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Electron spin resonance signal from a tetra-interstitial defect in silicon

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Abstract

The Si-B3 electron spin resonance (ESR) signal from agglomerates of self-interstitials was detected for the first time in hydrogen-doped float-zone-grown silicon samples subjected to annealing after electron irradiation. Previously this signal had been detected only in neutron- or proton-irradiated silicon samples. The absence of obscuring ESR peaks for the investigated samples at applied measurement conditions allowed an investigation of the hyperfine structure of the Si-B3 spectra. The analysis supports assignment of a tetra-interstitial defect as the origin of the signal.

1. Introduction

Interactions involving intrinsic defects, i.e., vacancies (V) and self-interstitials (I) in silicon (Si) are still of great interest because they affect nearly all possible defect reactions. Most V-related defects are electrically active and can be detected by various techniques, while detection and identification of I-related defects poses problems. Due to this, V-related reactions have been extensively investigated but much less is known about I-related reactions. Self-interstitial atoms are thought to play a crucial role in transient enhanced diffusion of dopants and in the formation of thermal donors and extended defects, such as rod-like and $\{311\}$ structural defects. The defect reactions and mechanisms, which lead to the formation of extended defects from I atoms are not established. Current theoretical calculations predict the crucial role of a tetra-interstitial (I_4) agglomerate as a building block in the formation of extended defects in Si [1–6]. In the model of an I_4 agglomerate [1] four additional silicon atoms are embedded in the silicon lattice in such a way that all atoms are four coordinated. Moreover, the distortions of bond lengths and angles against those of a perfect crystal are relatively small for the I_4 model. The defect is characterized by five-, six- and seven-member atomic rings and has D_{2d} point group symmetry. Experimental data on the existence and properties of the tetra-interstitial may elucidate many aspects of I-related reactions in Si.

Electron spin resonance (ESR) spectra labelled Si-B3 were first reported as a signature of ‘one more’ irradiation-induced defect [7]. The spectra soon attracted considerable attention due to the rare symmetry of the related defects [8, 9]. The structure of the defect responsible for

the Si-B3 spectra has remained controversial despite considerable investigation [8]. Recently, these spectra were proposed as a possible signature of the I_4 agglomerate in silicon [4, 5]. However, lack of thoughtful analysis of hyperfine (HF) structure of the spectra did not allow this assignment to be checked.

The striking feature of the Si-B3 spectra is their unusual tetragonal, i.e. D_{2d} point group, symmetry. To date, only a few ESR centres with similar symmetry have been reported for defects in irradiated Si. Other reported properties can be summarized as follows [4, 7–9]. The Si-B3 spectra were observed in neutron- or proton-irradiated float-zone-grown Si crystals upon annealing at $T > 200^\circ\text{C}$ and were stable up to 500°C . The Si-B3 centre has inherent, i.e. not related to the Jahn–Teller distortion, D_{2d} symmetry by virtue of its molecular structure. The centre of the defect should be vacant, with two equivalent Si atoms lying along the principal $\langle 100 \rangle$ axis. The defect is intrinsic, i.e. it contains no impurity atoms and is not related to the agglomeration of vacancies. The spectra originate from the single positive charge state of the defect with a total spin of $S = 1/2$. The HF structure was not analysed carefully in previous publications about the Si-B3 spectra [7–10]. Only one pair of HF peaks, related to two equivalent Si atom shells, was investigated in [8]. Other components of the HF structure were not analysed, probably due to obscuring ESR peaks of unknown origin in highly damaged proton- or neutron-irradiated samples.

Recently we detected Si-B3 spectra in hydrogen-doped silicon samples annealed at temperatures of $250\text{--}500^\circ\text{C}$ after electron irradiation for the first time. Appearance of the spectra in the electron-irradiated samples was strongly related to the hydrogen doping. However, the defect responsible for the Si-B3 spectra did not contain hydrogen atoms: admixture of deuterium to the doping ambient did not cause any change to the HF structure of the Si-B3 spectra. Results relating to the role of hydrogen and other impurity atoms in the formation of the defect and various ESR spectra observed in similar samples will be presented elsewhere. Due to the absence of obscuring peaks in our samples, it was possible to investigate all components of the HF structure of the spectra. In what follows, we present results of the investigation of the HF structure of the Si-B3 spectra and a comparison of obtained results with the model proposed in [4].

