Spin-dependent effects due to triplet centers in irradiated silicon

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A study has been made of the optical polarization of nuclei and spin-dependent photoconductivity in silicon crystals containing structural defects which are in excited triplet states when illuminated, with a nonequilibrium distribution of the populations of magnetic sublevels. Mixing of triplet states differing in spin projection is necessary for the onset of an optical polarization of nuclei as the nuclei participate in a hyperfine interaction with the triplet centers. A correlation is found between the angular distribution and the temperature dependence of the intensities of the ESR lines of triplet centers and of the degree of optical polarization of the nuclei. It is shown that the saturation of the ESR transitions of the triplet centers leads to a change in the photoconductivity of silicon crystals. A similar change in photoconductivity is observed at anticrossings of the magnetic sublevels of triplet centers.

1. INTRODUCTION

The irradiation of silicon crystals by high-energy particles gives rise to various structural defects, which may be paramagnetic, depending on their charge state. If the defects contain an even number of electrons, their ground state S_0 will generally be a singlet state with a spin $S = 0$. When the crystal is illuminated, the recombination of the photoexcited carriers may cause the defects to be in an excited triplet state T_1 and to have a spin $S = 1$.

Photoexcited triplet states of defects have several distinguishing features. First, they are metastable and generally have a fairly long lifetime, greater than 10^{-5} s, because the intercombinational transition $T_1 \rightarrow S_0$ is forbidden. In the case of a long lifetime and high light intensity, the steady-state concentration of defects in excited triplet states can be significant, on the order of 10^{11}–10^{13} cm^{-3}. A second distinguishing feature of photoexcited triplet states is the onset of a nonequilibrium population of the magnetic sublevels of the triplet states, with the consequence that some of the ESR lines in the spectra of these centers exhibit an inversion.

Despite the wide variety of defects which are induced in silicon by radiation, optically excited triplet states have been detected by the ESR method only for oxygen + vacancy complexes[1] (the ESR spectrum of Si-*SL* 1) and aluminum + vacancy complexes[2] (the spectrum Si-*G* 9). A method of optical detection of magnetic resonances has made it possible to detect and study the excited triplet state of a defect formed by two carbon atoms and an interstitial silicon atom.[3,4]

If the energy of the $T_1 \rightarrow S_0$ transition is on the order of kT, the triplet states which are excited are attainable thermally, and at a sufficiently high temperature their ESR spectra can be observed even without illuminating the crystal.[5]

The effects of excited triplet states of defects on the various physical properties of silicon and the role which these states play in recombination have not been studied adequately. It has been established that a change in the spin state of triplet centers under magnetic resonance conditions can lead to a change in luminescence intensity.[3,4] The presence in silicon of defects in excited triplet states with a nonequilibrium population of magnetic sublevels during illumination leads to several distinctive features in the optical polarization of nuclei.[6,7] Since the excitation of structural defects into the triplet state results from recombination of photoexcited carriers,[8] one would naturally expect to see effects of spin-dependent recombination, i.e., a resonant change in the photoconductivity of silicon crystals during saturation of ESR transitions of triplet centers. So far, effects of a spin-dependent recombination have been studied for only a limited number of centers in crystalline silicon: surface centers,[9] dislocations in plastically deformed silicon,[10,11] and impurity phosphorus atoms.[12]

In the present paper we report a study of the basic features of the processes of optical polarization of nuclei in silicon containing triplet centers and also effects on spin-dependent recombination which are manifested in ESR experiments.

2. DISTINCTIVE FEATURES OF THE OPTICAL POLARIZATION OF NUCLEI IN SILICON CONTAINING STRUCTURAL DEFECTS

It is well known that ^{29}Si nuclei can be optically polarized only if the silicon contain paramagnetic centers whose spin polarization during the illumination, P_e, differs from the equilibrium Boltzmann value P_{e0} in the magnetic field H_0 at the temperature T. Here the deviation of the average polarization P_n of the nuclei from its equilibrium value P_{n0} is described by[13,14]

$$P_n - P_{n0} = -f\xi(P_e - P_{e0}), \tag{1}$$

where the factor $f \leqslant 1$ describes the leakage of nuclear polarization due to foreign paramagnetic centers in the crystal which do not participate in the nuclear polarization process. The coefficient ξ depends on the electron spin, the nuclear spin, and the nature of the hyperfine interaction between the nuclei and the paramagnetic centers.

In silicon containing paramagnetic centers with spin $S = 1/2$, e.g., neutral phosphorus donor atoms, the spin po-

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larization of these centers can be changed by illuminating the crystal with circularly polarized or unpolarized light in the fundamental absorption region. Nonequilibrium polarization of paramagnetic centers results from the capture of optically oriented photoexcited electrons from the conduction band to donor levels or from the bulk scattering of oriented electrons by paramagnetic centers. The use of circularly polarized light results in a significantly higher degree of optical polarization of nuclei (OPN) than is achieved when the crystal is illuminated with unpolarized light. The reason is that the circularly polarized light makes it possible to make the degree of spin polarization of the photoexcited electrons deviate significantly more from its equilibrium value.

