ically induced self-compensation of chalcogens in silicon

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A quenching and a regeneration of photoconductivity have been observed in silicon containing tellurium, selenium, and sulfur centers during preliminary pumping by monochromatic light. These effects stem from the reversible photodissociation of a one-electron state of a deep double chalcogen donor in the silicon.

Chalcogen impurity centers in silicon are double do- . They form two interrelated deep levels in the band (Fig. 1). Electron-spin-resonance studies[1,2] have wn that a singly charged paramagnetic state of a deep cogen center in silicon is at a lattice site and is char- rized by a symmetry close to T_d. The Hall energies of the background electron $(+/++)$ and the corre- d electron $(0/+)$ of the double chalcogen donors are ntially the same as the corresponding energies for ther- ionization and photoionization (Table I). This fact, nbined with information on the helium-like wave func- of chalcogen impurities in silicon, might seem at first nce to imply that the chalcogens do not tunnel in the ice during charge exchange, so there are no related nifestations of metastability. However, photo-ESR spec- contain regions of a partial quenching and regeneration paramagnetic states.[1,2] That result, combined with fea- es of the temperature dependence of the cross sections trapping by chalcogen centers,[1,3] suggests that the de- t changes position in the silicon lattice during charge change. Accordingly, in order to refine the model of the nter and the positions of the charge states of the chalco- ns in a silicon lattice, it is worthwhile to study the be- vior of the impurity photoconductivity as the duration d wavelength of a preliminary monochromatic optical umping are varied. This pumping stimulates their charge xchange in electric fields of various strengths oriented long crystallographic axes.

In this paper we are reporting a study of *p*-type silicon amples doped with selenium, sulfur, and tellurium by igh-temperature diffusion (1100 °C, 30 h), followed by quenching in oil. The photoconductivity spectrum was measured for various wavelengths and durations of a preliminary monochromatic pumping. In the measurements, we varied the strength of the anisotropic electric field applied to the sample. We observed intervals of the optical pumping which resulted in a quenching of the photoconductivity signal over the entire spectrum (Figs. 2a–4a). The results also show that the spectrum can be restored when the samples are subsequently illuminated with monochromatic light in a different spectral region (Figs. 2b–4b). These effects are metastable at $T = 77$ K, and they do not disappear when the pump light is turned off. After each measurement cycle (quenching and regeneration) we carried out a thermal restoration of the photoconductivity signal by heating the test sample to room temperature. Note that Figs. 2–4 show the spectra of the quenching and regeneration of only the interband photoconductivity in silicon with chalcogen centers; a corresponding behavior of the quenching and regeneration was observed over the entire spectrum.

In the Si⟨Te⟩ samples we observed a quenching of the photoconductivity in the course of a preliminary optical pumping with photon energies in the interval $0.34 < h\nu < 0.69$ eV (Fig. 2a). Subsequent illumination with $0.1 \leqslant h\nu \leqslant 0.34$ eV or $0.75 < h\nu < 1.15$ eV (Fig. 2b) caused a regeneration of the photoconductivity signal.

In the silicon samples doped with selenium, we observed a more complex kinetics of the quenching and regeneration of the photoconductivity. For a short illumination time, preliminary optical pumping with photon energies $0.4 < h\nu < 0.75$ eV or $0.85 < h\nu < 1.0$ eV (Fig. 3a) stimulated a quenching of the photoconductivity, while an increase in the duration of the preliminary illumination resulted in a regeneration of the spectrum (Fig. 3b). In addition, the photoconductivity signal could be restored in the course of optical pumping with a photon energy $0.15 < h\nu < 0.4$ eV (Fig. 3b).

In Si ⟨S⟩ we also observed two spectral intervals of the preliminary-pumping light which stimulated a quenching of the photoconductivity ($0.4 < h\nu < 0.7$ eV and $0.7 < h\nu < 0.85$ eV; Fig. 4a). Subsequent illumination by light with $0.15 < h\nu < 0.3$ eV or $0.65 < h\nu < 1.1$ eV resulted in a restoration of the photoconductivity signal (Fig. 4b). In addition, in the sulfur-doped silicon samples we studied the effect of an external electric field, directed along the [111] axis. We observed that an increase in this field changed the spectra of the photoconductivity quenching and regeneration (Fig. 4). There was a pronounced weakening of the quenching in the energy interval $0.4 < h\nu < 0.7$ eV (Fig. 4a), while the second quenching region shifted toward higher values of the photon energy of the preliminary pumping (Fig. 4a). An electric field also caused a sharp intensification of the regeneration of the photoconductivity signal. It expanded the interval of pump photon energies ($0.15 < h\nu < 0.8$ eV) which resulted in a restoration of the photoconductivity (Fig. 4b).