2. Experimental details

We used high-resistivity ($1800\ \Omega\ \text{cm}$) float-zone-grown p-type (boron doped) Si samples. Doping of the samples with hydrogen (H) was accomplished by annealing the samples in gas-filled quartz capsules at 1300°C for 1 h. Fast quenching in iced water followed the doping procedure. The doped samples were irradiated at room temperature with 3 MeV electrons to dose $d = 4 \times 10^{17}$ electrons cm^{-2} . Annealing of irradiated samples was accomplished in an Ar flow at $T = 400^\circ\text{C}$ for 5 h.

We used a JEOL X-band ESR spectrometer equipped with a TM_{011} mode microwave (MW) resonator and a continuous helium gas-flow cryostat. The derivative of MW field absorption with respect to the magnetic field ($d\chi''/dB_0$) was measured using a lock-in amplifier and magnetic field modulation with an amplitude of 0.01–0.2 mT and a frequency of 100 kHz. It was possible to illuminate samples during ESR measurements through an optical window in the resonator. For the best signal-to-noise ratio, the Si-B3 signal was recorded under weak illumination of the sample with white light at a temperature of 45 K. Microwave power was 1 mW.

The measured ESR spectra for various mutual orientations of crystal axes and magnetic field were decomposed on components, i.e. individual peaks with Gaussian line shape and the same line width, relevant to Zeeman peaks and several shells of equivalent Si atoms surrounding

the paramagnetic electron. The best decomposition set should include a minimal number of shells and should give a good fit to all orientations of the sample toward the static magnetic field. For the best set an anisotropy of HF peak positions was plotted and analysed.

3. Results and discussion

It should be noted that all previously reported parameters of the Si-B3 spectra [7–10] coincided well with those obtained in our measurements [11]. This fact allowed us to make unambiguous identification of the detected spectra as the Si-B3. However, in the case of our samples, the total damage due to electron irradiation was substantially less than that due to neutron irradiation in [8]. After annealing of the samples at 400 °C for 5 h for the employed measurement conditions no obscuring ESR signals were detected. Thus, despite the worse spectral resolution (X-band in our case and K-band in [8]) and fast passage conditions, it was possible to analyse all components of HF structure.

We attempted to fit the experimental ESR spectra with various sets of HF peak pairs. For the sake of simplicity, we will label each set of pairs below using numbers of equivalent Si atoms in the successive shells followed by the period, i.e. the ‘2–8–12’ set means successive shells containing 2, 8 and 12 Si atoms. The number of equivalent Si atoms in the shell can be estimated from ratios (r) of the intensities of individual HF peaks (see 2, 8, 12 in figure 1) to that of the central peak for the group (Z in figure 1) and comparison of the obtained results with the relative abundance of Si isotopes. Fewer than three shells of equivalent atoms did not give reasonable fits of the spectra at various orientations of sample axes toward the static magnetic field. Several sets were investigated for the model of three successive shells, such as ‘2–8–12’, ‘2–4–12’, ‘2–8–4’, ‘2–8–8’ and others. For the best-fitted set of peaks the HF peak intensities corresponded to interactions of a paramagnetic electron with a ^{29}Si atom positioned in the shells consisting of 2 ($r \approx 0.05$), 8 ($r \approx 0.195$) and 12 ($r \approx 0.293$) atoms each, i.e. the ‘2–8–12’ set. Examples of experimental data (open circles), overall fitting curves (solid curve) and individual fitted ESR peaks (dotted curves) relevant to the Zeeman and HF structure of the signal for the [110] rotation axis of the sample are presented in figure 1. Three sets of curves in figure 1 correspond to various angles between the static magnetic field and the crystalline axes of the sample. The directions are indicated in the figure next to the curves. Similarly good fits for this set of peaks were obtained for all measured sample orientations. Our attempts to fit the experimental spectra with different sets of HF peaks originating from three shells of equivalent atoms gave significantly larger fitting errors. Slightly better fitting than that for the ‘2–8–12’ set was obtained for several sample orientations using a decomposition which included a set of four shells of equivalent atoms, comprising 2, 8, 4 and 8 Si atoms each (‘2–8–4–8’ set). However, the improvement was in the limits of fitting errors. Thus, it was decided to proceed with the ‘2–8–12’ set, keeping in mind that the 12 Si atom shell may comprise 4 Si and 8 Si shells, with similar HF parameters.

