Theory of cooperative interaction of point defects and the extrinsic photoconductivity of semiconductors

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We propose a model of concentration-dependent interaction of point defects (PDs) in semiconductors. The essence of the model is that the formation energy of a defect depends on the concentration of defects of a different type, and the model gives a phenomenological description of the cooperative behavior of point defects. We show that at the temperature at which cooperative interaction comes into play the spatially uniform distribution of point defects can separate into regions of high and low concentration. The separation is all the more effective the stronger the concentration-dependent reciprocal influence is. We estimate that a periodic distribution of impurities forms over distances of 10^{-5} cm within a time ranging from several seconds to minutes. The redistribution and clustering of point defects, which occur due to this cooperative interaction, give rise to the formation of complexes of point defects, in particular, multistable complexes. We determine how configurational restructuring of a bistable donor impurity center, occurring when the depth of the bound-electron levels changes, affects the amplitude and phase shift of the semiconductor photoconductivity. We show that it is possible to determine the electronic and configurational characteristics of these centers.

It is well known that point defects (PDs) in solids—vacancies, intrinsic interstitial atoms, impurities, and impurity complexes—significantly influence the elastic, thermal, electronic, and magnetic properties of materials. Point defects often give rise to radical restructuring of these properties as compared with more or less pure materials. This is especially characteristic for semiconductors, but point defects undoubtedly also play an important role in high-T_c superconducting ceramics, where, for example, oxygen plays an important role.

Here not only is the behavior of a single intrinsic point defect (IPD) or impurity important, but the role of the entire ensemble of defects as a whole, i.e., cooperative effects, increases, even when the concentrations of the defects are comparatively low.

In the present paper we analyze the experimental data on this subject and we show that cooperative interactions of point defects result in a nonuniform distribution of defects in space, formation of correlated pairs and complexes, and the existence of multistable defects (Sec. 1). Hence it is necessary to clarify the conditions which bring about such changes and the effect this has on the electronic properties of crystals. A general criterion for instability of a uniform distribution of impurities in semiconductors will be derived in Sec. 2, and a model of a restructuring "impurity-defect" complex and its effect on photoconductivity is studied in detail in Sec. 3.

1. ANALYSIS OF THE EXPERIMENTAL DATA

This section consists of two parts. In the first part we analyze diffusion and interaction of impurities; in the second part we discuss briefly the associated problems of multistability point defect complexes.

1. In the last few years many proofs have appeared of the fact that in semiconductors the profiles of the distribution of impurities are correlated even for comparatively low concentrations of impurities and intrinsic point defects of the order of 10^{14}–10^{17} cm^{-3} (see, for example, Refs. 1–8); diverse impurity pairs and impurity-defect complexes are formed.[9-12]

The ultraprecise degree of compensation of donor levels of phosphorus in silicon by acceptor gold, as observed in Ref. 1, indicates that there exists some mechanism for automatic grouping of impurities of different sign in space. The correlation in the arrangement of the impurities, as is pointed in Ref. 1, is determined by the directed diffusion of gold in the elastic field of donors.

Similarly, in Refs. 2 and 3 it was established that atoms of electrically active gold, occupying lattice sites in silicon crystals doped with a shallow donor impurity, are located predominantly some distance away from the atoms of the donor impurity. In other words, in crystals there exist correlated pairs of impurity atoms. The experimentally measured pair concentrations are one to two orders of magnitude higher than the concentrations computed for a random distribution. In addition, the average distance between Au atoms and the donor impurity (As, B, or P) for a correlated impurity distribution is approximately equal to 80, 50, and 50 A, respectively. In these papers the possible mechanism of formation of correlated pairs of atoms of donor and acceptor impurities was not discussed. Taking into account the Coulomb interaction between components of the pairs does not contribute significantly to the value of their concentration. Since the strain fields decay more rapidly than the Coulomb fields, the contribution of the strain fields is even smaller.