A completely different behavior of the OPN has been observed[6,7] in silicon crystals containing structural defects induced by bombardment with fast electons or neutrons, by heat treatment, or by plastic deformation and also in polycrystalline silicon. In these materials, the degree of OPN does not depend on the polarization of the pump light. A plot of the degree of OPN versus the strength H_0 of the magnetic field in which the illumination is carried out reveals peaks at certain values of H_0, which vary with the type of defect. In several cases, the factors P_n/P_{n0} by which the OPN exceeds its equilibrium value, which are reached during illumination with unpolarized light are greater than the maximum theoretical value $P_n/P_{n0} = 1 - \gamma_e/\gamma_n = -3310$ (γ_e and γ_n are the gyromagnetic ratios of the electron and of the ^{29}Si nucleus, respectively). The amplification P^n/P_{n0} of the nuclear polarization in silicon with structural defects reaches a value of several thousand, and in some samples of plastically deformed silicon a value $P_n/P_{n0} = 5\cdot 10^4$ has been found.

This behavior of the OPN indicates that the silicon crystals contain paramagnetic centers whose spin polarization differs markedly from the equilibrium value during illumination with unpolarized light.

3. OPTICAL POLARIZATION OF ^{29}Si NUCLEI DUE TO TRIPLET CENTERS IN IRRADIATED SILICON

In silicon crystals grown by the Czochralski method with an oxygen concentration $\sim 10^{18}$ cm^{-3}, one of the most abundant defects produced during bombardment with electrons or γ rays is the A-center, which is an oxygen + vacancy complex. In the ESR spectra of these silicon crystals, during illumination with light in their fundamental absorption region, one observes an intense Si-SL 1 spectrum,[1] which corresponds to the excited state of a neutral A-center. Some of the lines of the spectrum are inverted, providing evidence of a nonuniform distribution of the populations of the magnetic sublevels of this center.

Curve 1 in Fig. 1 shows the degree of optical polarization of ^{29}Si nuclei versus the magnetic field H_0 in silicon bombarded with 1-MeV electrons in a dose $\sim 10^{18}$ cm^{-2}. The samples contain triplet Si-SL 1 centers. The degree of OPN is determined from the intensification of the NMR signals of ^{29}Si nuclei after the sample is illuminated with unpolarized light from a 1-kW incadescent lamp at 77 K. Shown for comparison in this figure, by curve 2, is a part of the

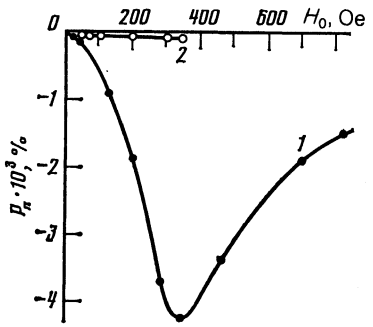

FIG. 1. Degree of optical polarization of ^{29}Si nuclei versus the magnetic field H_0 in silicon. 1—Bombarded with electrons during illumination with unpolarized light; 2—in the same sample, before the electron bombardment, during optical pumping by circularly polarized light.

degree of OPN in the same silicon sample before the electron bombardment; in this case, the sample was illuminated with circularly polarized light. During the illumination of the electron-bombarded silicon crystal with circularly polarized light, the OPN reaches the same values as during illumination with unpolarized light (curve 1). Negative values of P_n in Fig. 1 mean that the direction of the nuclear polarization is opposite the equilibrium direction. The maximum value of the degree of OPN in the bombarded silicon is reached during illumination in a magnetic field $H_0 \approx 350$ Oe, which corresponds to the point where anticrossing of magnetic sublevels of Si-SL 1 centers occur.

To describe the basic features of the OPN which occur in the course of a hyperfine interaction of nuclei with triplet centers, we need to examine the mechanisms which would lead to a nonequilibrium distribution of the populations of the magnetic sublevels of the triplet centers. We also need to examine the behavior of the degree of polarization P_e of the triplet centers in various magnetic fields. We can write the Hamiltonian of centers with spin $S = 1$ as

$$\mathcal{H} = g\beta \mathbf{H}_0 \mathbf{S} + D(S_z^2 - {}^1/_3 S^2) + E(S_x^2 - S_y^2). \qquad (2)$$

The parameters D and E describe the level splitting in a zero magnetic field due to (for example) the dipole-dipole interaction of two electrons which are localized at a center and which form a total spin $S = 1$. For the Si-SL 1 center, we have $D = -328.7\cdot 10^{-4}$ cm^{-1} and $E = 7.2\cdot 10^{-4}$ cm^{-1}.

Figure 2 shows the energies of three states of an Si-SL 1 center (W_1, W_2, and W_3) versus the magnetic field strength H_0 for the case in which the field H_0 deviates slightly (by an angle θ) from the symmetry axis of the center, $Z \| \langle 110 \rangle$. In the simplest case, in which the center is axisymmetric, and we have $E = 0$ and $H_0 \| Z$, the wave functions which are eigenfunctions of $\mathcal{H}$ are the eigenfunctions of the operator S: $|+1\rangle$, $|0\rangle$ and $|-1\rangle$. If H_0 is not parallel to the Z axis, these states become mixed, and at small values of θ the wave functions can be written as follows to within an accuracy sufficient for our purposes:

$$\varphi_1 = c_1|+1\rangle + c_2|0\rangle, \quad \varphi_2 = c_3|+1\rangle + c_4|0\rangle, \quad \varphi_3 = |-1\rangle. \qquad (3)$$

In this case, the eigenvalues of the Hamiltonian $\mathcal{H}$ (W_1, W_2, and W_3) and also the coefficients c_{1-4} are determined by

