Electron Exchange Interaction in $S = 1$ Defects Observed by Level Crossing Spin Dependent Microwave Photoconductivity in Irradiated Silicon

R. Laiho
Wihuri Physical Laboratory, University of Turku, FIN 20014 Turku, Finland

M. M. Afanasjev, M. P. Vlasenko, and L. S. Vlasenko
A. F. Ioffe Physico-Technical Institute of Russian Academy of Sciences, 194021 St.-Petersburg, Russia

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Spin dependent change of photoconductivity is observed for the first time at magnetic field induced crossing of a ground singlet ($S = 0$) and an excited triplet ($S = 1$) state levels of structural defects in irradiated silicon. These defects include two electrons localized on points of trigonal symmetry in the lattice. The results show that there exists in silicon radiation defects with low exchange energy, comparable with the Zeeman energy, between the two electrons responsible for the $S = 1$ state. New EPR spectra corresponding to transitions between Zeeman levels of the excited triplet state of these defects are observed by spin dependent microwave photoconductivity measurements. [S0031-9007(98)05307-1]

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Exchange interaction between two unpaired electrons localized on different atomic or molecular orbitals of a structural defect in silicon leads to formation of a ground singlet S_0 ($S = 0$) and an excited metastable triplet T ($S = 1$) states. In zero magnetic field these states are separated to the first approximation by the energy $J \cong E(T) - E(S_0)$ where J is the exchange interaction constant. Using conventional electron paramagnetic resonance (EPR) detection methods spectra of such defects in the $S = 1$ state can be observed only at sufficiently high defect concentrations [1–4]. The value of J has not been directly determined from $S = 1$ EPR spectra in Si but it is usually supposed to be many orders of magnitude higher than the Zeeman energy. EPR spectra of the excited triplet states of the aluminium + vacancy [1] and oxygen + vacancy complexes [2] have been observed under illumination of the samples [1,2]. Several $S = 1$ EPR spectra of radiation defects having J comparable to the thermal energy kT have been found also without illumination at relatively high temperatures ($T > 77$ K) [3,4].

At low defect concentrations the $S = 1$ EPR spectra can be detected only by highly sensitive methods based on optical detection of magnetic resonance [5] or on spin dependent recombination (SDR) effects. Using spin dependent microwave photoconductivity measurements, providing 4 orders higher sensitivity than the usual EPR method [6,7], spectra of the excited triplet states of a phosphorus + vacancy complex [8] and of a divacancy [9] have been found in Si.

In the present Letter we report measurements of spin dependent microwave photoconductivity in low dose irradiated Si. The results show existence of structural defects in the excited $S = 1$ states with J comparable to the Zeeman energy.

The results described below were obtained on float zone (FZ) grown n-type (300 Ω cm) silicon crystals irradiated at room temperature by 1 MeV electrons with the dose of 5×10^{16} cm^{-2}. Experiments were performed also with γ irradiated Si crystals having different phosphorus and oxygen concentrations. The detection method based on the SDR-induced change of microwave photoconductivity is described in details in Refs. [6–9]. We used an EPR spectrometer operating at the frequency of 9 GHz in the temperature range of 4–300 K, employing two modulation frequencies, 100 KHz and 100 Hz, of the magnetic field and detection of the second derivative of the signals. During measurements the sample was illuminated with a 100 W tungsten lamp.

SDR-induced change of the microwave photoconductivity observed in our samples at different temperatures for the magnetic field $B \parallel \langle 111 \rangle$ is shown by curves a–d in Fig. 1. The positions of the SDR lines are unusual since they are found in magnetic fields approximately twice as high as the field used to detect EPR spectra of paramagnetic centers with $g \approx 2$. The SDR line patterns are confined within a magnetic field interval of $\Delta B \approx 3$ mT under rotation of the field in the (110) crystal plane at any fixed temperature. Angular dependences of the positions of the SDR lines are shown in Fig. 2(a). They give evidence that the symmetry of the defect responsible for the spectrum is trigonal. If these lines would originate from saturation of the usual EPR transitions the components of the trigonal g tensor should have values of $g \approx 1$.