In Ref. 4 an "exchange" mechanism, involving the presence of a third point defect—a vacancy (V), which interacts actively with a phosphorus atom, forming an E-center, and a gold atom, thereby "holding" them at some distance away from one another—was proposed in order to explain the appearance of such correlated pairs of atoms. In so doing, it was assumed that the vacancy V does not affect the electrophysical parameters of P and Au at low temperatures.

The phenomenon of precise compensation (self-compensation) of the effect of an introduced impurity by intrin-

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sic defects in wide-bandgap 2–6 semiconductors was mentioned in Ref. 5. It was pointed out that this phenomenon can be explained at high temperatures by the association of existing defects in the crystal with impurities. In order to explain the correlated behavior of charged impurities and intrinsic point defects at low temperatures, a mechanism was proposed for the restructuring of the lattice near an impurity atom with the impurity atom itself or a neighboring lattice atom being expelled from the lattice site into an interstice.

A correlated distribution of implanted impurities in silicon after high-temperature annealing has been noted in other studies: boron and gallium (Ref. 6) and boron and hydrogen (Ref. 7). It was noted that the mutual diffusion of B and Ga is limited by their association into pairs and mutual oscillations of the concentrations of B and H is observed at submicron distances.

These facts indicate that point defects migrating in a crystal lattice interact effectively with one another. This interaction strongly affects the mutual concentration profiles of point defects and under certain conditions results in the formation of associations of defects and impurity pairs. In addition, the electronic properties of semiconductor materials are determined by such correlated behavior of impurities in the process of doping or annealing.

A very large number of papers, reviews, and monographs concerning diffusion of impurities in semiconductors has now been published. Here we confine our attention only to low-dislocation crystals (dislocation density less than 10^4 cm^{-2}). The large number of models and diffusion mechanisms that have been proposed indicates the complexity and diversity of diffusion processes in each specific case of impurity and semiconductor with different external factors. The first very simple models of impurity diffusion (interstitial, vacancy, and dissociative (see the monograph Ref. 12)) have gradually evolved into more complicated models in order to describe adequately the experimental facts.

Thus, for example, in Refs. 13–19 mechanisms were proposed for diffusion with the participation of several point defects: the kick-out mechanism;[14,15] migration by means of E-centers[16,17] and taking into account impurity-vacancy interaction (Ref. 18); and, an ensemble exchange mechanism of diffusion (Ref. 19). The effect of the Fermi level on the diffusion of charged impurities has been studied.[20,21]

In Refs. 22–25 different combinations or a change in the mechanisms of impurity diffusion under different conditions of diffusion were proposed in order to interpret the experimental data. Such corporate models, evidently, make sense, since they are based on numerous data on the change in the state of impurities and intrinsic point defects at different temperatures, depending on the type of doping, for different forms of irradiation, and levels of laser annealing (we mention only Refs. 26–34). According to these data, in different situations point defects can migrate by different mechanisms. From this standpoint, the sharp change in the diffusion and annealing temperatures and the types of external actions on the crystal are all factors that drive the system out of equilibrium, and the parameters of these perturbations are the criterion for the degree to which the process departs from equilibrium.

In connection with the intensive investigations of nonequilibrium phenomena in condensed media, there have appeared works concerning the analysis of the stability of prescribed distributions of point defects in crystals under substantially nonequilibrium conditions.[31–34] Different mechanisms, which are responsible for the instability of the uniform state of the defects, are proposed for the interaction of defects: elastic interaction of vacancies and interstitial atoms, produced by a particle flux in the crystals, with saturated sink–complexes;[31] uphill diffusion of irradiation-induced vacancies along the gradient of the concentration of a substitution impurity;[32] mechanism associated with the effect of a vacancy wind and deviation from local neutrality accompanying fluctuations of the impurity concentration;[33] and the nonlinear character of the interaction accompanying annihilation of defects on centers neglecting diffusion.[34]

