Correlations in distributions of donor and acceptor impurities in silicon

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The method of optical polarization of nuclear moments (OPNM) is used to find correlations in the distributions of shallow donor and deep-lying acceptor impurities in silicon single crystals. The behavior of shallow group-V donor impurities and of gold impurities, which form donor and acceptor levels in the forbidden band of silicon, were investigated. Also studied were the kinetics of the changes of the densities of the various components in a decaying solid solution of gold in silicon. It is shown that the electric properties and the thermal stability of silicon single crystals are determined by the presence of donor-acceptor pairs. A new mechanism was discovered of spin-lattice relaxation of a deep paramagnetic center in a semiconductor, due to exchange interaction with an electron trapped by a shallow donor center. This interaction is modulated at 77 K by thermal electron transitions between shallow donor levels and the conduction band. It is shown that a bottleneck exists in the described mechanism of the electron spin-lattice relaxation. The OPNM method yielded the distribution of the gold donor center density as a function of the electron spin-lattice-relaxation time; this distribution reduces to a distribution with respect to the distance between the components of the electron-acceptor pair. It is shown that the distribution obtained differs strongly from the random distribution of the donor and acceptor impurities in a silicon crystal.

Investigations of the optical polarization of nuclear moments (DPNM) in semiconductors have shown that its onset is due to the presence of impurity centers or lattice defects that in a nonequilibrium spin state under conditions of optical pumping.[1–4]

Nonequilibrium polarization of paramagnetic impurity centers sets in when photoexcited electrons that are nonequilibrium in spin are captured from the conduction band.[1)] Under optical conditions there exist two possibilities of producing a nonequilibrium spin system of electrons:

1. Irradiating the semiconductor by circularly polarized light in a maximum magnetic field.

2. Irradiating the semiconductor by unpolarized light in a magnetic field of arbitrary orientation. In this case an equal number of electrons with spin $+1/2$ and $-1/2$ are excited into the conduction band, so that the degree of polarization of the photoexcited electrons in the conduction band is zero. The equilibrium Boltzmann value of the projection of the electron spin n a magnetic field differs then from zero.

Optical pumping is more effective by circularly polarized than by unpolarized light, for in the former case one can produce a considerably larger deviation of the degree of polarization of the photoexcited electrons from its equilibrium Boltzmann value.[2)] It must be noted that the electron system nonequilibrium in spin can be produced both in interband and in impurity absorption of light.[8]

The hyperfine interaction between paramagnetic centers in a non-equilibrium state and the surrounding lattice nuclei polarizes the latter strongly.[1–4]

The polarization of the lattice impurity centers propagates into the entire volume of the crystal by diffusion of the nuclear spin.[2,9,10] The magnitude and direction of the OPNM in the crystal volume, recorded by determining the gain and phase of NMR signals, are determined by the characteristics of the impurity centers[1–4] (by impurity-level energy in the forbidden band, by the density, degree of compensation, homogeneity of the distribution, and others). Thus, in semiconductors containing shallow impurity-center donors, the OMNM is due to contact hyperfine interaction due to the nonzero density of the wave function of the impurity electron at the surrounding lattice nuclei. In semiconductors doped with deep-level impurities in the forbidden band, dipole-dipole hyperfine interaction predominates in the OPNM and leads to an opposite direction of the nuclear magnetization compared with the contact interaction.[1–4,8] Study of the hyperfine-interaction mechanisms permitted OPNM to be used to determine the fluctuations of the energy of the impurity levels in the forbidden band[11] and of the densities of the impurities of various kinds, which are simultaneously present in silicon single crystals[12] as well as to solve various problems dealing with decay and stabilization of solid solutions of impurities in semiconductors.[11,13,14] It must be noted that OPNM can be used to investigate the behavior of impurity centers in silicon crystals of large volume,[15] owing to the weak wavelength dependence of the coefficient of interband-light absorption.

One of the most interesting problems in the application of the OPNM technique is the investigation of the correlations in the distributions of donor and acceptor impurities in semiconductors, which practically always occur in the various methods of single-crystal doping. We demonstrate this in this paper using as the example investigations of the electron and nuclear spin-lattice relaxations by the OPNM in silicon containing group-V and gold donor centers.

EXPERIMENTAL PROCEDURE

Silicon single crystals containing group-V impurities (phosphorus, arsenic, bismuth) were doped with gold by high-temperature diffusion followed by quenching. The to-

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tal gold density was measured by neutron-activation analysis. To study the correlations in the distributions of the group-V impurities and of gold in silicon single crystals, stepwise annealing was carried out at $T = 500$ C. After each annealing step, the OPNM method was used to determine the densities of the various components of the solid solution of gold in the silicon.

