

New oxygen-related EPR spectra in proton-irradiated silicon

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Abstract

An electron-paramagnetic resonance (EPR) study of proton-irradiated silicon has revealed two new EPR spectra labeled Si-AA13 and Si-AA14. Spectrum AA13 has C_{3v} symmetry ($g_{\perp} = 1.9985$ and $g_{\parallel} = 2.0024 \pm 0.0002$), AA14 C_1 symmetry. These spectra correspond to positive (B^+) and negative (B^-) charge states respectively of a bistable defect in the B configuration. Another metastable configuration (labeled A) in positive charge state creates the known EPR spectrum Si-A18. Reversible transitions and electronic levels of the metastable defect are studied. A tentative model for this center is proposed: a self-interstitial–oxygen-interstitial complex (Si_i-O_i).

Keywords: Electron paramagnetic resonance; Silicon; Oxygen; Bistable defect

1. Introduction

It is well known that thermal treatment and irradiation by high energy particles of Czochralski-grown silicon introduce into crystals a lot of oxygen-related defects such as donors [1], precipitations [2], and point radiation defects: A-center ($V-O$) [3], K-center (O_i-C_i) [4], multivacancy clusters (V_n-O_m) [5]. In our paper two new EPR spectra, Si-AA13 and Si-AA14, are reported. These spectra were found to arise from an oxygen-related metastable defect. We will argue that interstitial oxygen atoms may capture a self-interstitial Si_i atom, and as result a bistable complex ($Si-O$)_i is created.

2. Experimental

Czochralski-grown and float-zone silicon (Si-Cz, Si-FZ) with initial resistivity at 0.1–10 Ωcm were irradiated at 77 K with 30 MeV protons. The typical value of fluency was 1×10^{15} – 5×10^{15} protons cm^{-2} . Hydrogen implantation in the bulk of the sample was completely avoided, since the 30 MeV proton range in silicon is of ~ 4.5 mm, while the thickness of the sample was of 0.3–0.5 mm. Thus only radiation defects were introduced. Immediately after irradiation the samples without intermediate heating were installed in a cavity. EPR measurements were carried out with a 35 GHz spectrom-

eter at a sample temperature of 77 K. Preferential alignment of the defects was achieved by applying a compressional stress ($\sim 1500 \text{ kg cm}^{-2}$) in the temperature range 77–300 K by using a special holder outside cavity. The stress was applied to the $\langle 011 \rangle$ axis at appropriate temperature and then the sample was cooled to 77 K under stress. The stress was then removed and the sample was placed into an EPR cavity for measurements at 77 K. Annealing and EPR measurements can be done in the dark as well as under illumination of the sample with band-gap light.

3. Results and discussions

The known EPR center A18 is the dominant one after 77 K proton irradiation of Si-Cz samples with resistivity $\sim 1 \text{ } \Omega\text{cm}$. Corbett et al. [6] have resolved the A18 spectrum in silicon electron-radiated at 100 K, and have determined the symmetry and thermal stability of the center. However, they did not identify the microscopic structure of the defect. In our case the A18 spectrum is observed in Si-Cz samples only and it is absent in Si-FZ samples. The A18 spectrum disappears during annealing in the dark at ~ 160 – 190 K and a new spectrum labeled Si-AA13 grows (Fig. 1, curve 1). The spectrum can be described as arising from an anisotropic defect C_{3v} symmetry with the spin Hamiltonian

$$H = \mu_B \tilde{H} \tilde{g} \tilde{S} + \sum_j \tilde{S} \tilde{A}_j \tilde{I}_j$$

with $S = 1/2$. The first term describes the electron Zeeman interaction, the second term corresponds to hyperfine interaction with a ^{29}Si nucleus ($I = 1/2$, 4.7% abundant). From angular dependence of the central lines and hyperfine satellites versus magnetic field orientation the values of the g and A tensors were determined. The principal values of g and A tensors are presented in Table 1 with the molecular wave-function coefficients (α_j^2 , β_j^2 , η_j^2).

A reduction of the AA13 spectrum intensity was observed immediately when the sample was illuminated with light. Simultaneously the 1:1 growth of a new EPR spectrum (labeled AA14) was observed (Fig. 2). Stopping sample illumination causes the disappearance of the AA14 spectrum and recovery of the AA13 spectrum. The AA14 spectrum can be described as arising from an anisotropic defect of C_i symmetry and $S = 1/2$. Its parameters are given in Table 2, and the angular dependence of the g values calculated from the experi-

Table 1

Observed g -tensor and ^{29}Si hyperfine interaction A -tensor for Si-AA13 spectrum (77 K) and molecular wave-function coefficients (η_j^2 the fraction of the total wave function at site j ; α_j^2 from the isotropic part; and β_j^2 from the anisotropic part of the hyperfine interaction)

$g(\pm 0.0002)$	$A(\text{MHz})$	α_j^2	β_j^2	No. of equivalent atoms	$\Sigma \eta_j^2$
$g_1 = 2.00245$	$A_1 = 144.5$	0.13	0.87	1	0.33
$g = 1.99852$	$A = 233.2$				
	$A_b = 49.0$	1		4 6	0.048–0.072
	$A_c = 28.8$	1		2	0.014

mental data is shown in Fig. 3.