After the pump light which stimulated the quenching of the photoconductivity in the silicon containing chalcogen centers was turned off, a restoration of this photoconductivity was not observed. Photoconductivity spectra could not be measured even after a prolonged wait at

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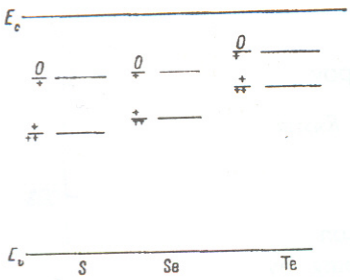

FIG. 1. One-electron band scheme of double chalcogen donors in silicon.

$T=77$ K. Only heating to room temperature restored the photoconductivity over the entire spectrum.

The results found here can be explained by the model of a reconstructed point defect for which the electron–vibrational interaction constant is a nonmonotonic function of the number of electrons at the center. In this model, a defect tunnels between positions characterized by different symmetries of the lattice of the semiconductor crystal in the course of a charge-exchange process.[4,5] The change in symmetry compensates for the effect of the Coulomb repulsion which arises in the course of the charge exchange of the deep center.[6] This model incorporates the characteristics of the charge states of the double chalcogen donors in silicon: The one-electron state D^+ is at a T_d lattice site, while the empty state D^{++} and the two-electron state D^0 are in respectively tetragonal (D_{2d}) and tetrahedral (C_{3v}) interstitial positions.

To pursue the analysis of the experimental results, we use two-electron adiabatic potentials, whose minima are separated by a distance corresponding to the actual po tions of the charge states of the S, Se, and Te centers silicon[4–6] (Figs. 5–7).

TABLE I. Activation energies of chalcogens in silicon found by various methods.

		Hall method E_c, eV	Capacitance measurements	Optical measurements E_c, eV
S	$+/++$	−0.59	−0.62	−0.63
	$0/+$	−0.3	−0.32	−0.36
Se	$+/++$	−0.52	−0.59	−0.65
	$0/+$	−0.28	−0.3	−0.32
Te	$+/++$	−0.36	−0.4	−0.45
	$0/+$	−0.19	−0.2	—

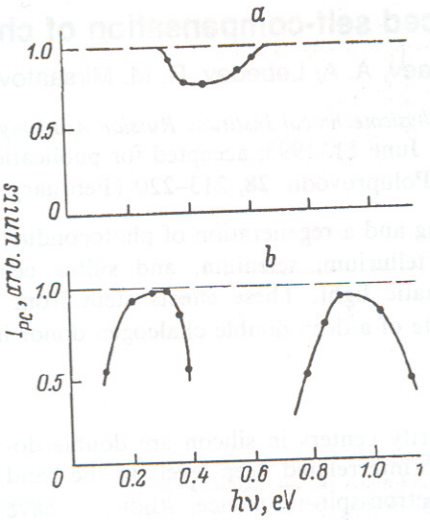

FIG. 2. Spectra of the quenching (a) and the regeneration (b) of interband photoconductivity in tellurium-doped silicon. The duratio the preliminary pumping (quenching) and of the subsequent pump (regeneration) was 20 min. The voltage across the sample was $U=4$ ($\varepsilon \approx 4 \times 10^4$ V/cm).

According to the model proposed here, the quenchi of the photoconductivity occurs after a preliminary pu ing by light with a photon energy $h\nu \geqslant I_1$ [Fig. 1), wh I_1 is the ionization energy of the background electron the defect: a (+/++) process], which stimulates a ph ionization of the D^+ state (Figs. 5–7):

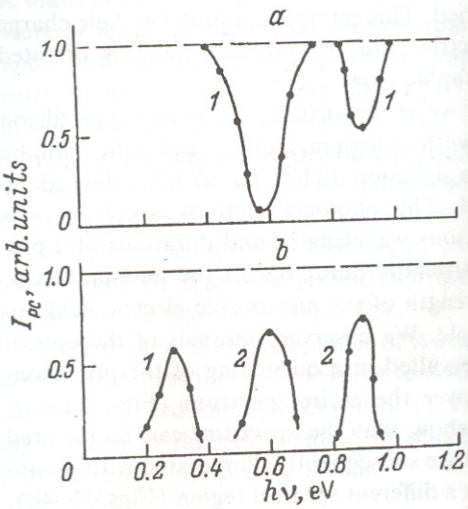

FIG. 3. Spectra of the quenching (a) and the regeneration (b) interband photoconductivity in selenium-doped silicon. The dura the preliminary pumping (the quenching) and that of the subse pumping (the regeneration) was (1) 10 and (2) 20 min. The across the sample was $U=40$ V ($\varepsilon \approx 4 \times 10^4$ V/cm).