The OPNM procedure is described in sufficient detail in Refs. 1–4, 13, and 15. We shall dwell briefly only on the principal features of the experiment. The samples were irradiated at $T = 77$ K by circularly polarized light from a 1-kW incandescent lamp in a longitudinal magnetic field whose strength was varied from 0.1 to 200 Oe. The duration of the irradiation after different successive annealing steps ranged from several minutes to tens of hours. After the irradiation, the samples were transferred to the magnet of an NMR radiospectrometer, where the magnetization of the ^{29}Si nuclei was determined from the phase and gain of the NMR signals recorded by the fast adiabatic passage method. In the course of the experiments in different magnetic fields and at various pump-light intensities we recorded exponential dependences of the degree of *pn* OPNM of ^{29}Si on the crystal irradiation time:

$$p_n(t) = P_{nm}(1-\exp(-t/T_1)).$$

These relations were used to determine the maximum OPNM degree P_{nm}, its direction, and the time of the nuclear spin-lattice relaxation with account taken of the diffusion of the nuclear spin T^1 determined by the impurity and defect densities in the lattice.

EXPERIMENTAL RESULTS

Figure 1 shows the experimental dependences of the OPNM degree and of the spin-lattice relaxation time of ^{29}Si nuclei on the magnetic field in which silicon doped with group-V impurities and with gold was optically pumped. Contributions to the OPNM are made both by contact interaction of the ^{29}Si nuclei with the electrons trapped by shallow group-V donor centers (region of positive values of P_{nm}) and by dipole-dipole hyperfine interaction of gold deep donor centers (eV + 0.35 eV) with the surrounding ^{29}Si nuclei (region of negative values of P_{nm}).

The dependences of P_{nm} and T_1 prior to annealing (curves 1 in Fig. 1) are determined mainly by spin-lattice relaxation of the ^{29}Si nuclei on the gold donor centers ($H_0' = 1/\gamma_e\tau_s$). An intensive contribution to these processes are made by electron nuclear flip-flop and flip-flip transitions induced by dipole-dipole interactions.[1,16]