It was found that prolonged illumination causes the simultaneous decrease of AA13 and AA14 spectra intensities and recovery of A18 spectrum (Fig. 1, curves 2 and 3). The kinetics of the process exponentially depends on the illumination time (Fig. 4). The rate of AA13 → A18 transition linearly increases with light power. Hence the A18 center can be converted to AA13 and AA14 by heating in the dark at 160–190 K and converted back by illumination of the sample at 77 K with ~ 1 eV light. The reversible transition is not accompanied by loss of spectral intensity.

Uniaxial compression experiments on samples containing AA13 spectra were also carried out. Stress of 1000–1500 kg cm⁻² was applied along a $\langle 011 \rangle$ axis of sample. We found that compression of the samples in

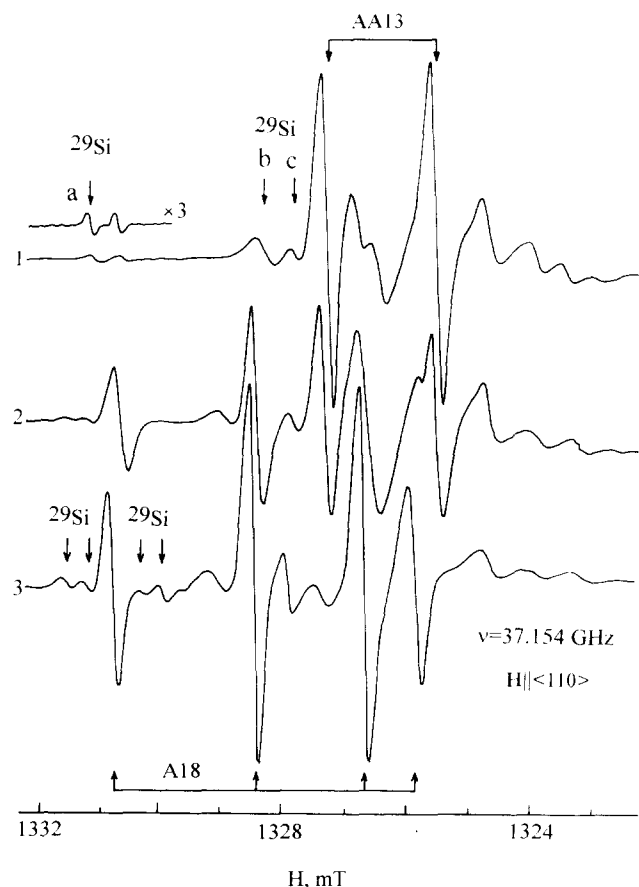


Fig. 1. EPR spectrum at 77 K of Si-Cz sample irradiated with 5×10^{15} protons cm⁻² at 77 K. 1, after annealing at 190 K for 5 min; 2, after light illumination at 77 K for 5 min; 3, after light annealing for 30 min. Arrows indicate positions of satellites resulting from hf interaction at one (a), 4–6 (b) and two (c) atom sites for the AA13 spectrum.

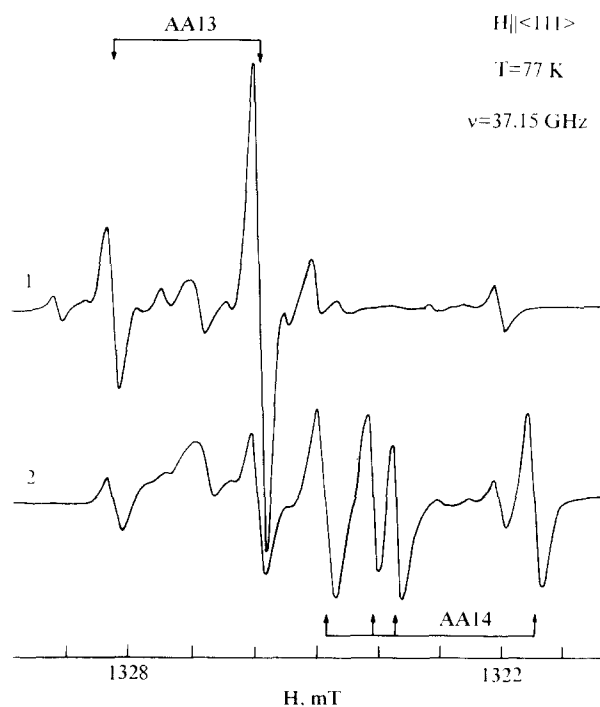


Fig. 2. EPR spectrum of Si-Cz sample irradiated with 5×10^{15} protons cm⁻² at 77 K and annealed at 190 K for 5 min. 1, EPR measuring in the dark; 2, under light illumination.