As a rule, instabilities of this type start with the appearance of certain structures: superlattice of pores, complexes of interstitial intrinsic atoms of the crystal, and "bubbles" of impurity atoms. In particular, it has been found that regular defect structures appear in semiconductors. For example, in silicon these are clusters of intrinsic point defects of the lattice, laminar defects, stacking faults, and swirl defects.[35–37] They characteristically are highly mobile and highly sensitive to variations in the concentrations of the vacancies and interstitial atoms as well as to the presence of even very weak internal and external mechanical fields. In addition, they are observed to be distributed in layers in planes, normal to the direction of the gradient of the mechanical stresses.[35] These planes are usually parallel to the surface of the crystal. In Ref. 7 it is shown that the boron and hydrogen concentrations oscillate, and it was proposed that the boron and hydrogen are concentrated on structural defects.

The facts presented above indicate that it is necessary to develop further the theory of diffusion and interaction of impurities in the process of doping and thermal annealing or other different external perturbations and to determine the effect of impurities on the electronic and structural properties of semiconductor materials.

2. As we have mentioned above, point defects can change significantly the properties of a semiconductor. But organized redistribution and clustering of point defects naturally give rise to the formation of clusters of defects—impurity-defect complexes, which in turn can strongly affect the same properties of semiconductor material, in particular, the thermal stability, radiation resistance, and degradation of electrophysical parameters. Further, the larger the number of point defects of different types in such clusters, the higher is the probability that complexes of defects will be multistable and will restructure from one stable state into another as a result of the input of energy. At the same time, the concept of multistability itself can be different. For this reason, we briefly review the restructuring defect-impurity complexes.

In Refs. 38 and 39 it was established that double thermally ionized donors, formed during heat treatment (573–733 K) of Ge crystals containing oxygen, are restructured with the Fermi level near E_c—0.04 eV between two configurations: X_2—with shallow $E_2^{0/+}$ and $E_2^{+/++}$ levels and X_1—with a deep level of a two-electron $E_1^{0/+}$ state. The restructuring of a thermally ionized donor, giving rise to inversion of the $E^{0/+}$ level and long-time relaxation of the nonequilibrium conductivity, have also been observed in silicon.[40]

In Ref. 41 it was found that in the same germanium there exists a modification of configurationally bistable thermally ionized donors with negative effective correlation energy ($U<0$), which are formed at the initial stages of heat treatment of oxygen-containing Ge crystals at temperatures $T\leqslant 673$ K.

A model of the attachment of minority current carriers in a semiconductor containing U^--centers was studied in order to explain the long-time decay of photoconductivity, when the attachment process is affected by a spatial transition of the impurity, accompanied by a change in the energy of the electronic state. In addition, it was assumed that U^--centers do not directly affect recombination processes. The theory was compared with experimental data obtained for two types of bistable donors in *n*-Si-crystals.

Another example of a multistable defect in silicon, but this time associated with the complex $\mathrm{Fe}_i\mathrm{Al}_s$ (iron atom at an interstice and an aluminum atom at a lattice site) was described in Ref. 43. Charge-controlled reorientation of an $\mathrm{Fe}_i\mathrm{Al}_s$ pair occurred for $\langle 111\rangle$ and $\langle 100\rangle$ configurations accompanying the changes $\mathrm{Fe}_i^{++}\leftrightarrow\mathrm{Fe}_i^{+}$.

A configurationally bistable *C*-center in silicon was described in Ref. 44. This center, as also the pair $\mathrm{Fe}_i\mathrm{Al}_s$, exhibits a hole-attracting character. It is also known that there exist in silicon bistable centers associated with the carbon complex $\mathrm{C}_i\mathrm{C}_s$ with different electronic levels in different configurations.[45]

An amphoteric bistable center, which in different configurational positions can be an electron and a hole trap, was obtained in silicon doped with phosphorus to a concentration of the order of $10^{17}\ \mathrm{cm}^{-3}$ (Ref. 46). This center is probably associated with phosphorus, and the transformation temperature of the center is equal to 300 K. Interstitial boron in silicon also exhibits amphoteric *U*-negative properties.[47] A long lattice relaxation time is apparently characteristic for this center.