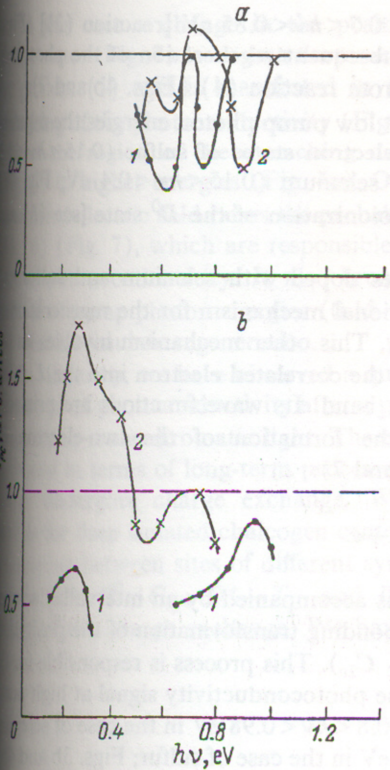

FIG. 4. Spectra of the quenching (a) and the regeneration (b) of the interband photoconductivity in sulfur-doped silicon. The duration of the preliminary pumping (quenching) and of the subsequent pumping (regeneration) was 20 min. 1—The voltage across the sample, was 40 V ($\varepsilon \approx 4 \times 10^4$ V/cm); 2—120 V ($\varepsilon \approx 1.2 \times 10^5$ V/cm).

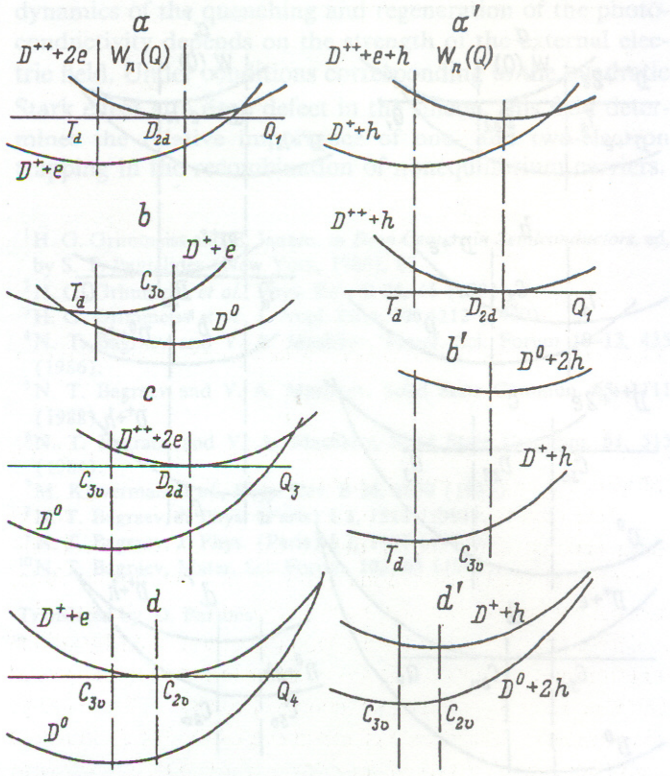

FIG. 5. Adiabatic potentials of the charge states of a tellurium center in silicon in the absence of an electric field corresponding to (impurity level)–(conduction band) transitions (a, b, c, d) and to (valence band)–(impurity level) transitions (a′, b′, d′).

$$\left.\begin{array}{l} D^+ + h\nu(I_1) \to D^{++} \\ D^{++}+2e \to D^0 \end{array}\right\} \qquad (1)$$

$$2D^+ + h\nu(I_1) \to D^0 + D^{++}.$$

This photoionization is accompanied by two-electron trapping.[5] The new long-lived state D^0+D^{++} is a center for intense Auger recombination,[7,8,9]

$$D^0+h\nu(h\nu \approx E_g) \to D^0+e+h \to D^+ + e \to D^{++}+2e \to D^0, \qquad (2)$$

which leads to a sharp decrease in the lifetime of the nonequilibrium carriers and a corresponding quenching of the photoconductivity over the entire spectrum.