In the case of stepwise annealing of the samples, an in-

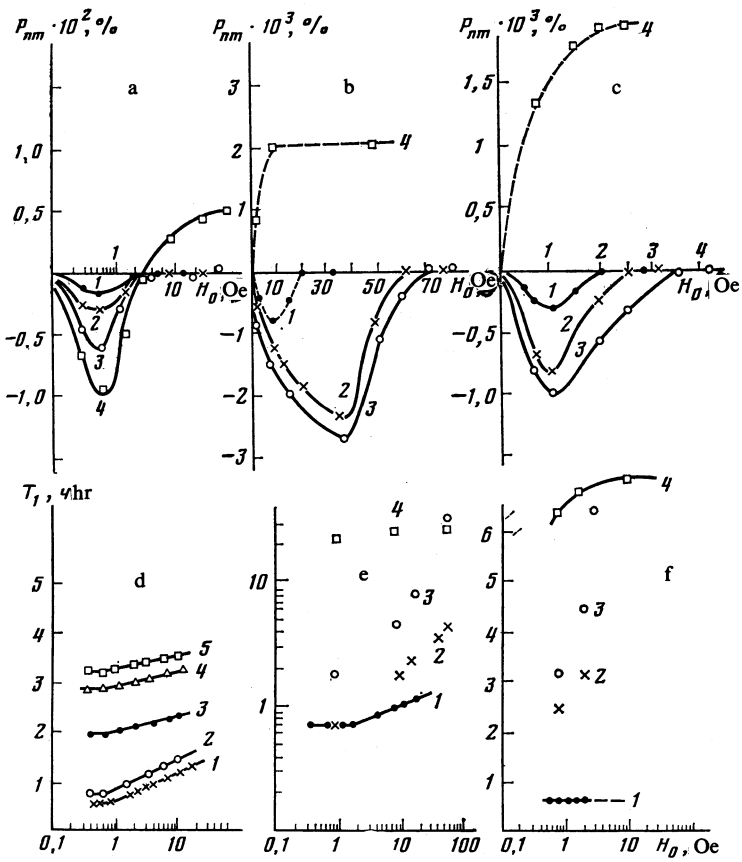

FIG. 1. Dependences of P_{nm} and T_1 on H_0 in stepwise annealing ($T = 500$ °C) of silicon doped with V-group impurities and gold. a) In silicon doped with phosphorus and gold ($N(\mathrm{P}) \approx 10^{15}\,\mathrm{cm}^{-3}$, $N(\mathrm{Au}) \approx 2.1\times10^{16}\,\mathrm{cm}^{-3}$): 1—initial state, $t_{ann} = 20$ min, 2—$t_{ann} = 40$ min, 3—$t_{ann} = 1$ hr, 4—$t_{ann} = 2$ hr. b) In silicon doped with arsenic and gold ($N(\mathrm{As}) \approx 5\times10^{15}$ cm^{-3}, $N(\mathrm{Au}) = 1.2\times10^{16}$ cm^{-3}): 1—$t_{ann} = 0$, 2—$t_{ann} = 1$ hr, 3—$t_{ann} = 3$ hr, 4—$t_{ann} = 6$ hr. c) In silicon doped with bismuth and gold ($N(\mathrm{Bi}) \approx 10^{15}$ cm^{-3}, $N(\mathrm{Au}) \approx 3\times10^{16}$ cm^{-3}): 1—$t_{ann} = 0$, 2—$t_{ann} = 1$ hr, 3—$t_{ann} = 3$ hr, 4—$t_{ann} = 6$ hr. d) Same as in case a, curve 5—$t_{ann} = 9$ hr. e) Same as in case b. f) Same as in case c.

crease of T_1 and a change of the dependence of T_1 on H_0 are observed. In addition, quantitative and qualitative changes of the dependences of P_{nm} on H_0 take place. These changes of the OPNM characteristics are due to the decay of the solid solution of the gold in the silicon, which takes place in the stepwise annealing. In the course of the gold solid-solution decay the concentration relations between its various components change (impurity in the form of individual atoms, donor-acceptor pairs, groups of impurity atoms, impurity atoms that have diffused to dislocations and to the surface of the crystal[13,14] which leads to the experimentally observed changes in the dependences of P_{mn} and T_1 on H_0.

In the case of long times of stepwise annealing, the main contribution to the polarization and to the spin-lattice relaxation of ^{29}Si nuclei is made already by group-V centers (see curves 4 of Fig. 1), since the density of the donor gold is already practically zero under these conditions. We shall consider below in detail the kinetics of the variation of the densities of the various components of the solid solution of gold in silicon with change of annealing time.

Particular interest attaches to the change, with annealing time, of the dependences of P_{nm} on H_0 in dipole-dipole interaction. The increase of the magnetic field at which P_{nm} vanishes and the shift of the maximum of P_{nm} towards the region of large H_0 (Figs. 1a, c, e, f) are evidence that gold donor centers with different spin lattice relaxation times appear in the course of the stepwise annealing ($H_0' = 1/\gamma_e \tau_s$ is the magnetic field at which P_{mn} vanishes.[1)] This is reflected also in a steeper dependence of T_1 on H_0 (see Figs. 1e, 1f). A similar behavior of the dependences of P_{mn} and T_1 on H_0 is due to dissociation, during the heat treatment, of the donor-acceptor pairs (group-V donor center + gold atom at the lattice site). In this case the energy of the forbidden-band impurity level corresponding to the gold acceptor center varies in the range form E_c—0.49 eV to E_c—0.54 eV, depending on the distance between the components in the donor-acceptor pair.[17] In the process of thermal dissociation of the donor-acceptor pair, the gold atom goes from the lattice site to a noncentral interstitial position, and a donor center (EV + 0.35 eV) is produced[11,17,18] thereby and takes part in the OPNM.

It should be noted that the fact that the levels E_V–0.54 eV and E_V + 0.35 belong to different centers of the gold was unequivocally established with the aid of various methods.[17,18,19,20]

The gold donor centers produced as a result of thermal dissociation of donor-acceptor pairs will have different times of electron spin-lattice relaxation, depending on the distance to the nearest group-V center, since donor-acceptor pairs with different distances between their components (E_c–0.4 eV to E_c–0.54 eV) dissociate during the stepwise annealing. It will be shown below that exchange interaction between optically oriented electrons captured by gold donor centers and electrons captured by arsenic and bismuth centers act as a strong channel for electronic spin-lattice relaxation.

Thus, gold donor centers with different values of τ_s are induced during the thermal annealing and contribute to the OPNM of silicon doped with arsenic and bismuth (see Figs. 1b, c, e, f). With further annealing the gold donor centers diffuse towards the solid-solution decay centers, leading to absence of OPNM induced by dipole-dipole interaction (see curve 4, Figs. 1b, c).

A solid solution of gold in silicon containing phosphor decays somewhat differently than in arsenic- or bismuth-containing silicon (see Figs. 1a, d). The reason is that a temperature 500 °C is patently insufficient for dissociation of even remote paired phosphorus + gold acceptor center pairs.[11] This is also attested by the fact that the resistivity ($\rho \approx 10^5\ \Omega\cdot$cm) does not change in the course of the stepwise annealing of silicon doped with phosphorus and gold, whereas in silicon doped with gold and containing bismuth or arsenic a decrease of ρ with annealing time is observed, attesting to dissociation of the donor-acceptor pairs.