Two important features of this spectrum were found. First, the observed strong temperature dependence of its position in the magnetic field [curve (e) in Fig. 1] is unusual for paramagnetic centers in silicon. Another important result is the *independence* of the line position on the *microwave frequency*. Figure 3 shows that the lines (a, b) detected at frequencies f_1 and f_2 ($f_1 - f_2 = 38.9$ MHz), respectively, appear at the same magnetic field, but the positions of the EPR-SDR lines (c, d)

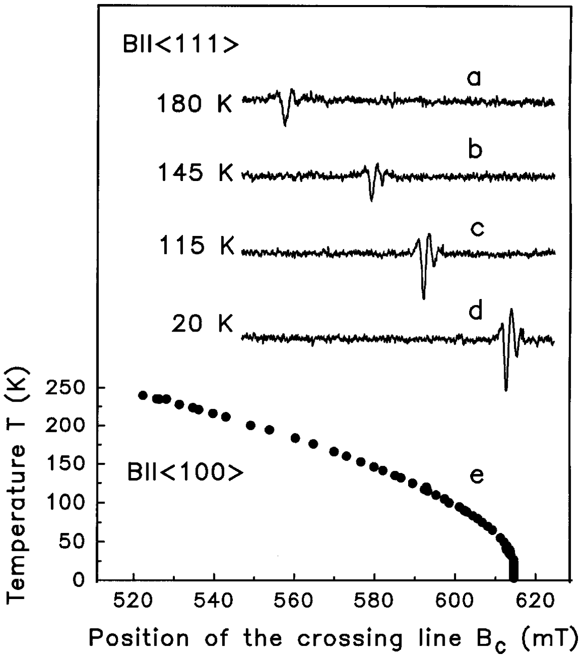

FIG. 1. Spectra of the microwave photoconductivity in irradiated Si at different temperatures for $B \parallel \langle 111 \rangle$ (traces a–d) and the temperature dependence of the position of the S_0-T^- crossing line at $B \parallel \langle 100 \rangle$ (e).

differ significantly. Hence the lines shown in Figs. 1 and 3 (traces a, b) are *not* caused by the change of the photoconductivity due to EPR transitions between the magnetic levels of the defect, but rather by change of the photoconductivity at specific points of the magnetic level structure, similar to anticrossing of the magnetic levels of excited triplet states [6,10]. So, we can attribute the SDR-induced change of the microwave photoconductivity in Fig. 1 to crossing of the S_0 state with the T^- level having the spin projection $S_z = -1$. The energy separation $E(T) - E(S_0)$ corresponding to the exchange constant $J = g\mu_B B_C$ (here $g \approx 2$ is the g factor and μ_B is the Bohr magneton) can be determined from the line position, B_C, at $B \parallel \langle 100 \rangle$. Within the temperature range of 4–30 K B_C is constant and has the value of 614.6 mT (see curve e in Fig. 1) which leads to $J \cong 17.2$ GHz (in frequency units). Usually J depends exponentially on the distance between two unpaired electrons in the defect concerned. Consequently, the temperature dependence of the line position shown in Fig. 1(e) can be explained by thermal expansion of the silicon lattice.

Within experimental accuracy the angular dependences of the lines shown in Fig. 2(a) are temperature independent. They can be described by anisotropies of the g factor and the magnetic dipole-dipole interaction between the electrons. Let us consider a two electron Hamiltonian

$$H = \mu_B \mathbf{B} \mathbf{g}_1 \mathbf{S}_1 + \mu_B \mathbf{B} \mathbf{g}_2 \mathbf{S}_2 + J \mathbf{S}_1 \mathbf{S}_2 + \mathbf{S}_1 \mathbf{D} \mathbf{S}_2 \,, \quad (1)$$

taking into account the Zeeman interaction between the applied magnetic field **B** and the electron spins S_1 and S_2, the isotropic exchange interaction $J\,\mathbf{S}_1\mathbf{S}_2$, and the anisotropic magnetic dipole-dipole interaction $\mathbf{S}_1\,\mathbf{D}\mathbf{S}_2$, where **D** is a symmetric traceless tensor. We assume that the g tensors of the electrons are identical and have trigonal symmetry defined by the components $g_\parallel$ and $g_\perp$. The energy levels obtained from the Hamiltonian (1) for the orientation $B \parallel \langle 111 \rangle$ are shown in Fig. 4(a). In particular, it may be observed that at $B = 0$ the T^0 and $T^\pm$ levels are separated by the zero field splitting constant D determined by the trigonal **D** tensor.