A quenching of the photoconductivity can also arise during optical pumping with $h\nu = E_g - \Delta I$ in the process

$$D^+ + h\nu \quad (h\nu = E_g - \Delta I) \to D^0 + h, \qquad (3)$$

where ΔI is the ionization energy of the correlated electron, $I_1 + \Delta I = I_2$, and I_2 is the energy of two-electron photoionization of the center[6] (Figs. 5–7).

Regeneration of the photoconductivity spectra becomes possible when the test sample is illuminated by light with a photon energy[5,8,9] $h\nu = E_g - I_1$ (Figs. 5–7):

$$\left.\begin{array}{l} D^{++}+h\nu(E_g-I_1) \to D^+ + h \\ D^0 + h \to D^+ \end{array}\right\} D^{++} \qquad (4)$$

$$+ D^0 + h\nu(E_g - I_1) \to 2D^+.$$

In the course of this process, the concentration of D^+ states is restored, and the lifetime of nonequilibrium carriers increases.

In addition, regeneration of the D^+ state can be induced during optical transitions into the conduction band in the course of an ionization of the long-lived D^0 state (Figs. 5–7):

$$D^0 + h\nu(\Delta I) \to D^+ + e. \qquad (5)$$

The quenching and regeneration spectra separate in greatest detail in the tellurium-doped silicon samples, in which the quenching of the photoconductivity in the photon energy interval $0.34 < h\nu < 0.69$ eV (Fig. 2a) is due to process (1) (Fig. 5). A regeneration of the photoconductivity spectrum becomes possible during optical pumping with $0.1 < h\nu < 0.34$ eV (Fig. 2b), by virtue of reaction (5) (Fig. 5), and in the interval $0.75 < h\nu < 1.15$ eV (Fig. 2b), in the course of process (4) (Fig. 5).

In Si⟨S⟩ and Si⟨Se⟩, the pump photon energies which stimulate quenching and regeneration are approximately equal. Accordingly, the kinetics of the photoconductivity signal during the preliminary optical pumping is most

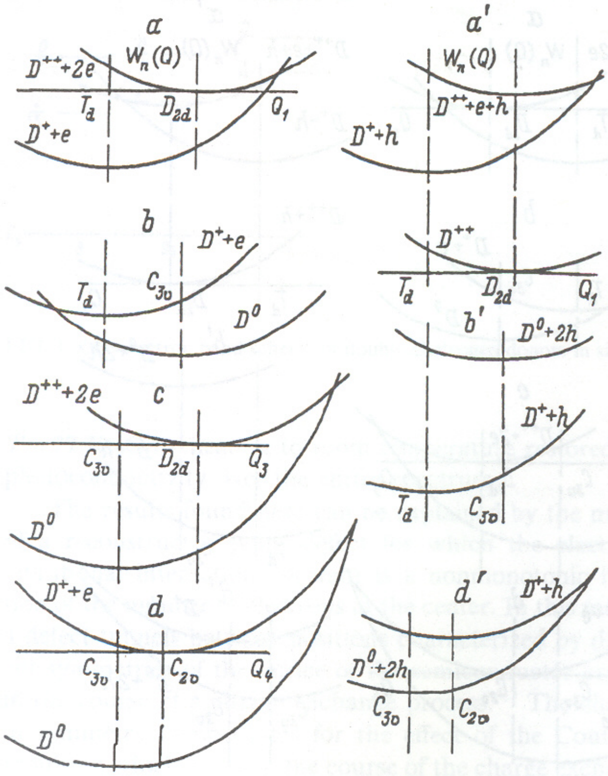

FIG. 6. Diagrams of the adiabatic potentials of charge states of a selenium center in silicon in the absence of an electric field corresponding to (impurity level)–(conduction band) transitions (a, b, c, d) and (valence band)–(impurity level) transitions (a′, b′, d′).

complex in this case (Figs. 3 and 4). In the case of selenium, the quenching of the photoconductivity during preliminary pumping with $0.4 < h\nu < 0.75$ eV (Fig. 3a) is due to process (1) (Fig. 6), while at $0.85 < h\nu < 1.0$ eV (Fig. 3a) it is stimulated by reaction (3) (Fig. 6). As the duration of the preliminary pumping is increased, the probability for reaction (4) increases (Fig. 6), with the result that process (1) is completely suppressed (Fig. 6).