Thus, by determining the densities of the gold atoms with different values of τ_s we can record in practice the distribution of the gold impurity as a function of the distance between the components in the donor-acceptor pairs, and thus obtain information on the degree of its correlation with the distribution of the V-group donor centers. We shall demonstrate the solution of this problem with the aid of the OPNM.

a) OPNM and nuclear spin-lattice relaxation in liquid solutions of impurities in semiconductors

The degree of OPNM in a semiconducting crystal containing impurity centers of several types is described by the following expression[1,2]:

$$P_{nm}=P_{nm\,\mathrm{V}}+\sum_{n=1}^{n} P_{nm\,\mathrm{Aud}n}=\xi_{\mathrm{V}} f_{\mathrm{V}} P_{e\mathrm{V}}+\sum_{n=1}^{n} \xi_n f_n P_{en}. \qquad (1)$$

The first term of (1) describes the degree of OPNM produced in the crystal by the contact hyperfine interaction of the ^{29}Si nuclei with the electrons captured by V-group centers. The second term describes the summary OPMN due to n different types of gold donor centers (the gold donor centers have different electron spin-lattice relaxation times), P_{eV} and P_{en} are respectively the degrees of polarization of the electrons trapped by the V–group centers and by the nth gold donor center:

$$P_e=0.125\frac{\tau_{se}}{\tau_{se}+\tau}\frac{\tau_{sd}}{\tau_{sd}+\tau_d}, \qquad (2)$$

where τ_{se} is the spin-lattice relaxation time of the electrons in the conduction band, τ is the electron lifetime in the conduction band, τ_{sd} is the spin-lattice relaxation time of the impurity electron, and τ_d is the lifetime of the electron on the impurity center.

For shallow donor centers in silicon at $T = 77$ K we have $\tau_d \ll \tau_{sd}$, i.e., $P_{\mathrm{eV}} = 0.125\tau_{se}/(\tau_{se} + \tau)$. The degree of polarization of the electrons captured by deep impurity levels is determined by relaxation both in the conduction band and on the center [see (2)]. In the case of an n-type compensated semiconductor it must be taken into account that under the conditions of optical pumping $1/\tau_{dn} = N_n \langle V \rangle \sigma_{\mathrm{ph}\ n}$ (Refs. 17 and 20), where $\langle V \rangle$ is the thermal velocity of the electrons N_n and $\sigma_{\mathrm{ph}\ n}$ are the density and the photoionization cross section of the gold donor centers with spin-lattice relaxation time τ_{sn}.

The quantities ξ_V and ξ_n in (1) take into account the relative contributions of the contact and dipole-dipole interactions to the OPNM[2]:

$$\xi=\left[\frac{5}{20}-\frac{16}{9}\eta^2\left(\frac{\rho}{b}\right)^6\exp\left(-\frac{4\rho}{b}\right)\right]\left[\frac{7}{20}+\frac{6}{20}(1+\omega_e^2\tau_c^2)+\frac{16}{9}\eta^2\left(\frac{\rho}{b}\right)^6\exp\left(-\frac{4\rho}{b}\right)\right]^{-1}, \quad (3)$$

where $\eta = 186$ is the localization density of the electron wave function in the silicon conduction band, ρ is the radius of the region of the hyperfine interaction between the electrons captured by the impurity centers and the surrounding lattice nuclei. For V-group centers it is necessary to take into account in the OPNM both the contact and the dipole-dipole interactions. Therefore ξ_V is described by expression (3), where b is the Bohr radius of the impurity center. In this case we have for ρ_V (Ref. 2):

$$\rho_V=\frac{b}{4}\ln\left[\frac{16\gamma_e^2\gamma_n^2\hbar^2\eta^2}{9b^6}\frac{n_d}{N_d}\frac{a^2}{D}\frac{2\tau_c}{1+\omega_e^2\tau_c^2}\right], \quad (4)$$

where γ_e and γ_n are the gyromagnetic ratios of the electron and the nucleus, respectively, $a = 6.5$ Å is the average distance between the ^{29}Si nuclei in silicon, $D = 2.4\times10^{-14}$ cm^2/c is the nuclear-spin diffusion coefficient in silicon, $\omega_e = \gamma_e H_0$, and τ_c is the correlation time of the electron field of the impurity center at the surrounding nuclei of the lattice. In silicon containing V-group centers τ_c is determined by the frequency of the thermal ejection of the electrons from the donor level into the conduction band ($\tau_c = 1.8\cdot10^{-10}$ sec for phosphorus in silicon, $\tau_c = 10^{-9}$ sec for arsenic in silicon, and $\tau_c \approx 6\cdot10^{-9}$ sec for bismuth in silicon[2]) if the OPNM is observed at $T = 77$ K; n_d/N_d is the degree of the occupation of the V-group centers by electrons under optical pumping conditions.