Table 2

Principal values of g -tensor ($T = 77$ K) and relevant principal axes (defined by giving their direction cosines with respect to the cubic axes) for one of the 24 orientations of AA14 center

$g(\pm 0.0002)$	n [100]	n [100]	n [001]
$g_1 = 2.00237$	0.9374	-0.0083	-0.3482
$g_2 = 2.00472$	0.2083	-0.7878	0.5796
$g_3 = 2.00926$	0.2792	0.6158	0.7368

the dark at $T < 230$ K did not cause visible preferential alignment. However, considerable alignment of the AA13 center was observed in the same temperature range, 180–200 K, under illumination. The preferential alignment of the defects was found to have been frozen-in at 77 K as measured by the relative intensities of the corresponding spectral lines. The defects whose $\langle 111 \rangle$ axes were perpendicular to the stress directions were decreased in intensity, and the defect whose $\langle 111 \rangle$ axes were 35.3° from the $\langle 110 \rangle$ stress direction were increased. Consequently defect energy is reduced when the defect is compressed in the direction along g_{11} and A_{11} axes. It is important to note that after the AA13 \rightarrow A18 transition a preferential alignment of the A18 defect was observed. The loss of alignment of the AA13 center and its thermal annealing takes place almost at the same temperature (~ 240 – 260 K). Acti-

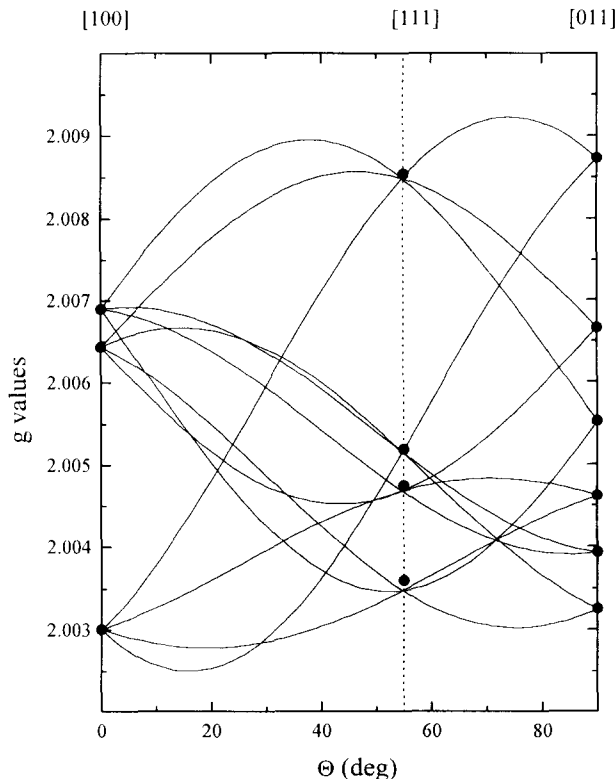


Fig. 3. Angular dependence of the g values for the Si-AA14 spectrum at 77 K with H in the $\{011\}$ plane.

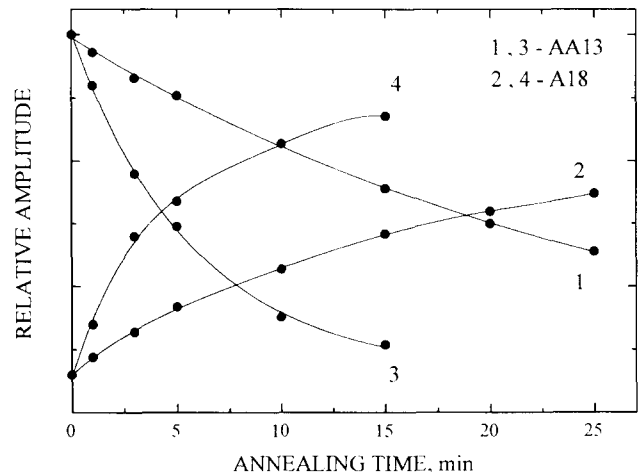


Fig. 4. Conversion of AA13 spectrum into A18 during band-gap light illumination at 77 K. The sample was initially irradiated with 30 MeV protons at 77 K and then annealed at ~ 200 K. Curves 1 and 2 correspond to light power of 0.095 W, and 3 and 4 to 0.44 W.

vation energy for the atomic reorientation process was found to be 0.8 ± 0.05 eV. A similar activation energy for the atomic reorientation process and defect migration is a typical property of interstitial centers [7].