A defect associated with a phosphorus-vacancy-oxygen or carbon atom complex in silicon exhibits configurationally multistable properties. We also mention Refs. 49–54, where it was found that *A*-centers, thermally ionized donors, and other radiation-induced defects in silicon exhibit bistability.

A wide diversity of multistable centers has also been observed in semiconductors other than silicon and germanium. We mention only some of them: *EL* 2-center,[55] *DX*-center,[56] Be-As-complex in GaAs;[57] *M*-center with charge-controlled structural relaxation[58] and *W*-multistable center without a change in the charge state (because of strong electron-lattice interaction) in InP.[59] Finally, a new radiation-induced bistable defect, differing from the well-known defects of this type in GaAs in that its states exhibit temperature inversion, was studied in Ref. 60.

Thus it is becoming clear that multistability of defects in semiconductors is a widespread phenomenon and can be distinguished by its physicochemical content. Defects of the following type exist: thermal inversion multistable defects;[44–60] charge-controlled bistable centers;[43,44,47] configurationally bistable centers with a high degree of lattice relaxation;[59,61] defect centers manifesting U^--properties;[40,41,47,62] charge-controlled multistable centers with a high degree of lattice relaxation;[58] amphoteric bistable centers;[46,47] etc. Apparently, all possible types of multistable centers have not yet been identified and their structural characteristics and the types of electronic interactions at centers as a function of the type of semiconductor material have yet to be determined. These problems can be solved by developing theoretical models of such centers and by developing experimental methods for determining the electrophysical and structural parameters of these centers.

Thus the aim of the present paper is to construct a theory of cooperative interaction of different types of point defects and the effect of such an interaction on the distribution of these defects and the possible formation of clusters of impurities and intrinsic point defects, and to investigate photoconductivity in semiconductors with multistable impurity-defect complexes.

2. COOPERATIVE INTERACTION OF POINT DEFECTS AND THEIR SPATIAL DISTRIBUTION

1. A significant change in the conditions to which a semiconductor is exposed, for example, thermal annealing, can alter the behavior of point defects as a result of the change in the state and number of the defects themselves and the resulting change in the character and strength of the interaction between the defects. In the process, it is possible that cooperative interaction between point defects of different types will be manifested according to the thermodynamic model studied in Ref. 63.

This model of concentration-dependent reciprocal influence of point defects of different types is based on the concentration dependence of the increment to the free energy of a crystal as a result of the introduction of one point defect into the matrix of the lattice without the entropy part—the formation energy—$G_i(C_j)$ (the indices *i* and *j* are not equal to one another; they label the type of defect).

For example, in a system containing two types of point defects the increment to the free energy of the crystal can be written as follows:[63]

$$\Delta G=N_1G_1(C_2)+N_2G_2(C_1)-TS_c, \tag{1}$$

where $N_j=N_0C_j$ is the number of point defects of the *j*th type, N_0 is the number of lattice sites per unit volume, and S_c is the configurational entropy.

For sufficiently low concentrations, $C_j\ll 1$, the elastic interaction of the particles is weak. For this reason, elastic concentration-dependent reciprocal influence of point defects of the same type is usually taken into account for concentrations of the order of $10^{19}\ \mathrm{cm}^{-3}$ and higher,[64] while the facts presented in Sec. 1.1 as well as the data on the reciprocal influence on the solubility and migration of intrinsic point defects and impurity atoms[65] indicate that a dynamic interaction between defects of different types also occurs for much lower concentrations. This is the justification for introducing a cooperative interaction of the form (1) between point defects of different types.