In hyperfine interaction between gold donor centers and silicon lattice nuclei, account must be taken of only the dipole-dipole interaction, since the wave function of the impurity electron is strongly localized in this case. We therefore have from ξ_n from (3)

$$\xi_n=5/(13+6\omega_e^2\tau_c^2), \quad (5)$$

where $\tau_c = \tau_{sn}$ is the spin-lattice relaxation time of the nth gold donor center. f_V and f_n in (1) are the leakage coefficients of the nuclear polarization for the V-group centers and for the nth gold donor center, respectively; $f_V = T_1/T_V$, where T_1 is the total time of nuclear spin-lattice relaxation in the silicon crystal, and T_V is the time of the spin-lattice relaxation due to the interaction of the ^{29}Si nuclei with the electrons captured by the V-group centers[2,6,21]:

$$1/T_V=\pi N_V D b[1+(1+4\rho_V/b)^2]. \quad (6)$$

For the OPNM induced by the nth gold donor center, the centers for the leakage of the nuclear polarization are not only the V-group donor centers, but also the $n-1$ gold donor centers that have other values of the electron spin-lattice relaxation time: $f_n \approx T_1/T_{1n}$, where T_{1n} is the relaxation time of the ^{29}Si nuclei on account of the dipole-dipole interaction with the nth donor center of the gold:

$$1/T_{1n}=4\pi N_n D\rho_n. \quad (7)$$

Here $\rho_n = 0.68(C_n/D)^{1/4}$ is the radius of the hyperfine interaction in the case of free diffusion in dipole-dipole interaction,[9] and

$$C_n=0.3\gamma_e^2\gamma_n^2\hbar^2\left[\frac{\tau_{sn}}{1+\omega_n^2\tau_{sn}^2}+\frac{7}{3}\frac{\tau_{sn}}{1+\omega_e^2\tau_{sn}^2}\right]. \quad (8)$$

It is easily seen from (1) that, depending on the densities of the group-V and of the Au^0 centers, the degree of the OPNM can change during the solid-solution decay both in magnitude and in direction. If Au^0 donor centers with smaller values of τ_s are produced during the thermodissociation of the donor-acceptor pairs, the dependence of P_{nm} on H_0 is shifted towards stronger magnetic fields (see Figs. 1b and 1c), so that the "break in the hyperfine interaction" [$\omega_e^2\tau_{sn}^2 \gg 1$, see (5)] takes place for the rapidly relaxing Au^0 donor centers in stronger magnetic fields.

In the course of the decay of a solid solution of gold in arsenic-containing silicon, the maximum of the dependence of P_{nm} on H_0 shifted towards stronger fields. This is evidence, as we shall show below, of the strong correlation in the distributions of the arsenic and of the gold in the crystal.

We consider now the processes that lead to a change in the time of the nuclear spin-lattice relaxation in the decay of a solid solution of gold in silicon.

The total time T_1 of the nuclear spin-lattice relaxation with allowance for the nuclear diffusion in a dislocation-free silicon crystal is described by the expression[22]

$$\frac{1}{T_1}=\sum_{n=1}^{n}4\pi N_n D\rho_n+\frac{4\pi N_2' D\rho_1}{1+(\nu-1)\rho_1/2\rho_0}+\pi N_V D b\left[1+\left(1+\frac{4\rho_V}{b}\right)^2\right], \quad (9)$$

where the second term describes the contribution made to the nuclear spin-lattice relaxation by the gold-atom groups produced in the decay of the solid solution. (In dislocation-free silicon crystals at $T = 500$ °C the principal gold solid-solution decay centers are oxygen thermodonors around which are produced during the annealing groups consisting of 4–5 gold atoms.[11,12,14]). In Eq. (9), ρ_1 is the hyperfine-interaction radius of the gold donor center, with an electron spin-lattice relaxation time $\tau_s \approx 2\cdot10^{-8}$ sec,[1] which is located at a considerable distance from the V-group donor centers; $\rho_0 = a_0\nu^{1/3}$ is the radius of the impurity group, where $a_0 = 1.44$ Å is the gold-atom radius and ν is the number of gold atoms in the group ($\nu \approx 4$–5).

It is easily seen that if gold-atom groups are produced in the solid-solution decay, the time T_1 does not depend on the value of the external magnetic field H_0. If the active component (impurity in the form of single atoms) predominates in the impurity solid solution, T_1 depends on the external magnetic field [see the first term of (9)]. With increasing H_0, starting with a certain value $H_0' \approx 1/\gamma_e\tau_{sn}$, T_1 begins to increase because of the break in the hyperfine interaction [see (8), (9), and Figs. 1d–1f]. P_{nm} begins to decrease at H_0 in synchronism with the increase of T_1 [see (1) and Figs. 1a–1c]. The gold donor centers with the smaller values of τ_{sn} begin to contribute to the growth of T_1 in stronger magnetic fields than the gold centers with the longer spin-lattice relaxation times [see (9) and Figs. 1e and 1f].