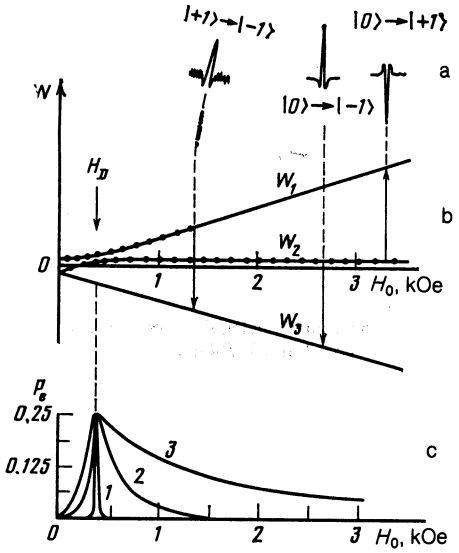

FIG. 2. a—ESR signals from Si-*SL* 1 centers; b—energy-level diagram of these centers in a magnetic field; c—degree of polarization of the Si-*SL* 1 centers, P_e, vers H_0. 1($\theta = 1°$; 2) 5°; 3) 10°.

solving the second-order secular equation. For the energy of the magnetic sublevels of the triplet centers, W_{1-3}, and for the mixing coefficients c_{1-4} we find

$$W_{1,2} = \frac{g\beta}{2}\left\{\frac{H_D}{3} + H_0 \pm [(H_0 - H_D)^2 + 2H_0^2 \sin^2\theta]^{1/2}\right\},$$

$$W_3 = -g\beta(H_D/3 + H_0), \quad |c_1|^2 = |c_4|^2, \quad |c_2|^2 = |c_3|^2, \tag{4}$$

$$|c_{1,2}|^2 = {}^1/_2 \pm {}^1/_2 (H_0 - H_D) \times [(H_0 - H_D)^2 + 2H_0^2 \sin^2\theta]^{-1/2}. \tag{5}$$

Here H_D is the magnetic field corresponding to the point where anticrossing of magnetic sublevels occurs; its value is $H_D = |D|/g\beta \approx 350$ Oe for Si-*SL* 1 centers.

The degree of spin polarization P_e of the triplet centers can be found from

$$P_e = \sum_{i=1}^{3} \mu_i N_i \Big/ \Big[g\beta \sum_{i=1}^{3} N_i \Big], \quad \mu_i = dW_i/dH_0, \tag{6}$$

where N_1, N_2, and N_3 are the populations of the states φ_1, φ_2, and φ_3, respectively. Using the expressions (4) for c_{1-4}, and ignoring the small terms containing $\sin^2\theta$, we find the following expression for P_e:

$$P_e = \frac{N_1 - N_2}{N_1 + N_2 + N_3}|c_1|^2 + \frac{N_2 - N_3}{N_1 + N_2 + N_3}. \tag{7}$$

We turn now to the processes which give rise to the excited triplet states and to their acquisition of a nonequilibrium spin polarization. Neutral *A*-centers in the excited triplet state, A^{0*}, appear when an electron-bombarded silicon crystal is illuminated with light in its fundamental absorption region, as a result of the successive capture of photoexcited electrons (e) and holes (h) in accordance with the schemes

$$A^0 + \begin{cases} e \to A^- + h \searrow \\ h \to A^+ + e \nearrow \end{cases} A^{0*} \xrightarrow{R} A^0. \tag{8}$$

Here A^0, A^-, and A^+ are the various charge states of the *A*-center.

As we mentioned in the Introduction, the intercombinational transition $A^{0*} \to A^0$ (or $T_1 \to S_0$) is forbidden. However, the spin-orbit interaction causes a mixing of the state S_0 with the states φ_1, φ_2, and φ_3; consequently, transitions of this type become possible. Their probabilities are different for the different spin states of the triplet; i.e., these transitions are spin-selective.[15,16] As was shown in Ref. 8, these are the transitions which are responsible for the appearance of a nonequilibrium distribution of the populations of the magnetic sublevels of triplet *A*-centers (Si-*SL* 1 centers) and for the inversion of the lines in their ESR spectrum (Fig. 2a). For the populations of the magnetic sublevels of the triplet centers (n^+, n^0, and n^-) in a strong magnetic field, in which case the states φ_1, φ_2, and φ_3 are "pure," we can write the following simple kinetic equations:

$$\begin{aligned} \dot{n}^+ &\to \Gamma^+ - n^+R^+ - (n^+ - n^0)W, \\ \dot{n}^0 &= \Gamma^0 - n^0R^0 - (2n^0 - n^+ - n^-)W, \\ \dot{n}^- &= \Gamma^- - n^-R^- - (n^- - n^0)W, \end{aligned} \tag{9}$$

where Γ^+, Γ^0, and Γ^- are the rates at which triplet centers are produced in the states $|+1\rangle$, $|0\rangle$ and $|-1\rangle$, respectively; R^+, R^0, and R^- are the probabilities for transitions per unit time from these states to the singlet ground state; and W is the probability for the relaxation transitions $|+1\rangle \leftrightarrow |0\rangle$ and $|-1\rangle \leftrightarrow |0\rangle$. Here we are ignoring the Boltzmann polarization and the relaxation transitions $|+1\rangle \leftrightarrow |-1\rangle$. If the magnetic field H_0 makes a small angle θ with the Z axis (the axis of the center), the populations n^+, n^0, and n^- are related to N_1, N_2, and N_3 by

$$N_1 = n^+|c_1|^2 + n^0|c_2|^2, \quad N_2 = n^0|c_1|^2 + n^+|c_2|^2, \quad N_3 = n^-. \tag{10}$$