The anisotropy of HF peak splitting obtained using the ‘2–8–12’ set is presented in figure 2 and parameters of the HF tensor are presented in table 1. Values of the HF parameters in table 1 correspond to the isotropic (a) and anisotropic (b) parts of the axially symmetric HF tensor. These parameters were calculated from the principal values of the HF tensor, i.e. A_{\parallel} and A_{\perp} , using expressions $A_{\parallel} = a + 2b$ and $A_{\perp} = a - b$. A value for localization of the paramagnetic electron on the atoms of various shells can be estimated using the values of a and b . An example of similar estimations with explanations can be found in [12]. The localization values for the case of the Si-B3 spectra are also presented in table 1 (see column L).

Results obtained for the 2 Si atom shell coincide well with results of [8]. Unpaired electronic function is strongly p-like with 94% anisotropic component. For the 8 Si and 12 Si

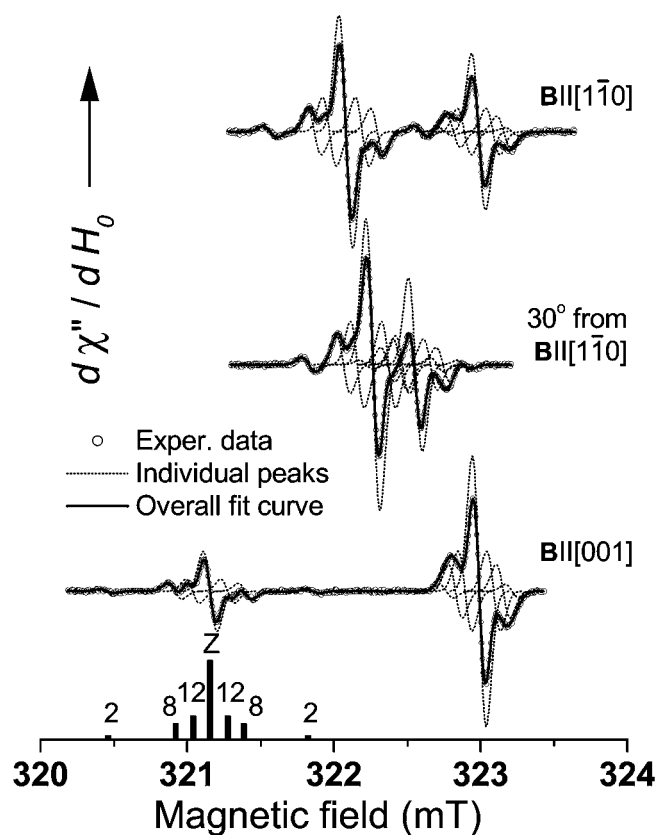


Figure 1. The Si-B3 ESR spectra at 45 K under weak white light illumination and $f_{RES} = 9.04$ GHz. Experimental data, overall fitted spectra and individual fitted ESR peaks are presented for various mutual orientations of crystal axes and static magnetic field. The magnetic field was rotated in the (110) crystal plane. Under the lower-field group of peaks, a stick diagram is shown explaining the position and intensity of individual peaks in the group for sample orientation $B \parallel [001]$.

Table 1. Hyperfine structure parameters for the Si-B3 spectra. The number of atoms in the shell and tentative assignment are given in first column (see also figure 3). Parameter a represents isotropic and parameter b anisotropic parts of the axially symmetric HF tensor. Parameter L represents localization of the unpaired wavefunctions on the atoms of the relevant shell.