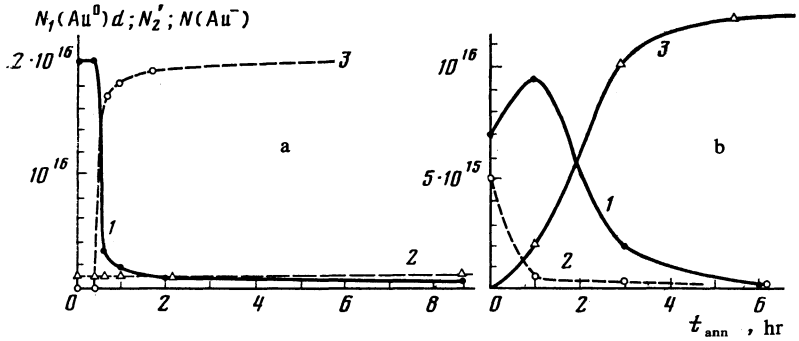

FIG. 2. Dependences of densities of various components of a solid solution of gold in silicon doped with phosphorus and gold (a) and with arsenic and gold (b) on the annealing time at $T = 500°C$: 1—$\Sigma_{n=1}^{n} N_n$, 2—$N(Au^-)$, 3—N_2'.

If the distribution of the density of the gold donor centers in the silicon crystal is discrete with respect to the distance to the nearest V-group center, this should be reflected in a more abrupt nonuniform increase of T_1 with increasing H_0 (see curves 2 and 3 of Fig. 1e).

The contribution of the V-group donor centers to T_1 [see (9) and Figs. 1d–f] in the initial state ($t_{ann} = 0$) is quite small. However, after a prolonged stepwise annealing the nuclear spin-lattice relaxation is due to gold in the form of groups (N_2') and V-group centers (see curves 4. Figs. 1e, f). In this case T_1 does not depend on H_0. From curves 4 one can depend the degree n_d/N_d of occupation of the V-group centers by electrons.

Using (1) and (9), we determine from the relations on Fig. 1 the densities of the various gold and silicon solid-solution components at different times of the stepwise annealing (see Fig. 2). InSi⟨Bi⟩ the gold solid-solution decay proceeds in the same manner as in Si⟨As⟩.

The kinetics of the solid-solution decay (curves 1, Fig. 2) is well described by Ham's exponential relations[23] for the case of nucleation centers of constant size. Practically the entire gold solid solution decays with formation of minute clusters consisting of 4–5 atoms (curves 2, Fig. 2). The growth of

$$\sum_{n=1}^{n} N_n$$

During the initial section of the time dependence of the decay of the solid solution of gold in silicon doped with arsenic is due to the intensive dissociation of the donor-acceptor pairs (see curves 3 of Fig. 2). In silicon doped with gold and phosphorus, no thermodissociation of the donor-acceptor pairs takes place at $T = 500°$ C (see Fig. 2a), and the gold solid solution decays on by diffusion of the Au^0 donor centers towards the nucleation centers (see curve 1, Fig. 2a).

To determine whether the distributions of the V-group and gold donor centers are correlated, we must obtain the dependence of the density of the gold that participates in the formation of the donor-acceptor pairs on the distance between the components inside the pair. It is therefore of interest to consider the distribution of the donor centers Au^0 produced in thermal dissociation of the donor-acceptor pairs (See Figs. 3a, 3b) with the values of τ_{sn} which, as we shall show below, reduces to a distribution in the distance between the components of the donor-acceptor pairs.

b) Spin-lattice relaxation of a deep paramagnetic center under conditions of exchange interaction with an electron captured by a shallow donor center

We consider the mechanism of the electron spin-lattice relaxation (SLR) in the case to be modulation of the exchange interaction between the shallow and deep centers on account of the phonon-induced transitions between the