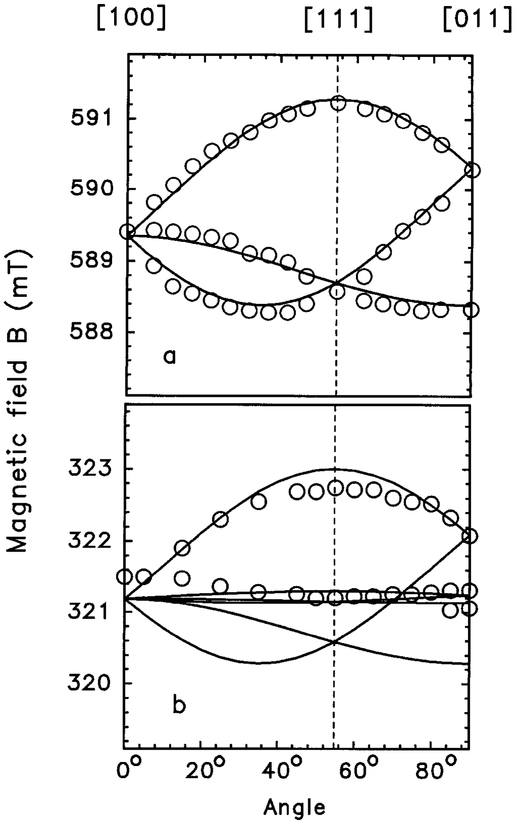

FIG. 2. Angular dependence of the observed SDR line positions (circles) for the level crossing spectrum (a) and for the spectrum Si-WL2 (b). In both cases the measurements were carried out at $T = 125$ K and the microwave frequency 9.0298 GHz. The solid lines describe the best fits of the observed data by using the Hamiltonian (1).

According to the level schema shown in Fig. 4(a) anticrossing of the T^0 ($S_z = 0$) and T^- ($S_z = -1$) levels is expected in a magnetic field B_{ac}. To observe this phenomenon we investigated changes of the photoconductivity of the sample when scanning the magnetic field through zero value. Indeed, as shown in Fig. 4(b), weak lines were observed symmetrically around $B = 0$ at $B_{\mathrm{ac}} = \pm 0.85$ mT for the orientation of $B \parallel \langle 111 \rangle$. With increasing the angle between **B** and the $\langle 111 \rangle$ axis these lines disappeared gradually. Such angular dependence is specific for the change of photoconductivity due to the anticrossing of levels [10]. From the value of $B_{\mathrm{ac}} = \pm 0.85$ mT that of $|D| \cong 23.8$ MHz could be determined.

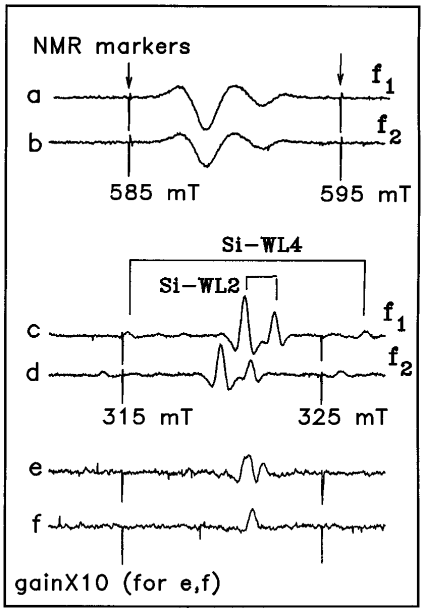

FIG. 3. SDR spectra of level crossing lines (a, b) and SDR-EPR lines (c, d) detected at frequencies of $f_1 = 9.0266$ GHz (a, c) and $f_2 = 8.9877$ GHz (b, d) at $B \parallel \langle 111 \rangle$. The Si-WL2 spectra observed for $B \parallel \langle 110 \rangle$ and $B \parallel \langle 100 \rangle$ are shown by the traces e and f, respectively. All spectra are recorded at $T = 125$ K.