Atoms (figure 3)	HF parameters ($\times 10^{-4} \text{ cm}^{-1}$)		
	a	b	$L(\%)$
2X	7.17	2.98	9.24
8Y	3.64	0.61	2.04
12Z	2.23	1.82	0.54

atom shells the anisotropic component gradually decreases, yet remains the prevailing one (85% and 64% respectively). The results fit well the structure of the tetra-interstitial defect presented in figure 3. Broad agreement of the results with the theoretical calculations presented in [4] is evident. However, there are some differences as well. In theoretical calculations [4], the Mulliken analyses showed that about 3% of the unpaired wavefunction is localized on the

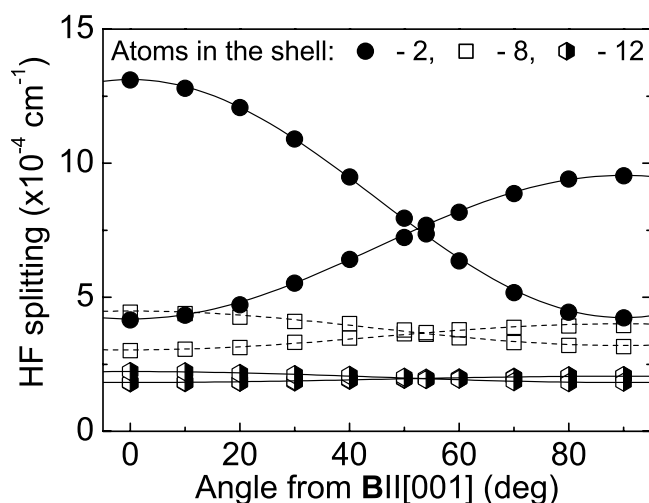


Figure 2. Experimental data (symbols) and fitted curves for an anisotropy of the separation of pairs of HF peaks. Assignment is presented in the figure. Experimental conditions are the same as given in figure 1.

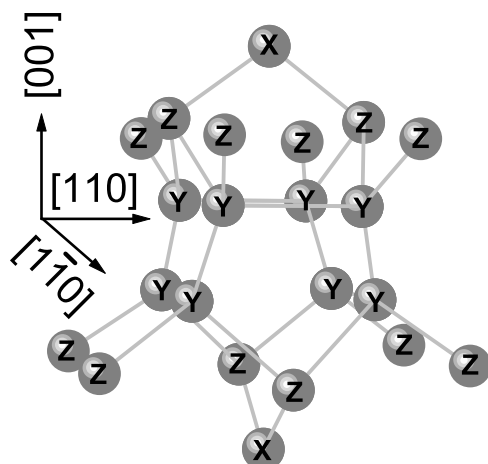


Figure 3. Atoms of a tetra-interstitial defect participating in a HF interaction. Atoms included in the 2 Si shell are marked with 'X', those included in the 8 Si shell are marked with 'Y' and those included in the 12 Si shell are marked with 'Z'.

sites labelled Y and a similar value on four Z atoms bounded to the X atoms (see figure 3). The value for the Y sites is in perfect agreement with our results (2%, see table 1). However, our calculations gave much less localization on the Z sites (0.5%). Besides that, the model for the unpaired wavefunction proposed in [4] will require 2 Si, 8 Si and 4 Si equivalent atom shells (the '2-8-4' set). Our attempts to find a solution for the HF structure consistent with such an arrangement failed. On the other hand, if the wavefunction of the unpaired electron, presented in [4] (see figure 2 of that publication), is rotated 90° around the [001] crystal axis, only minor changes will be needed to get excellent agreement of theoretical predictions with our experimental data.

However, data obtained for the HF structure of the Si-B3 spectra do not agree with the (001) split interstitial model or the (001) interstitial model proposed in [8]. Namely, the existence of 8 Si and 12 Si equivalent atom shells with D_{2d} symmetry cannot be expected for these models. Moreover, the sets of shells expected for the HF structure of these structures (such as '2–4–12', for example) do not fit the experimental results.

In conclusion, Si-B3 ESR spectra from agglomerates of self-interstitials were detected for the first time in hydrogen-doped float-zone-grown Si samples subjected to annealing after electron irradiation. Absence of obscuring ESR signals allowed investigation of the HF structure of the spectra. Three shells of equivalent atoms were detected and parameters of the HF structure were calculated. According to the best-fit model, the shells consisted of 2, 8 and 12 Si atoms in D_{2d} symmetry. Obtained results are in good agreement with the theoretical model of the tetra-interstitial defect in silicon [1–4].

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