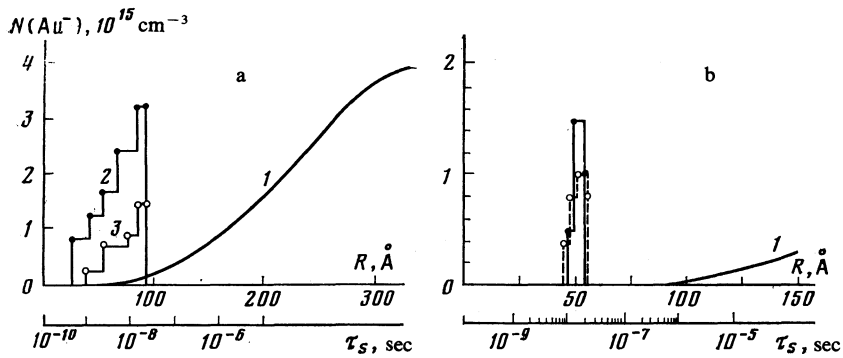

FIG. 3. Distribution of the density of gold present in a crystal in the form of donor-acceptor pairs, vs the distance between the components in the pair. a) Silicon doped with gold and arsenic: 1—calculated dependence for random gold and arsenic distribution in the crystal; Distribution $N(Au^-) = f(R)$ after $t_{ann} = 1$ hr at $T = 500°$ C, 3—distribution $N(Au^-) = f(R)$ after $t_{ann} = 3$ hr. b) Silicon doped with gold and bismuth: 1—calculated dependence for random distribution of bismuth and gold in silicon crystal, ●—distribution $N(Au^-) = f(R)$ after $t_{ann} = 1$ hr, ○—distribution $N(Au^-) = f(R)$ after $t_{ann} = 3$ hr.

ground and excited states of the shallow center. Thus, substantial modulation of the exchange interaction occurs for photoinduced transitions between $1s$ and $2p_z$ states of a shallow center (z is the axis joining the shallow and deep centers). The operator of the exchange interaction between shallow and deep centers can be represented in the form[24]

$$\mathcal{H}_{\text{exch}}=-2I_0\delta(\mathbf{r}_{\text{sh}}-\mathbf{R}_{\text{dp}})\mathbf{S}_{\text{sh}}\mathbf{S}_{\text{dp}}, \tag{10}$$

$$I_0=\iint \Psi(\mathbf{r}_{\text{dp}}^{(1)})\frac{e^2}{|\mathbf{r}_{\text{dp}}^{(1)}-\mathbf{r}_{\text{dp}}^{(2)}|}\Psi(\mathbf{r}_{\text{dp}}^{(2)})\,d\tau_{\text{dp}}^{(1)}\,d\tau_{\text{dp}}^{(2)}, \tag{11}$$

where $\mathbf{r}_{\text{dp}}$, $\mathbf{S}_{\text{dp}}$, Ψ_{dp}, and $\mathbf{R}_{\text{dp}}$ are respectively the electron coordinates, the spin operator, the wave function, and the coordinate of the deep-center nucleus, and $\mathbf{r}_{\text{sh}}$ is the coordinate of the shallow-center electron.

The spin Hamiltonian of the exchange interaction in the $1s$ state and in the excited $2p_z$ state of the shallow center takes then the form

$$\mathcal{H}_{1s}=\frac{-2I_0|U_0|^2}{\pi b^3}\exp\left(-\frac{2R_r}{b}\right)\mathbf{S}_{\text{sh}}\mathbf{S}_{\text{dp}},$$
$$\mathcal{H}_{2p_z}=\frac{-I_0|U_0|^2R_r^2}{16\pi b^5}\exp\left(-\frac{R_r}{b}\right)\mathbf{S}_{\text{sh}}\mathbf{S}_{\text{dp}}, \tag{12}$$

$|U_0|^2$ is the square of the modulus of the Bloch factor at the location of the deep center. It follows from (12) that owing to the transitions between the ground and excited states of the shallow center, a time-fluctuating exchange interaction takes place in the form

$$\mathcal{H}'_{\text{exch}}=\mathcal{H}_{1s}\left[-\exp\left(-\frac{R_{\text{dp}}}{b}\right)+\frac{R_{\text{dp}}^2}{32b^2}\right]\frac{(P(t)+1)}{2}, \tag{13}$$

where $P(t)=\pm 1$ is a random function of the time.

A calculation of the rate of the SLR of the deep center in the investigated case, carried out in analogy with Ref. 25, leads to an expression for $1/T_s$ in the form

$$\frac{1}{T_s}=\frac{4}{\pi^2\hbar^2}|\langle -+|S_{\text{sh}}\,S_{\text{dp}}|+-\rangle|^2|U_0|^4I_0^2\exp\left(-\frac{2R_{\text{dp}}}{b}\right)\frac{1}{b^6}$$
$$\times\left[\frac{R_{\text{dp}}^2}{32b^2}-\exp\left(-\frac{R_{\text{dp}}}{b}\right)\right]^2\frac{\exp(\Delta/kT)}{(\exp(\Delta/kT)+1)^2}$$
$$\times\frac{w_\uparrow(1+\exp(\Delta/kT))n_d}{w_\uparrow^2[(1+\exp(\Delta/kT))^2+(\omega_s^{\text{dp}}\omega_s^{\text{sh}})^2]N_d}, \tag{14}$$

Δ is the energy difference between the $1s$ and $2p_z$ states of the shallow center, $w_\uparrow$ is the probability of a phonon-induced $1s\to 2p_z$ transition, ω_s^{dp} and ω_s^{sh} are the frequencies of the spin splitting of deep and shallow centers, respectively. Expression (14) was obtained for the case of high temperatures: $kT\gg g\beta H$.

