantitative specifications of the EPR spectrometers

	X band	*K* band
Microwave frequency	9.2 GHz	23.3 GHz
Field modulation	12.3 Hz	83.2 Hz
Tuning mode	Dispersion	Dispersion
Cavity	TE_{011}	TE_{011}
Q factor	43 000	5000
Temperature	6 K	4.5 K
Microwave power	−25 dBm	−22 dBm

cylindrical cavities with high *Q* factors. To these cavities low-power microwave radiation, in the μW range, was applied. The sample could be *in situ* illuminated with white light from a tungsten source, guided to the sample through a quartz rod. Further, quantitative, details are given in Table 1.

3. RESULTS

Following the sample preparations as described above, several EPR spectra could be detected upon illumination. In the hydrogen-implanted sample a superposition of three different spectra could be resolved and identified, as can be seen in Fig. 1 (top trace), where these spectra are plotted for the magnetic field along a ⟨1 0 0⟩ crystallographic direction, as acquired at the *X*-band spectrometer. First, the figure reveals a slightly anisotropic spectrum (α), which is not further discussed in this paper. Another spectrum, which could be identified by its angular dependence, is the spectrum associated with the self-interstitial, Si-B3 [2], first observed by Daly [1].

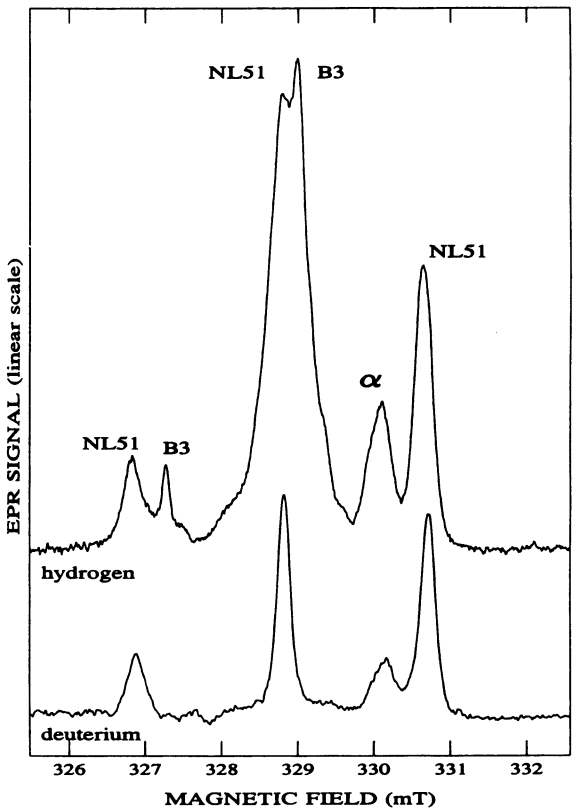
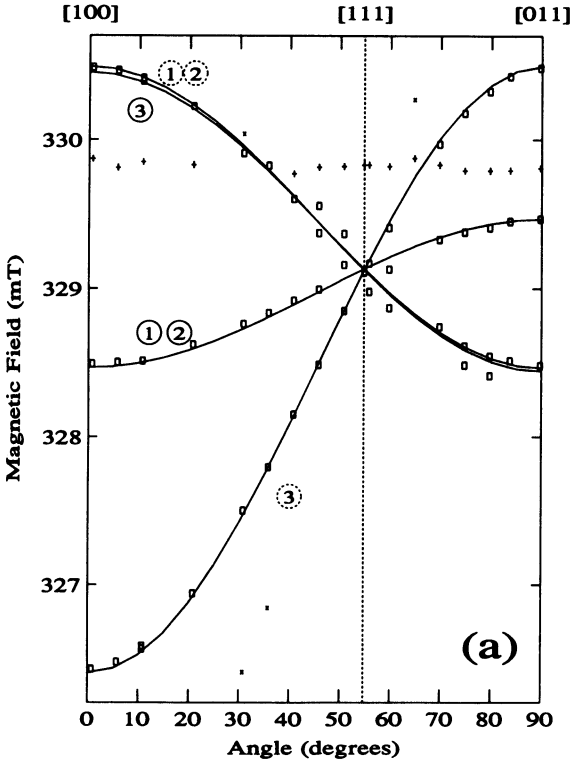


Fig. 1. EPR spectra of the hydrogen (top trace) and deuterium (bottom trace) implanted samples, observed at *X* band, with the magnetic field parallel to ⟨1 0 0⟩. The first sample was annealed at 380°C in air, while the latter underwent a likewise treatment at 540°C.