In the sulfur-doped silicon we again observe two regions of photoconductivity quenching, $0.4 < h\nu < 0.7$ eV [process (1)] and $0.7 < h\nu < 0.85$ eV [reaction (3)] (Figs. 4a and 7). The subsequent regeneration of the photoconductivity results from reaction (4) (Figs. 4b and 7).

In addition, at low pump photon energies the regeneration of the one-electron states of sulfur ($0.15 < h\nu < 0.3$ eV; Fig. 3b) and selenium ($0.15 < h\nu < 0.4$ eV; Fig. 4b) results from photoionization of the D^0 state [see (5) and Figs. 6 and 7].

In the samples doped with selenium and sulfur, we observed an additional mechanism for the regeneration of photoconductivity. This other mechanism involves an optical excitation of the correlated electron into the L valley of the conduction band. Its wave functions are primarily responsible for the formation of the two-electron D^0 state[8,10] (Figs. 6 and 7):

$$D^0 + h\nu \rightarrow D^+ + e. \tag{6}$$

This process is accompanied by an intervalley scattering with a corresponding transformation of the position of the center ($C_{3v} \rightarrow C_{2v}$). This process is responsible for the regeneration of the photoconductivity signal at high pump photon energies ($0.8 < h\nu < 0.98$ eV in the case of selenium and $0.8 \leqslant h\nu < 1.1$ eV in the case of sulfur; Figs. 3b and 4b). Note that the one-electron state forms at a lattice site predominantly from wave functions of the valence band or from the Γ valley of the conduction band in the case in which the center has the T_d symmetry. Its position characterized by a C_{2v} symmetry is related to the [110] minimum of the conduction band.[10] In turn, the empty state is formed predominantly from the wave functions of the X valley of the conduction band.[10]

In the case in which the electron–vibrational interaction is a nonlinear function of the number of electrons at a center, the quadratic Stark effect induced by an external electric field shifts the charge states of the defect and causes corresponding changes in the energies of direct optical transitions and in the kinetics of the charge exchange of deep centers.[5,8,9] We studied the kinetics of the quenching and regeneration of photoconductivity with an electric field directed along the [111] axis (Fig. 6) in sulfur-doped silicon.

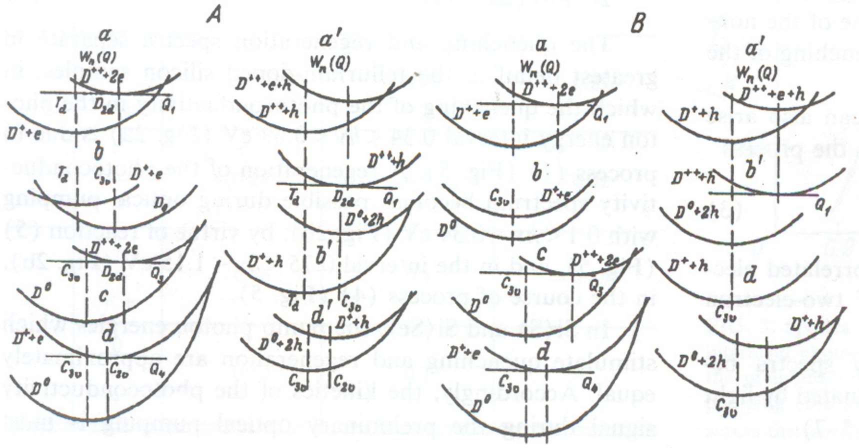

FIG. 7. Diagrams of the adiabatic potentials of the charge states of a sulfur center in silicon in the absence of an electric field (A) and in an electric field directed along the [111] axis (B). These diagrams correspond to (impurity level)–(conduction band) transitions (a, b, c, d) and (valence band)–(impurity level) transitions (a′, b′, d′).

ase a change in the position of the defect
(Fig. 7) leads to a decrease in the probability
1) and is manifested in a decrease in the
the photoconductivity (Fig. 4a) and also in a
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photoconductivity after a preliminary optical
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terms of long-term processes in which a deep
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D^0-C_{3v}, D^+-T_d, and $D^{++}-D_{2d}$) in the
charge exchange. We have shown that the
dynamics of the quenching and regeneration of the photoconductivity depends on the strength of the external electric field. Under conditions corresponding to the quadratic Stark effect at a deep defect in the silicon, this field determines the relative importance of one- and two-electron trapping in the recombination of nonequilibrium carriers.

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