In the case in which we have $\Gamma^+ = \Gamma^0 = \Gamma^- = \Gamma$ and $R^+ = R^- = R \neq R^0$, as we do in the case of Si-*SL* 1 centers,[8] we find from (9) the steady-state population values

$$n^+ = n^- = \frac{R^0 + 3W}{RR^0 + R^0W + 2RW}\Gamma, \quad n^0 = \frac{R + 3W}{RR^0 + R^0W + 2RW}\Gamma. \tag{11}$$

Using these expressions along with (7) and (10), we find the degree of polarization of the triplet centers to be

$$P_e = 2|c_1|^2|c_2|^2\mathscr{P}_{max}\frac{2R^0 + R}{2R^0 + R + 9W}, \tag{12}$$

where $\mathscr{P}_{max} = (R^0 - R)/(2R^0 + R)$ is the maximum polarization between the $+1\rangle$ and $0\rangle$ levels which is reached during illumination in a strong magnetic field in the absence

of relaxation ($W=0$). From (11) we can also find an expression for the intensities of the ESR lines, $I_1 = n^+ - n^0$ and $I_2 = n^0 - n^-$:

$$I_1 = -I_2 = \Gamma \frac{R^0 - R}{RR^0 + R^0 W + 2RW}. \quad (13)$$

It can be seen from expression (12) that the behavior of P_e as a function of the magnetic field H_0 is determined entirely by the H_0 dependence of the mixing coefficients $c_{1,2}$. Figure 2c shows the dependence $P_e \sim |c_1|^2|c_2|^2$ calculated from (12) for various values of the angle θ. We see that the maximum values of P_e are reached at $H_0 = H_D$, where mixing of the $|+1\rangle$ and $|0\rangle$ states occur. The mixing of states has the further consequence that in magnetic fields $H_0 > H_D$ the level W_1 is found to be populated to a greater extent than W_3 is. It therefore becomes possible to observe "forbidden" transitions between these levels, transitions with "$\Delta m = \pm 2$." As can be seen from Fig. 2a, the ESR line of these transitions is inverted and corresponds to the emission of microwave power.

The degree of OPN, P_n, should reflect the behavior of the degree of polarization of the triplet centers, according to expression (1). Taking into account the equilibrium Boltzmann polarization of the triplet centers, we easily find the following result from the relations derived here for P_e:

$$P_n - P_{n0} = -f\xi(2\mathscr{P}_{max}|c_1|^2|c_2|^2 - P_{10}|c_1|^2 - P_{20}) \frac{2R^0 + R}{2R^0 + R + 9W}. \quad (14)$$

Here

$$P_{10} = \frac{N_1^0 - N_2^0}{N_1^0 + N_2^0 + N_3^0}, \quad P_{20} = \frac{N_2^0 - N_3^0}{N_1^0 + N_2^0 + N_3^0},$$

where N_1^0, N_2^0, and N_3^0 are the equilibrium populations of the levels W_1, W_2, and W_3.

In the case of an isotropic hyperfine interaction between triplet centers and nuclei and with short correlation times for the random field of the electrons at the nuclei, the quantity ξ is essentially independent of the magnetic field.[6] The plot of P_n versus H_0, like that of P_e versus H_0, has an extremum at $H_0 = H_D$. If the crystal contains various triplet centers with different constants D, the H_0 dependence of P_n will have several extrema, corresponding to anticrossings of levels for each type of center. Figure 3 shows P_n versus H_0 in an electron-bombarded silicon crystal in which ESR measurements have revealed Si-*SL* 1 and Si-*P* 4 centers. The latter consist of an excited triplet state of a complex of three vacancies + oxygen,[5] with a level anticrossing at $H_D \approx 40$ Oe. The apparent reason for the opposite direction of the nuclear polarization due to the Si-*P* 4 centers is that the constant D of the centers has the other sign.

It follows from expressions (13) and (14) that P_n, the degree of OPN, and the intensity of the ESR lines of triplet centers should depend on the spin relaxation rate W, which can be reduced by reducing the temperature of the sample.[8] Experimentally, there is good agreement between the temperature dependence of the intensity of the ESR lines of the Si-*SL* 1 centers and the degree of OPN due to these centers.

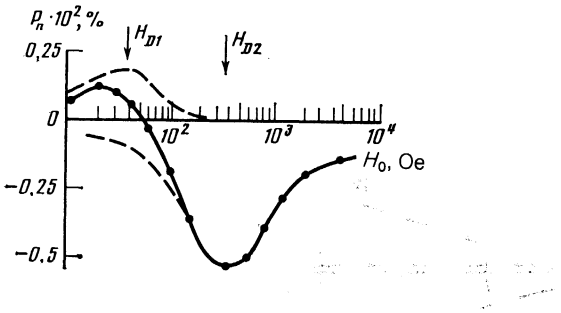

FIG. 3. Degree of optical polarization of nuclei, P_n, versus H_0 in electron-bombarded silicon containing Si-*SL* 1 and Si-*P* 4 centers.

These results are shown in Fig. 4. This behavior as a function of the temperature also shows that as the temperature is lowered from 77 to 20 K it is possible to increase the degree of optical polarization of the ^{29}Si nuclei by an order of magnitude.