In the diffusion equations for point defects

$$\partial_t C_j=\operatorname{div}\mathbf{J}_j \tag{2}$$

such a cooperative interaction can be taken into account either through the concentration dependence of the diffusion coefficient or by adding to the expression for the fluxes a term which determines the drift of point defects of one type in the gradient field of the concentration of point defects of a different type.

It is well known[66] that on the basis of linear nonequilibrium thermodynamics the fluxes of point defects can be represented as a linear combination of thermodynamic forces acting in the system. For isothermal diffusion these forces are the gradients of the particle chemical potentials of the point defects. For this reason, the expressions for the fluxes of point defects can be written as

$$\mathbf{J}_j=-\sum_{k=1}^{N}\frac{L_{jk}}{T}\nabla\mu_k. \tag{3}$$

In our case the indices denote the following: 1—vacancies (V), 2—interstitial intrinsic atoms of the lattice (I), 3—site impurity (A_s), 4—interstitial impurity (A_i), 5—intrinsic lattice atoms at a lattice site (S), and 6—unoccupied interstices (J).

The restriction to two elementary diffusion mechanisms—vacancy mechanism of diffusion (VMD) and interstitial mechanism of diffusion (IMD)—makes it possible to divide the system (3) into two subsystems of fluxes (along different sublattices), depending on the corresponding thermodynamic forces:

$$\text{a) } k,j=\{1,3,5\} - \text{for VMD; b) } k,j=\{2,4,6\} - \text{for IMD}. \tag{3'}$$

In the general case, of course, the off-diagonal coefficients L_{ik}, which, according to their physical meaning, express the correlation in the motion of particles of different types in the crystal, though they are not equal to zero are nonetheless negligibly small compared with the diagonal terms L_{ii}, which determine the correlation in the motion of particles of the same type.[67] As pointed out in Ref. 67, for VMD and IMD the motion of vacancies and site atoms as well as unoccupied interstices and interstitial atoms are correlated, i.e., a jump of an atom to a neighboring unoccupied site means a jump of the unoccupied site in the reverse direction. For this reason, because of the direct spatial correlation between atoms and unoccupied sites (or vacancies or unoccupied interstices) the corresponding off-diagonal kinetic coefficients will be of the same order of magnitude as the diagonal coefficients. We point out once again that there is no such direct correlation in the random jumps of atoms of different types. On the basis of the above remarks, K. P. Gurov *et al.*[67] analyzed the diffusion fluxes in a binary metallic system taking into account the short-range order of the interaction of atoms in the first configuration sphere for the vacancy mechanism of diffusion. This corresponds to the case a) of a subsystem of fluxes in the expression (3), when it is assumed that the diffusion interaction of atoms of different types is equal to zero, i.e., $L_{35}=L_{53}=0$. In addition, relations were derived between the diffusion coefficients of the particles.

We give a similar analysis for subsystems a) and b) of the expressions (3) taking into account the cooperative interaction introduced in Ref. 63 for point defects of different types. Calculating the partial chemical potentials $\mu_j=\partial\Delta G/\partial N_j$, we represent their gradients in terms of the gradients of the concentrations of the point defects:

$$\nabla\mu_j=\frac{kT}{C_j}\sum_k\varphi_{jk}\nabla C_k, \tag{4}$$

where the elements φ_{jk} have the form

$$\varphi_{jk}=\frac{C_j}{C_k}\frac{\partial\ln f_j}{\partial C_k}.$$

The matrix φ_{jk} is

$$\begin{pmatrix} 1 & -\varphi_{24} & 0\\ -\varphi_{42} & 1 & 0\\ 0 & 0 & 1\end{pmatrix},$$

in the case IMD (Ref. 63) and

$$\begin{pmatrix} 1 & 0 & \varphi_{31}\\ 0 & 1 & 0\\ \varphi_{31} & 0 & 1\end{pmatrix}.$$

in the case of VMD. The matrix of Onsager coefficients has the form

$$\begin{pmatrix} L_{22} & 0 & 0\\ 0 & L_{44} & 0\\ 0 & 0 & L_{66}\end{pmatrix}$$

for IMD (Ref. 63) and

$$\begin{pmatrix} L_{11} & L_{13} & L_{15}\\ L_{31} & L_{33} & 0\\ L_{51} & 0 & L_{55}\end{pmatrix}$$

for VMD.