Thus, the reversibility of A18 \rightarrow AA13 transitions and conservation of preferential alignment level at these transitions confirms that the observed EPR spectra arise from two different molecular configurations (labeled A^+ and B^+ respectively) of the same bistable center. Neutral charge states of these centers (A^0 and B^0) are nonparamagnetic. $B^+ \rightarrow B^0 + h$ transition occurs in the temperature range 100–120 K with activation energy 0.19 ± 0.03 eV. After this anneal, the AA13 signal was regenerated at 77 K with a short burst of light. This way, the defect produces in the band gap the donor level with energy $E_v + 0.19$ eV. The acceptor level ($B^0 \rightarrow B^- + h$ transition) is rapidly emptied at 77 K, and the AA14 spectrum is seen only under relatively high intensity of illumination. Consequently the level has to be placed higher than $E_c - 0.15$ eV. A study of the recharging process kinetics for A state ($A^+ \rightarrow A^0 + h$) yields a value of donor level depth of $E_v + (0.42 \pm 0.05)$ eV. The barrier for the conversion $A^0 \rightarrow B^0$ was determined to be $\sim 0.27 \pm 0.05$ eV. The energy diagram corresponding to experimental data is shown in Fig. 5(a).

Finally, we have discussed the possible nature of the revealed bistable center. It is clear that an impurity atom is involved in the structure of the center. Carbon and oxygen impurities are the main contaminations in Si-Cz samples. Obviously, carbon atoms cannot be included in the center structure since the A18 and AA13 spectra intensities did not depend on carbon concentration in the range from 2.6×10^{16} to 3.2×10^{17} atoms cm^{-3} . At the same time the spectra are absent in

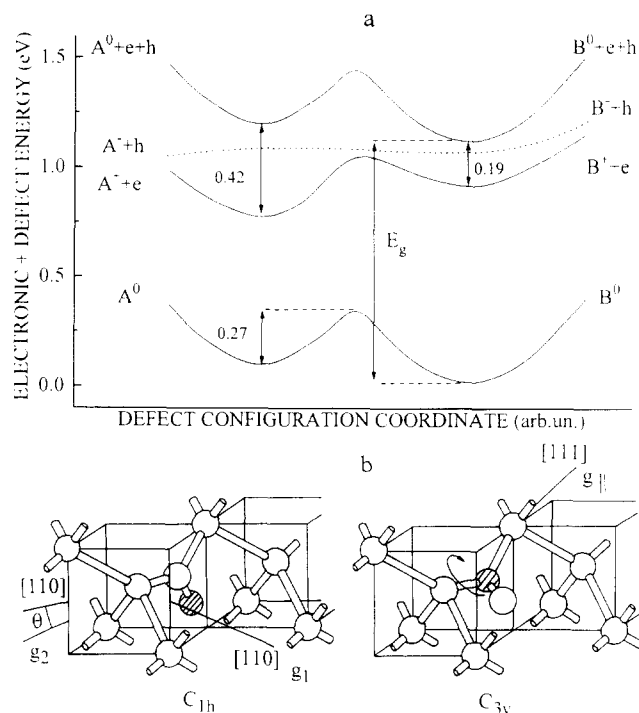


Fig. 5. Configurational-coordinate energy curves (a) and tentative models (b) for metastable states: A^+ (A18, C_{1h} symmetry), B^+ (AA13, C_{3v} symmetry) and B^- (AA14, C_1 symmetry). In the models, the hatched atoms are oxygen.

Si-Fz samples with a low concentration of oxygen impurity. Therefore we deduced that the bistable center includes oxygen atom. Simple intrinsic defects such as vacancy or self-interstitial could also be involved in the center, since these defects are mobile at 77 K. The weak localization of wave function on the Si atom for the AA13 center ($\sim 33\%$) is confirmation of the interstitial character of the bistable center. The resulting A18 center resonance was of sufficient intensity to observe the strong ^{29}Si hyperfine. No hf was observed with the

exception of slight splitting satellites (~ 50 MHz, Fig. 1(c)). This would be a result of preferential localization of paramagnetic electron on the oxygen atom.

Thus we suggest a tentative model for the bistable center complex of self-interstitial-oxygen-interstitial. It has been reported [8] that oxygen may be the trap for self-interstitial Si_i . Since oxygen interstitial O_i in silicon has unshared lone pair electrons and Si_i in $3s^23p^2$ state has an empty orbital, a donor-acceptor bond between these atoms may be formed. In the resulting complex $\text{Si}_i\text{-O}_i$ the C_1 symmetry is created. However, the symmetry may be raised to C_{3v} at 77 K by rotation of the defect around the $\langle 111 \rangle$ axis (Fig. 5(b)). Transition between metastable configurations A and B is realized by means of exchange of Si_i and O_i atom positions with corresponding bond-switching transformation.

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