We now consider the angular dependence of the degree of OPN due to triplet centers. It follows from expression (5) and (14) that the coefficients $c_{1,2}$ and P_n depend on θ, the angle between the magnetic field and the axis of the center, the Z axis. In silicon crystals containing triplet Si-*SL* 1 centers, however, one observes a very weak change in the degree of OPN as the magnetic field H_0 is rotated in the {110} plane of the crystal (Fig. 5a). The reason is that the silicon lattice contains six equivalent ⟨110⟩ directions, along which the Z axes of the *A*-centers can be oriented with equal probabilities. Since all of the defects oriented along the different directions contribute to the polarization, the polarization of the nuclei of the entire volume of the crystal will be averaged over the various orientations of the defects with respect to the direction of the magnetic field. The angular dependence of the degree of polarization in Fig. 5a correlates well with the angular dependence of the intensity of the line of forbidden transitions "$\Delta m = \pm 2$," shown in Fig. 5b. The position of this line in the ESR spectrum of the Si-*SL* 1 centers (Fig. 2a) is essentially independent of the orientation of the crystal in the magnetic field, and all six different orientations of the defects contribute to its intensity. The intensity of this line reflects the magnitude of the polarization of the excited triplet states of all of the *A*-centers in the crystal, so that one should observe a correlation between the angular dependence of the intensity of this line and the angular dependence of the degree of OPN of the ^{29}Si.

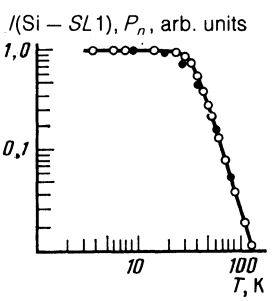

FIG. 4. Intensity of the ESR lines of Si-*SL* 1 centers (○) and degree of polarization of ^{29}Si nuclei, P_n (●), versus the temperature T.

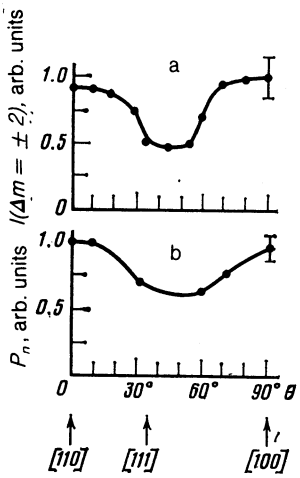

FIG. 5. Angular dependence of the intensity of the lines of "forbidden" ($\Delta m = 2$) transitions of Si-*SL* 1 centers (a) and degree of optical polarization of the nuclei, P_n (b).

A pronounced anisotropy of the onset of OPN has been observed in pure silicon crystals grown by float zoning, with an oxygen concentration less than 10^{16} cm^{-3}. After these crystals are bombarded with electrons and γ rays, one observes new triplet centers, designated as Si-*PT* 1 centers, in these crystals. The symmetry axis (the Z axis) of these centers runs along the ⟨111⟩ axis of the crystal. A deviation of the magnetic field from the ⟨111⟩ axis gives rise to a decrease in the amplitude of the ESR lines of the Si-*PT* 1 centers. Figure 6a shows the angular dependence of the amplitude of the lines of the spectrum. The Si-*PT* 1 centers have a constant $D = 402 \cdot 10^{-4}$ cm^{-1}, which corresponds to a level anticrossing point (at $E = 0$) $H_D \approx 430$ Oe. Figure 6b shows the angular dependence of the degree of optical polarization of the ^{29}Si nuclei which occurs in a silicon crystal containing Si-*PT* 1 centers, for various orientations of the external magnetic field H_0 in which the crystal is illuminated. This dependence is M-shaped and is described well by the relations derived above. At $H_0 \gtrsim H_D$, if the magnetic field is

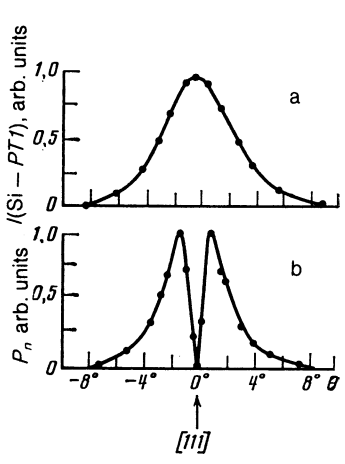

FIG. 6. Intensity of the lines of the Si-*PT* 1 spectrum (a) and degree of optical polarization of nuclei, P_n (b), versus the angle (θ) between the magnetic field and the ⟨111⟩ axis of the crystal at $H_0 \simeq 500$ Oe.

directed precisely along the axis of the center ($\theta = 0$), the states φ_1, φ_2, and φ_3 are pure ($|c_2|^2 = 0$), and the nuclei do not become polarized, as follows from expression (14). Even a small deviation of H_0 from the ⟨111⟩ axis, however, causes mixing of the $|+1\rangle$ and $|0\rangle$ states. In this case we have $|c_2|^2 \neq 0$, and a nuclear polarization appears. It initially increases with increasing angle θ and then decreases, reproducing the curve of the decay of the ESR signal amplitude.

In summary, these experimental results confirm the interpretation of the optical polarization of nuclei through excited triplet states of defects in silicon which was offered above. Theoretically, the maximum value of the degree of OPN which can be achieved during illumination with unpolarized light in silicon with triplet centers is 50%, while this value would be 25% in silicon containing centers with spin $S = 1/2$, during illumination with circularly polarized light.

4. SPIN-DEPENDENT PHOTOCONDUCTIVITY AND ESR IN IRRADIATED SILICON

As was mentioned above, the triplet centers appear during the successive capture of photoexcited electrons and holes according to the schemes (8). The defects in the excited triplet state may be thought of as intermediate centers which are formed in the course of the recombination of photoexcited carriers. Weakly bound electron-hole pairs in a triplet state were suggested in Ref. 17 in an effort to explain the effects of spin-dependent recombination in semiconductors. In the schemes (8), the last recombination event is a transition of the defect from a triplet excited state to the singlet ground state. In this case the saturation of the ESR transitions of the triplet centers by the alternating resonant magnetic field H_1 should change the rate of triplet-singlet transitions and thus the rate at which electrons and holes recombine.