Thus, with the help of the expression (4), the fluxes $\mathbf{J}_j$ in Eq. (3) can be represented as

$$\mathbf{J}_j=-\sum_k D_{jk}\nabla C_k, \tag{5}$$

where the so-called mutual diffusion coefficients D_{jk} have the form

$$D_{jk}=k\sum_i\frac{L_{ij}}{C_j}\varphi_{jk}.$$

The above assertion that the number of particles in the system is constant

$$\sum_i C_i=1,$$

$$\text{a) } i=2,\ 4,\ 6,\quad \text{b) } i=1,\ 3,\ 5$$

makes it possible to obtain some relations between the mutual diffusion coefficients from the expressions (5) for a) IMD and b) VMD.

Summing the kinetic equations for IMD and VMD, given by Eqs. (1), we obtain

$$\sum_i \operatorname{div}\mathbf{J}_i=0.$$

For the one-dimensional case we have

$$\sum_i\mathbf{J}_i=0.$$

This condition and the expressions for the fluxes in VMD and IMD permit the off-diagonal kinetic Onsager coefficients to be expressed in terms of the diagonal coefficients:

$$L_{26}=L_{62}=-L_{22};\ L_{46}=L_{64}=-L_{44};\ L_{66}=L_{22}+L_{44};$$
$$L_{15}=L_{51}=-L_{55};\ L_{13}=L_{31}=-L_{33};\ L_{11}=L_{33}+L_{55}.$$

Thus the matrix of diffusion coefficients can be represented in terms of the self-diffusion coefficients and the reciprocal influence coefficients:

a) for IMD

$$\begin{pmatrix} D_2^* & D_2^*\varphi_{24} & -D_2^*\dfrac{C_2}{C_6} \\ D_4^*\varphi_{42} & D_4^* & -D_4^*\dfrac{C_4}{C_6} \\ -(D_2^*+D_4^*\varphi_{42}) & -(D_2^*\varphi_{24}+D_4^*) & \left(D_2^*\dfrac{C_2}{C_6}+D_4^*\dfrac{C_4}{C_6}\right) \end{pmatrix}, \tag{6a}$$

b) for VMD

$$\begin{pmatrix} D_3^*\left(\dfrac{C_3}{C_1}+\varphi_{31}\right)+D_5^*\dfrac{C_5}{C_1} & -D_3^*\left(\dfrac{C_3}{C_1}\varphi_{13}+1\right)-D_5^*\dfrac{C_5}{C_1}\varphi_{13} & -D_5^* \\ -D_3^*\left(\dfrac{C_3}{C_1}+\varphi_{31}\right) & D_3^*\left(\dfrac{C_3}{C_1}\varphi_{13}+1\right) & 0 \\ -D_5^*\dfrac{C_5}{C_1} & D_5^*\dfrac{C_5}{C_1}\varphi_{13} & D_5^* \end{pmatrix}. \tag{6b}$$

It is obvious directly from the explicit expression for the elements of the matrix of diffusion coefficients that these coefficients are linked with one another by the relations for VMD and IMD separately:

$$\sum_i D_{ij}=0. \tag{7}$$

The expressions (7) indicate that when all migrating particles are taken into account the sum of the particle fluxes produced by an arbitrary gradient of the concentration of particles of a definite type is equal to zero, essentially because the number of sites (interstices) per unit volume is conserved.