Estimates have shown[3] that SLR rates of the order of 0.5×10^8 sec^{-1} (approximately equal to the SLR rate not connected with the contribution of the donors to the SLR) are reached at $R_{\text{dp}}=150$ Å for P, As, and Bi in Si⟨Au⟩ only if account is taken of the fact that the outer $6s^1$ electron of the deep Au^0 center has moved over to the orbitals of the ligands of the first coordination sphere. The corresponding wave function of the deep Au^0 center takes in the LCAO model the form $\Psi_{5d^{10}}=1/2\,(\Psi_1+\Psi_2+\Psi_3+\Psi_4)$, where Ψ_1 is the wave function of an electron localized on the ith Si atom of the first coordination sphere. As a result, the parameter I_0 of the exchange interaction increases. The SLR rate (14), which is proportional to I_0^2, also increases. The calculation results are represented by the second scales of Figs. 3a and 3b [$\tau_{sn}=f(R)$]. The calculation of τ_{sn} as a function of the distance between the components in the donor-acceptor pair was carried out for values determined experimentally from Fig. 1, $n_d/N_d=10^{-3}$ in the case of silicon doped with arsenic and gold, and for $n_d/N_d\approx 10^{-4}$ in the case of silicon doped with bismuth and gold.

It should be noted that there is a bottleneck for the described exchange SLR mechanism. For very shallow donor centers at $T=77$ K this mechanism is ineffective, since the degree of occupation n_d/N_d is very small, while for too deep donor centers its effectiveness falls off because of the abrupt decrease of the probability of thermal ejection of an electron from a donor level to the conduction band [see (14)]. For example, in silicon doped with gold and arsenic (E_c–0.052 eV), the SLR exchange mechanism is much more effective than in silicon doped with bismuth and gold (E_c–0.068 eV).

The estimates have shown thus that such an SLR mechanism via exchange interaction between shallow and deep donor centers is effective enough to explain the acceleration of the SLR of the Au^0 donor centers in the presence of shallow group-V donor centers in silicon.

On the basis of the dependences of τ_{sn} on R we obtain the density distribution of the gold that participates in the formation of the donor-acceptor pairs on the distance between the pair components (see the first scales of Figs. 3a and 3b). The same figure shows the calculated random distribution of the gold donor centers and the V-group centers in silicon. It is difficult to obtain the density distribution of the gold at large values of R, for in this case the time τ_{sn} governed by the relaxation exchange mechanism becomes of the order of the SLR time which is not connected with the contribution of the V-group donors ($\tau_s\approx 2\cdot 10^{-8}$ sec, Ref. 1). The restriction on the N_n distribution in the region of small R is due to the need for taking the Coulomb interaction into account and to the fact that the exchange-interaction mechanism becomes less effective if R becomes smaller than the radius of the orbit of the donor electron in the $2p_z$ state (Fig. 3).

Lowering the pump-light intensity in the experiments led, in accord with (1)–(4) to a lowering of the degree of occupation of the arsenic centers and to a corresponding decrease of the value of P_{nm}, and also to a shift of the dependence of P_{nm} on H_0 into the region of weak magnetic fields. This is due to the weakening of the SLR exchange mechanism with decreasing degree of occupation of the shallow donor levels by electrons.

It can be seen from Fig. 3 that a strong correlation exists in the distributions of the gold and of the V-group centers in silicon. Thus, close donor-acceptor pairs predominate in the distributions. We have carried out similar investigations of the correlations in the distributions of shallow and deep impurity levels in silicon as functions of the doping method and conditions. Deviation from a random distribution, to one degree or another, was observed practically always at all densities of the shallow and deep impurity; this deviation is

apparently due to the influence of the elastic field of the shallow donor centers.

Thus, we determined with the aid of the DPNM the densities of the different component of a solid solution of gold in silicon containing group-V impurities. It was shown that the mechanism of the exchange interaction between the centers and the shallow and deep levels in the forbidden band can contribute to the SLR of latter. We observed by the DPNM method strong correlations in the distributions of the donor and acceptor impurities in silicon; these distributions exert a significant influence on the electrophysical properties, thermal stability, and photosensitivity of the materials.

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[1)]Optical polarization of paramagnetic centers and accordingly of lattice nuclei can be due to exchange scattering of spin-oriented photoexcited conduction electrons.[5,6,7]

[2)]In semiconductors containing various defects with spin $> 1/2$ the use of circularly polarized light offers no advantage whatever, for in this case the polarization of the paramagnetic centers is due to selective population of the magnetic sublevels.[4]

[3)]In the estimates of the SLR rate we have assumed that $w_\uparrow = w_d$, where w_d is the probability of thermal ejection of an electron from a donor level into the conduction band, since it is precisely the $1s \rightarrow 2p_z$ excitation which is here the "bottleneck" of the relaxation channel.

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