If the number of transitions from the triplet excited state to the singlet ground state increases when the resonant field H_1 is imposed, the steady-state concentration of triplet centers, $N_T = n^+ + n^0 + n^-$, should decrease. At a constant light intensity, this effect will increase the concentration of centers in the ground state and increase the rate of recombination of photoexcited carriers. In other words, when the ESR transitions of the triplet centers saturate, the photoconductivity of the crystal should decrease.

From equations (9) we can find the steady-state concentration of triplet centers in the absence of the alternating field H_1:

$$N_T(H_1=0) = \Gamma \frac{R+2R^0+9W}{RR^0+R^0W+2RW}. \tag{15}$$

When the field H_1, which corresponds to transitions between the sublevels $|+1\rangle$ and $|0\rangle$, is turned on, we should add to Eq. (9) terms describing these transitions, with a probability W_1:

$$\begin{aligned} \dot{n}^+ &= \Gamma - n^+R - (n^+ - n^0)(W+W_1), \\ \dot{n}^0 &= \Gamma - n^0R^0 - (2n^0 - n^+ - n^-)W - (n^0 - n^+)W_1, \\ \dot{n}^- &= \Gamma - n^-R - (n^- - n^0)W. \end{aligned} \tag{16}$$

From these equations we find an expression for the con-

centration of triplet centers. In the case of a strong alternating field H_1, with $W_1 \gg W$, R, and R^0, we find

$$N_T(H_1)=\Gamma\frac{5R+R^0+9W}{RR^0+R^0W+2RW+R^2}. \quad (17)$$

For the change in the concentration of triplet centers when the ESR transition saturates, we find from (15) and (17)

$$\Delta N_T=N_T(H_1)-N_T(0)$$

$$=-\Gamma\frac{(R+W)(R-R^0)^2}{(RR^0+R^0W+2RW)(R^2+RR^0+R^0W+2RW)}. \quad (18)$$

From this expression we see that the relation $\Delta N_T<0$; consequently, as we mentioned earlier, there should be a decrease in the photoconductivity of the sample at the resonance. The saturation of the $|0\rangle\leftrightarrow|-1\rangle$ transition leads to the same result for ΔN_T. It follows that in measurement of the ESR spectra of triplet centers on the basis of the change in the photoconductivity of the crystal, the lines corresponding to the transitions $|+1\rangle\leftrightarrow|0\rangle$ and $|0\rangle\leftrightarrow|-1\rangle$ will have the same sign, while these signs would be different for ordinary ESR lines.

It also follows from the relations derived here that the photoconductivity of crystals containing triplet centers should change when the magnetic field changes at the anticrossings of the magnetic sublevels of the triplet centers. From (9), using (10) for N_T, assuming the case $H_0=H_D$, and assuming that the magnetic field is oriented precisely along the axis of the defect (the Z axis), in which case we have $|c_1|^2=|c_2|^2=1/2$, we find the expression

$$N_T(H_0=H_D)=\Gamma\frac{5R+R^0+9W}{RR^0+R^0W+2RW+R^2}, \quad (19)$$

which is the same as (17). For the change in the concentration of triplet centers during the scanning of the magnetic field near the value $H_0=H_D$ we find an expression identical with (18). Consequently, in silicon crystals containing triplet centers one should see a change in the photoconductivity when the ESR transitions of the centers saturate and also a change in the photoconductivity at the anticrossings of the magnetic sublevels without the imposition of an alternating magnetic field. Such effects have in fact been observed in irradiated silicon crystals.[18,19]

In conventional experiments on spin-dependent recombination, the signals reflecting the change in the photoconductivity at saturation of ESR transitions are measured by measuring the photocurrent through the sample by means of contacts. Under conditions such that the silicon crystal, held in the resonator of the ESR spectrometer, is illuminated with light in its fundamental absorption region, the resonator of the ESR spectrometer "senses" not only the absorption of the microwave power by the paramagnetic centers but also the change in the concentration of photoexcited carriers. If the concentration of paramagnetic centers is low, on the order of 10^{12}–10^{13} cm^{-3}, the change in the quality factor of the resonator is caused primarily by a change in the photoconductivity of the sample at resonance. The sign of the signals detected by the ESR spectrometer will depend on whether there is a resonant increase or decrease in the rate of recombination of photoexcited carriers. An ordinary ESR spectrometer can thus be used to detect effects of spin-dependent recombination in semiconductors without using contacts and to detect ESR signals from paramagnetic recombination centers, whose concentration is extremely low in ordinary ESR measurements.