Apart from these two spectra, Fig. 1 discloses a third, previously undiscovered spectrum, which we label Si-NL51. Switching from protons to deuterons as an implantation species does not change the line positions or line widths of this spectrum. This is illustrated in the bottom trace of Fig. 1, where a scan is shown for an identical sample, except for the implantation type (deuterium instead of hydrogen) and the anneal temperature (here 540°C, instead of 380°C for the top scan). Such a result suggests the absence of hydrogen in the defect, but in the next section we will present an alternative reason for this lack of difference. Comparison of the two scans in Fig. 1 reveals another interesting feature, namely the absence of Si-B3 in the lower scan. This is caused by the difference in anneal temperature. The comparatively high temperature of 540°C already anneals out Si-B3 (consistent with Fig. 1 of [2]), while Si-NL51 is more persistent and subsists.

To further analyse the spectrum the angular dependencies were measured. The results are shown in Fig. 2(a) and 2(b) for *X* and *K* band, respectively. The first task is to find the components of the spin Hamiltonian, in other words to determine the cause of the separation of the different parts of the spectrum. In view of this, it is interesting to note that a change of splitting of the lines occurs when going from the low-frequency *X*-band, to the higher-frequency *K*-band spectrometer. This eliminates the possibility of the splitting being caused by a hyperfine interaction, which is in first order magnetic-field independent. It can also be excluded that the spectrum is entirely due to an electronic Zeeman interaction, since this can never account for the intricate changes of the structure when altering the microwave frequency. First, a pure Zeeman interaction $\mathcal{H} = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S}$ would produce a spectrum whose splitting would be directly proportional to the microwave frequency. Secondly, no symmetry gives rise to the observed patterns as disclosed in Fig. 2. This leaves behind the involvement of a crystal-field term in the Hamiltonian for the explanation of the observed



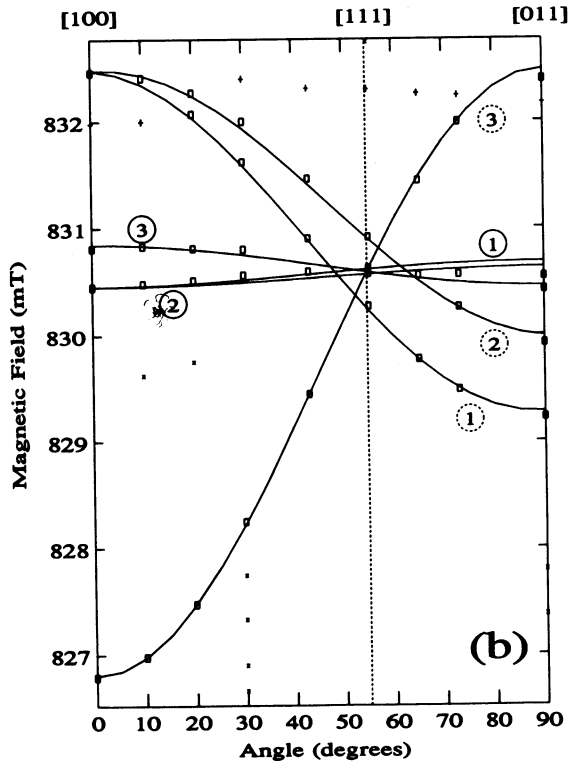


Fig. 2. Angular dependence of Si-NL51 for X band (a) and K band (b) with the magnetic field in the $(0\,1\,\bar{1})$-plane. The experimental points of Si-NL51 (□), α (+) and unidentified resonances (×) are marked. Along the solid lines, which indicate simulations with the Hamiltonian as described in the text for microwave frequencies of 9.226106 GHz (a) and 23.282640 GHz (b), the arbitrary labeled defect orientations are plotted (with 3 corresponding to [1 0 0]). The circles around the orientations indicate the electron spin state transitions (dashed circles: $m_s = -1$ to $m_s = 0$, solid circles: $m_s = 0$ to $m_s = 1$,). For (b) a misorientation of the sample of 4.1° was introduced into the simulation to more accurately follow the observed line positions. The Si-B3 spectrum was absent in this sample.

line positions. The lowest value of an electron spin for which crystal fields can affect the spectrum is $S = 1$. We therefore propose to describe the Si-NL51 spectrum with a spin Hamiltonian containing an (electronic) Zeeman and a crystal-field term

$$\mathscr{H} = \mu_B \mathbf{B}\cdot\boldsymbol{g}\cdot\mathbf{S} + \mathbf{S}\cdot\boldsymbol{D}\cdot\mathbf{S}, \tag{1}$$

where we take for both $\boldsymbol{g}$ and $\boldsymbol{D}$ tetragonal tensors of second rank possessing $\langle 1\,0\,0\rangle$-axial symmetry, and $S = 1$, corresponding to a triplet state. The experimentally determined values of $\boldsymbol{g}$ and $\boldsymbol{D}$ can be found in Table 2, together with the spin-Hamiltonian parameters of the other spectra detected in the studied material.