In situations in semiconductors for which $C_x \gg C_2$, C_4 and $C_5 \gg C_1$, C_3 the matrices of coefficients (6) can be reduced to the following form:

$$\begin{pmatrix} D_2^* & D_2^*\varphi_{24} \\ D_4^*\varphi_{42} & D_4^* \end{pmatrix} \tag{6''a}$$

for IMD and

$$\begin{pmatrix} D_3^*\left(\dfrac{C_3}{C_1}+\varphi_{31}\right)+D_5^*\dfrac{C_5}{C_1} & -D_3^*\left(\dfrac{C_3}{C_1}\varphi_{13}+1\right)-D_5^*\dfrac{C_5}{C_1}\varphi_{13} \\ -D_3^*\left(\dfrac{C_3}{C_1}+\varphi_{31}\right) & D_3^*\left(\dfrac{C_3}{C_1}\varphi_{13}+1\right) \end{pmatrix} \tag{6''b}$$

for VMD. Naturally, in contrast to Eq. (6), the expressions (6″) do not permit relations similar to (7) to be derived.

We note that the drift fluxes of point defects in the cases of VMD and IMD are not identical—reciprocal influence (determined by the coefficients φ_{ij}) and direct spatial correlation (determined by the off-diagonal coefficients L_{ij}) of the corresponding particles in VMD are present together with concentration gradients, while in IMD there is no direct spatial correlation between the corresponding particles.

2. The model developed in the preceding section for the reciprocal influence of point defects of different types in semiconductors is one way to describe the possible changes occurring in the behavior of the defects. This suggest the obvious problem of studying the transformations ensuing in the spatial distribution of such defects when the departure from equilibrium is included and as a result of which a new annealing temperature of the semiconductor is established quite rapidly.

We shall perform a linear analysis of the stability of prescribed distributions point defects under conditions when the system of defects is driven out of equilibrium. For definiteness we assume that after the temperature changes the kinetics of the point defects is determined by the kick-out mechanism[14] taking into account the reciprocal influence of concentrations of migrating defects, which is described in our model by the drift term in the kinetic equations. Three types of defects participate in the kick-out mechanism. The reaction between these defects proceeds according to the scheme

$$A_i \underset{\nu_i k_I}{\overset{\nu_i}{\rightleftarrows}} A_s + I, \tag{8}$$

where $k_I = k_i C_s = C_i/C_I$, and ν_i and k_i are the rate and the equilibrium constant of the quasichemical reaction. Assuming that $C_s \gg C_i$, C_I holds, a system of kinetic equations can be written for two types of interstitial point defects—the intrinsic lattice atoms and impurity atoms—in the form

$$\begin{aligned} \partial_t C_i &= D_i \partial_{xx}^2 C_i - \partial_x (C_i m_{iI} \partial_x C_I) + \nu_i (k_I C_I - C_i), \\ \partial_t C_I &= D_I \partial_{xx}^2 C_I - \partial_x (C_I m_{Ii} \partial_x C_i) - \nu_i (k_I C_I - C_i), \end{aligned} \tag{9}$$

where

$$m_{jk} = -D_j^* \varphi_{jk} = D_j \frac{1}{kT}\left(\frac{\partial G_j}{\partial C_k} + \frac{\partial G_k}{\partial C_j}\right).$$

It is obvious that this system is quite general, since if we appropriately interpret the quantities in the equations the system will describe the kinetics of site impurity atoms and vacancies.