Figure 7 shows ESR spectra detected from the change in the quality factor of the resonator of an ESR spectrometer due to the change in the photoconductivity of silicon sam-

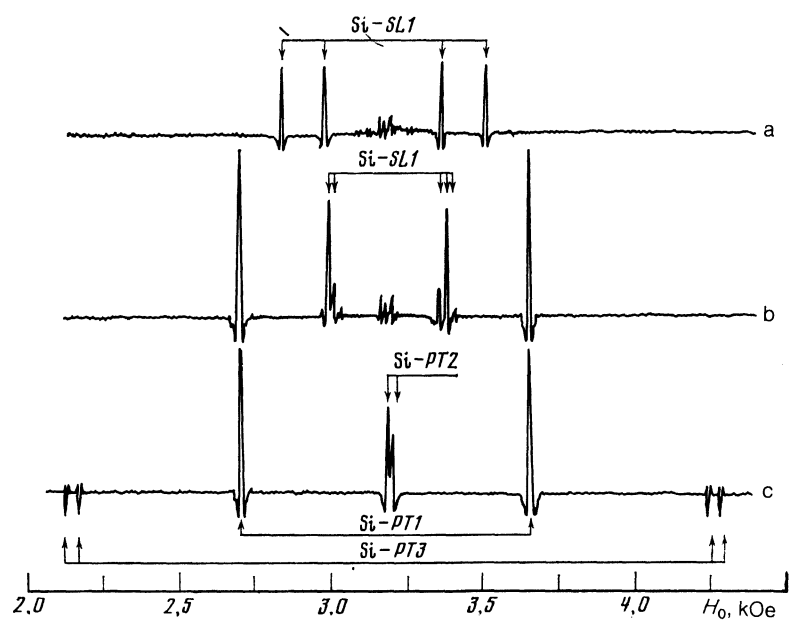

FIG. 7. ESR spectra measured from the change in the photoconductivity of silicon crystals irradiated with γ rays (the notation is explained in the text proper). a—The field H_0 is directed along the ⟨110⟩ axis; b, c—the ⟨111⟩ axis. The frequency is $\gamma_0=9.124$ GHz.

ples bombarded with small doses of γ rays. The spectrum in Fig. 7a was obtained in n-type silicon containing oxygen, bombarded with a dose of $5\cdot10^{13}$ γ rays/cm^2. In the case $H_0\|\langle110\rangle$ we see the familiar Si-*SL* 1 spectrum, but all the lines of this spectrum have an identical phase, corresponding to an increase in the quality factor of the resonator. In the case $H_0\|\langle111\rangle$ (Fig. 7b), a new spectrum, Si-*PT* 1, is observed in this sample. At the center of the spectrum we also observe ESR lines from phosphorus atoms and from other radiation defects with spin $S = 1/2$. In pure silicon grown by float zoning with a phosphorus concentration of $2\cdot10^{13}$ cm^{-3}, after bombardment with γ rays in a dose of $5\cdot10^{14}$ cm^{-2}, we observe the Si-*PT* 1 spectrum and also a spectrum of triplet centers (Si-*PT* 3) and a spectrum of Si-*PT* 2 centers with spin 1/2 (Fig. 7c). These spectra were recorded with a 3-cm-range ESR spectrometer. In the measurements of the spectra, the spectrometer was adjusted to record the second derivative of tthe absorption line. The samples were illuminated with light from a 100-W incandescent lamp. It was found that the amplitude of the ESR lines increases linearly with increasing light intensity. The maximum intensity in the spectra is reached at temperatures in the interval 25–30 K.

The parameters of the new spectra of triplet centers observed by this new procedure, Si-*PT* 1 and Si-*PT* 3, are described in detail in Refs. 18 and 20. The Si-*PT* 3 spectrum arises from *E*-centers (phosphorus + vacancy complexes) in an excited triplet state. It can be seen from Figs. 7c that the lines of this spectrum have a phase corresponding to a decrease in the quality factor of the resonator, i.e., to a decrease in the rate of recombination of photoexcited carriers. This result can be explained on the basis that the *E* centers in this state are charged, in contrast with the *A*-centers, which are neutral in the excited triplet state. In the case of the charged centers, the capture of carriers would be more effective. Consequently, when the triplet centers are themselves carrier-capture centers the decrease in the concentration of triplet centers when their ESR transitions saturate may lead to a decrease in the recombination rate of photoexcited carriers.

When the silicon crystals are bombarded with γ rays, the rate at which radiation defects are produced is 10^{-2}–10^{-3} cm^{-1}. Accordingly, at irradiation doses of 10^{13}–10^{14} cm^{-2} the concentration of defects in the crystals is on the order of 10^{10}–10^{12} cm^{-3}, and the relative number of these defects which are in excited triplet states is on the order of 10^{-2}. The sensitivity of the ESR method making use of spin-dependent recombination effects is thus several orders of magnitude higher than the sensitivity of the ordinary ESR method, which makes it possible to observe the ESR signals from radiation defects in silicon after bombardment with far greater doses, e.g., more than 10^{17} cm^{-2} in the case of γ rays.

Figure 8 shows the intensity of the Si-*SL* 1 and Si-*PT* 1 spectra versus the irradiation dose. We see that these spectra initially intensify with increasing dose and then fade. The decrease in the intensity of the spectra is due not to the decrease in the concentration of defects but to a decrease in the sensitivity of the detection method. The increase in the concentration of defects with increasing dose leads to an in-

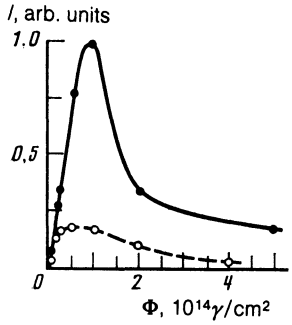

FIG. 8. ●—Intensity of the Si-*PT* 1 spectra; ○—intensity of the Si-*SL* 1 spectra versus the irradiation dose Φ.

crease in the rate of recombination of photoexcited carriers, shortening of the lifetime of these carriers, and therefore a decrease in their steady-state concentration. As a result, the sensitivity of the resonator of the spectrometer decreases and the photoconductivity of the crystal changes.