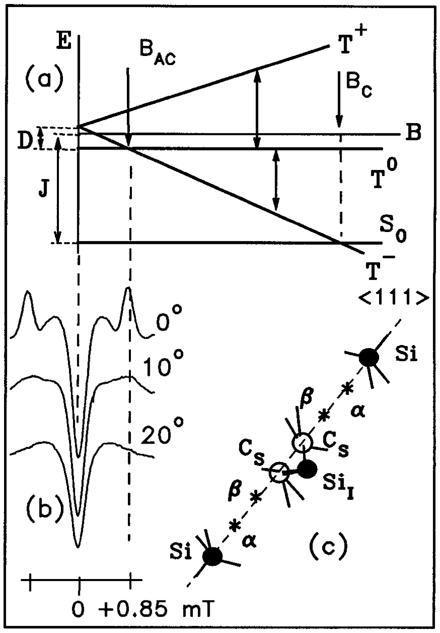

FIG. 4. Energy levels of a system of two electrons in a magnetic field $B \parallel \langle 111 \rangle$ (not to scale) (the arrows show the expected positions of the SDR lines) (a), SDR-induced lines of the microwave photoconductivity recorded in our samples at $T = 125$ K near the zero magnetic field at different angles between B and the $\langle 111 \rangle$ axis (b), and positions of the nearest tetrahedral interstitials α and β in Si lattice near a (C_s-Si_i-C_s) complex along the $\langle 111 \rangle$ axes (c).

This value is too small to explain the angular dependence of the lines at $B = B_C$ [see Figs. 1 and 2(a)] without taking into account the anisotropy of the g factor.

Using the SDR-EPR detection method a new spectrum, labeled Si-WL2, was found in our samples just above 320 mT [see Fig. 3 (traces c–f)]. The observed spectrum is not completely resolved and shows strong angular dependence of the line intensity, so that not all orientations of the defects responsible for it could be traced. This is a common feature of the spectra detected so far by the SDR method for different $S = 1$ centers [6–9]. We attribute this spectrum to the transitions $T^0 \leftrightarrow T^{\pm}$ also predicted by the level schema in Fig. 4(a). The angular dependence of the line position of the Si-WL2 spectrum in Fig. 2(b) corresponds to trigonal symmetry. No hyperfine structure of the spectrum was detected. Its linewidth measured between the maxima of the first derivative lines at $B \parallel \langle 111 \rangle$ is ≈ 0.8 mT in the temperature range of 80–150 K and increases gradually to 1.5 mT between 150–300 K. Below 80 K this spectrum overlaps with other spectra and was not investigated in detail. The traces of the Si-WL2 spectrum at $B \parallel \langle 110 \rangle$ and $B \parallel \langle 100 \rangle$ are shown in Fig. 3 (traces e, f), respectively. For these orientations the line intensities are more than 10 times lower than for $B \parallel \langle 111 \rangle$. The width of the level crossing lines [Fig. 3 (traces a, b)] gradually increases from 1.5 mT at 4–30 K to 4 mT near room temperature.

The angular dependences of the spectra at $B \sim B_C$ and Si-WL2, calculated from the Hamiltonian (1) with the parameters $g_{\parallel} = 2.0027 \pm 0.0002$, $g_{\perp} = 2.0117 \pm 0.0002$, J ($T = 125$ K) $= 16\,570$ MHz, and $D = 23.8$ MHz are shown by solid lines in Fig. 2. The best fits with the experimental data require that J and D have the same sign. If we suppose $J > 0$, corresponding to the ground singlet state, the D constant must also be positive. Because these spectra can be described by the same parameters and are detected in the same temperature region (up to room temperature) we can conclude that they arise from the same defect. It should be noted that the signs of the anticrossing line and the lines of the Si-WL2 spectrum are the same. Both of them correspond to the decrease of the photoconductivity. The lines corresponding to the crossing of the S_0 and T^- levels, shown in Fig. 1 (traces a–d), have the sign which is opposite to that of the Si-WL2 spectrum. This difference is likely to be related to the mechanism of SDR through the excited triplet states and should be investigated in details separately.

The observed spectra of spin dependent change in the microwave photoconductivity of irradiated silicon cannot arise from a close pair of two defects, as was found for phosphorus atoms in heavily doped silicon [11] because the total concentration of defects of different types in Si does not exceed 10^{15} cm^{-3} at the low irradiation dose used. The dose applied to our samples would lead to the average distance of ~1000 Å between the defects. The distance R between the two electron spins responsible for the observed spectra can be estimated from the value of D taking into account the $1/R^3$ dependence of the dipole-dipole interaction and the calculations and experimental data for different $S = 1$ centers summarized in [2,4]. For $D = 23.8$ MHz ($\cong$0.85 mT) we get $R \cong 12.8$ Å.