4. DISCUSSION

Spectrum Si-NL51 exhibits tetragonal symmetry (point group S_4 or D_{2d}), indicating a symmetry axis along a $\langle 1\,0\,0\rangle$ direction. This is quite rare in silicon, where only about 5% of the known centres [5] have this symmetry. All of them are radiation defects (without presence of the radiation species) [6, 7] or are $\langle 1\,0\,0\rangle$-uniaxial strain-induced signals [8, 9]. Since seemingly the identical spectrum is produced for hydrogen- and deuterium-implanted material it would be tempting to ascribe the centre to a radiation defect, without incorporation of implantation particles.

An analysis of the $\boldsymbol{D}$-tensor reveals further information about the defect. The magnitude of $\boldsymbol{D}$ is very small for a triplet spectrum. When we use the approximation of two interacting point-dipoles at a mutual distance r we get

$$\boldsymbol{D}_\perp = \frac{\mu_0}{4\pi}\cdot\frac{\mu^2}{r^3}, \tag{2}$$

where $\mu = \mu_B = 9.2740154 \times 10^{-24}\,\mathrm{J\,T^{-1}}$ and $\mu_0 = 4\pi \times 10^{-7}\,\mathrm{N\,A^{-2}}$. The experimental value of $\boldsymbol{D}_\perp$

Table 2. Spin-Hamiltonian parameters of the discussed spectra

Centre	Symmetry	Spin	Term	//	⊥	Unit	Reference
Si-NL51	tetragonal	$S = 1$		⟨1 0 0⟩			This
	⟨1 0 0⟩-axial		g	2.00707	2.00069		paper
			D	−37.9	19.0	MHz	
Si-B3	tetragonal	$S = 1/2$		⟨1 0 0⟩			[2]
	⟨1 0 0⟩-axial		g	2.0166	2.0054		

then yields an inter-dipole distance of nearly 9 Å. A careful search for ^{29}Si or other hyperfine lines within 50 mT of the Zeeman lines was made for the Si-NL51 spectrum, but none were found. It is important to note that there is also no hint of any structure in the Zeeman lines which can be associated with ^{1}H or ^{29}Si hyperfine interactions. It is also important to note that the EPR signal is very sensitive to the sample temperature; it vanishes for temperatures above approximately 20 K. In view of these results, the structure of the spin-triplet Si-NL51 center as arising from interacting dipoles which belong to two different cores at a distance of 9 Å with high localization is not very likely. More plausible is an extended, one-core defect, in which the value of 9 Å should be interpreted as a measure for the radius of the hydrogen-like effective-mass wavefunction. Such an extended core eliminates the possibility of observing hyperfine interactions of any nucleus, since even the strongest (closest) interactions would not be resolved in the spectrum. In this way we can still not exclude the involvement of hydrogen (deuterium) in the defect.

Because of the high electron spin ($S = 1$) and the fact that it is seen only upon illumination Si-NL51 is most likely to arise from an excited state. On basis of the angular and frequency dependence we propose as a model for Si-NL51 an excited state of a ⟨1 0 0⟩-oriented complex. It should be noted that the possibility of Si-NL51 and Si-B3 arising from the same structure cannot be excluded. The absence of Si-B3 from the higher-temperature heat-treated (540°C) sample should then be explained by an annealing-induced shift of the Fermi level. In this case it would be logical to assign Si-NL51 to an excited, neutral charge state of the di-interstitial $(SiSi)^{0*}_{Si}$. Nevertheless, such a possibility seems not very likely, since Si-NL51 has not been observed in the elaborate study of Si-B3. On the other hand, if we do not assign it to the di-interstitial, the range of self-interstitials seems to be exhausted. This is in favour of a model which includes hydrogen (deuterium) in the structure. Though the involvement of hydrogen in the defect cannot be deduced from the experimental data presented here.

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