As we mentioned earlier, in silicon crystals containing triplet centers one should observe a change in the photoconductivity at values of the magnetic field corresponding to anticrossing points of the magnetic sublevels of triplet centers. Figure 9 shows this change in the photoconductivity in silicon containing Si-*SL* 1 centers, which have an anticrossing point $H_0 = H_D = 352$ Oe. When the magnetic field is oriented exactly along the axis of the center, $Z\|\langle110\rangle$, we see a narrow line (Fig. 9a). This line becomes broader when H_0 is turned slightly away from the $\langle110\rangle$ axis (Figs. 9b and 9c).

When the magnetic field is oriented along the $\langle111\rangle$ axis of the crystal, we observe the photoconductivity to vary along a line corressponding to an anticrossing point of levels of Si-*PT* 1 centers (Fig. 10). In the temperature interval 10–30 K, the position of this line corresponds to $H_0 = 387.6$ Oe.

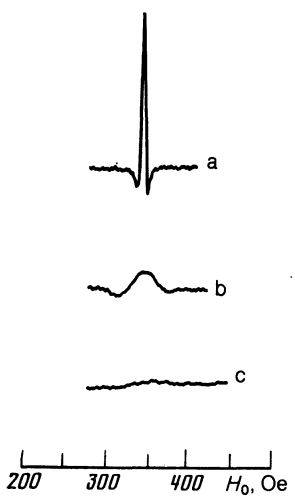

FIG. 9. Change in the photoconductivity of a γ-irradiated silicon crystal as the magnetic field strength H_0 is varied. a—$H_0\|\langle110\rangle$; b—$\theta = 0.5°$; c—$\theta = 2.5°$ (θ is the angle between H_0 and the $\langle110\rangle$ axis).

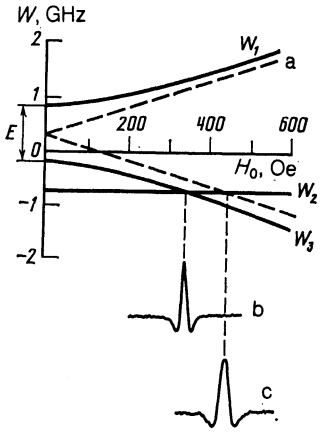

FIG. 10. a—Energy-level diagram of the Si-*PT* 1 center; b—signal showing the change in the photoconductivity at $T = 25$ K; c—the same, at 80 K.

As the temperature is raised from 30 to 60 K, the line shifts into stronger fields, and for $T > 60$ K its position is $H_0 = 430$ Oe. This change in the position of the line can be attributed to a temperature-induced change in the constant E of the Si-*PT* 1 centers. At $E \neq 0$, the position of the level anticrossing point is determined from the relation $H_{ac} = (D^2 - E^2)^{1/2}/g\beta$. The constant D can be determined from the splitting of the lines of the Si-*PT* 1 spectrum (Figs. 7b and 7c); in the case $H_0 \| \langle 111 \rangle$ this splitting is 858.7 Oe and corresponds to $D = 400.7 \cdot 10^{-4}$ cm^{-1}. From the value $H_0 = H_{ac} = 387.6$ Oe we find $E = 171.1 \cdot 10^{-4}$ cm^{-1}. At temperatures $T > 60$ K the position of the level anticrossing point corresponds to $E = 0$. Since the parameter E is a measure of the deviation of the symmetry of the center from axial symmetry, it can be concluded from these results that there is a change in the symmetry of the Si-*PT* 1 center as the temperature is changed.

At present we have no model for the Si-*PT* 1 center, but the intensity of the components of the hyperfine structure of this spectrum, due to the interaction with ^{29}Si nuclei, shows that the defect contains a single silicon nucleus. It can therefore be suggested that this defect is an interstitial silicon atom on a bond oriented along the $\langle 111 \rangle$ direction of the crystal. A deviation of the center from axial symmetry may be caused by a slight displacement of this atom from the axis of the bond. In this case, the change in the symmetry with increasing temperature may be due to rotation of the interstitial atom around the $\langle 111 \rangle$ axis. For triplet Si-*SL* 1 centers, the temperature dependence of the position of the line corresponding to the anticrossing point of the levels of the center has not been observed.

These results show that the effects of a spin-dependent photoconductivity can be exploited in the ESR spectroscopy of silicon crystals to study structural defects, especially if these defects have a low concentration. The model of spin-dependent recombination which we have been discussing here, involving a change in the number of triplet-singlet ($T_1 \rightarrow S_0$) transitions at a magnetic resonance or at anticrossings of magnetic sublevels of triplet centers, gives a qualitatively good description of the experimental results. The same processes are probably responsible for the change in the luminescence intensity at saturation of ESR transitions and at the level anticrossings which has been observed in silicon carbide crystals by the technique of optical detection of magnetic resonance.[21]

5. CONCLUSION

These studies have shown that the presence of structural defects in excited triplet states with a nonequilibrium spin polarization during illumination in silicon crystals leads to the appearance of a strong dynamic polarization of lattice nuclei. The nonequilibrium population distribution among the magnetic sublevels of the triplet centers is a result of spin-selective transitions from an excited triplet state to the ground singlet state.

It has been shown experimentally that the saturation of ESR transitions of triplet centers leads to a change in the photoconductivity of silicon crystals and to effects of a change in the photoconductivity at anticrossings of the magnetic sublevels of the triplet centers.

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