The symmetry of the spectra and the conditions of their creation and decay allow us to discuss a possible defect model. It was found that the described spectra arise after 1 MeV electron or γ irradiation of very pure (high resistance) FZ silicon. Maximum intensity of the lines is found at the electron irradiation dose $\Phi_e \approx 5 \times 10^{16}$ cm^{-2}. When Φ_e is further increased the intensity starts to decrease. For γ irradiation the line intensity increases in the range of doses from 10^{17} to 5×10^{17} cm^{-3}. The spectra are very sensitive to concentrations of phosphorus and oxygen atoms and are not observed for concentrations of phosphorus higher than 5×10^{13} cm^{-3}. In these samples the spectrum Si-PT3 [8] of the excited triplet states of the phosphorus + vacancy ($\mathrm{P} + V$) complexes is observed. The oxygen also prevents the creation of the spectra. The presence of oxygen atoms in the investigated samples was determined from SDR-EPR spectra Si-SL1 [2] of the excited $S = 1$ state of the $(\mathrm{O} + V)^0$ complexes.

The intensity of the level crossing lines and the Si-WL2 spectrum correlate with the carbon concentration and with the intensity of the Si-PT1 spectrum arising from the excited $S = 1$ state of the carbon-silicon complex $(\mathrm{C}_s\text{-}\mathrm{Si}_I\text{-}\mathrm{C}_s)^0$ [5–7]. These complexes are the dominant defects in the irradiated FZ silicon and the intensity of the Si-PT1 spectrum exceeds 10^2–10^3 times the intensity of the other detected spectra. Isochronal (10 min) annealing experiments show that the spectra described here and the Si-PT1 spectrum disappear in the same temperature range of 270–300 °C.

It can be supposed that in pure silicon two interstitial carbon atoms can be localized near the dominant defect ($\mathrm{C}_s\text{-}\mathrm{Si}_I\text{-}\mathrm{C}_s$) at the nearest tetrahedral interstitial positions along the ⟨111⟩ axes [points α and β in Fig. 4(c)]. It is well established [12] that interstitial C_I atoms produced under irradiation are mobile at room temperature and form stable complexes ($\mathrm{C}_I + \mathrm{C}_S$) [13,14], ($\mathrm{P}_S + \mathrm{C}_I$) [14], and ($\mathrm{O}_I + \mathrm{C}_I$) [15]. The probability of the formation of multiatom complexes is low and perhaps this reflects the low intensity of the observed lines. The presence of the P and O atoms prevents formation of complexes of many C atoms.

In silicon lattice the distance $R(\alpha\text{-}\alpha)$ is 11.75 Å and $R(\beta\text{-}\beta)$ is 7.05 Å. According to estimations [2,4] of the energy of the magnetic dipole-dipole interaction these distances correspond to the D constants (in units of magnetic field) $D_{\alpha\alpha} \approx 1$ mT (in agreement with the experimentally determined value of $D \cong 0.85$ mT) and to $D_{\beta\beta} \approx 5.5$ mT. There is the possibility that C_I atoms occupy β places [see Fig. 4(c)]. Perhaps the weak new spectrum Si-WL4 of trigonal symmetry, shown in Fig. 3(*c*), originates from the $\beta\beta$ configuration. This spectrum is observed in the temperature range of 100–165 K with the angular dependences of the line positions and the line intensity similar to the Si-PT1 spectrum [7], but has a lower D constant (6 mT) which is close to $D_{\beta\beta}$. However, further extensive work is needed to establish the details of the defect model.

To summarize, we have investigated defects produced by irradiation in silicon at concentrations too low to detect them by conventional EPR techniques. Using measurements of spin dependent photoconductivity the magnetic field induced crossing of the ground singlet ($S = 0$) and the excited triplet ($S_z = -1$) levels of a defect in silicon have been observed for the first time. Similarly, a new spectrum, labeled Si-WL2, has been detected by spin dependent recombination EPR measurements. From the angular dependence of the observed spectra, with respect to the applied magnetic field, it is concluded that the defect concerned is oriented along the ⟨111⟩ crystalline axes. From fits of the calculated angular dependences with the experimental data of (i) the T^0/T^- anticrossing, (ii) the S_0/T^- crossing, and (iii) the SDR-EPR transitions $T^0 \leftrightarrow T^{\pm}$, the components of the electron **g** tensor, zero field splitting constant D, and the electron-electron exchange interaction constant J are determined. It is likely that the defect concerned has two additional C_I atoms at tetrahedral interstitial positions along the ⟨111⟩ axes near the ($\mathrm{C}_s\text{-}\mathrm{Si}_I\text{-}\mathrm{C}_s$) complex.

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