We now analyze the stability of the spatially uniform distribution C_{a0} with respect to small deviations. Taking the perturbation in the form $\delta C_a \simeq \exp(\lambda t + iqx)$ and linearizing the system (9) we obtain [assuming that $m_{iI}(x)$, $m_{Ii}(x) = \mathrm{const}$] the dispersion relation

$$\lambda^2+B_0\lambda+C_0=0,$$

where

$$B_0=\nu_i(1+k_I)+q^2(D_i+D_I),\ C_0=P_0q^4+R_0q^2,$$
$$P_0=D_iD_I-M_{i0}M_{I0},\ R_0=\nu_i(D_I+k_ID_i-k_IM_{I0}-M_{i0}),$$
$$M_{i0}=m_{iI}C_{i0},\quad M_{I0}=m_{Ii}C_{I0}.$$

Since λ is complex, the region of instability will be determined by the condition $\mathrm{Re}\,\lambda > 0$. For $q = 0$ the roots of the dispersion equation are $\lambda_{1,2} = 0, \ -\nu_i(1 + k_I)$, whence it follows that for large-scale fluctuations the system is always stable! Only the presence of fluctuations with $q = 0$ can lead to instability. The condition of instability with respect to the fluctuation wave vectors has the form

$$P_0q^2+R_0<0 \tag{10}$$

For certain values of P_0 and R_0 the condition (10) on q becomes a threshold condition. In this case the sufficient condition for development of threshold instability is

$$q^2>q_c^2=-\frac{R_0}{P_0}>0. \tag{10''}$$

The growth time of spatially nonuniform fluctuations, which is defined as the inverse of the positive root λ in the approximation $4|C_0|/B_0^2 \ll 1$, which presumes either that the corresponding values of the fluctuation wave vectors are small or the difference between the relative magnitude of the drift fluxes and the purely diffusion fluxes is small, is expressed as $\tau_n \approx B_0/C_0$, or in expanded form,

$$\tau_n \approx \frac{\tau_0^{-1}+q^2(D_i+D_I)}{(M_{i0}M_{I0}-D_iD_I)q^4+\tau_0^{-1}(1+k_I)^{-1}(M_{i0}-k_ID_i+k_IM_{I0}-D_I)q^2}, \tag{11}$$

where τ_0 is the decay time of spatially uniform fluctuations:

$$\tau_0^{-1}=\nu_i(1+k_I).$$

On the basis of the model adopted for the reciprocal influence of point defects of different types, with respect to the signs of the reciprocal influence coefficients 1) m_{iI}, $m_{Ii} < 0$ and 2) m_{iI}, $m_{Ii} > 0$ the expression for P_0 remains unchanged, in contrast to R_0, which is

$$\tau_0^{-1}\left(1+\frac{C_{i0}}{C_{I0}}\right)^{-1}\left(D_I+D_i\frac{C_{i0}}{C_{I0}}+|m_{iI}|C_{i0}+|m_{Ii}|C_{I0}\right)$$

in the first case and

$$\tau_0^{-1}\left(1+\frac{C_{i0}}{C_{I0}}\right)^{-1}\left(D_I+D_i\frac{C_{i0}}{C_{I0}}-|m_{iI}|C_{i0}-|m_{iI}|C_{I0}\right)$$

in the second case.

In the first case the inequality $R_0 > 0$ always holds. Then, in order for instability to appear, it follows necessarily from the condition (10) that $P_0 > 0$. This means that the product of drift fluxes should not exceed in magnitude the product of the diffusion fluxes for both types of point defects.

The values of P_0 are negative only when we have

$$\frac{1}{kT}\left|k_I^{-1/2}\frac{\partial G_I}{\partial \tilde{C}_i}+k_I^{1/2}\frac{\partial G_i}{\partial \tilde{C}_I}\right|>1, \tag{12}$$

where $\tilde{C}_j = C_j/C_{j0}$. The condition (12) is physically reasonable, and its seems that it can actually be satisfied, since it is determined not by the formation energy of intrinsic point defects itself, which is estimated to be several eV, but rather by the change in this energy as a result of the reciprocal influence of the concentrations. The magnitude of this change is comparable to kT. For example, for $kT \sim 0.1$ eV, which corresponds to 1000 °C, then in order for instability to arise the change must not be less than 0.1 eV. A sufficient condition for instability to arise is that the wave vectors of the fluctuations must exceed some critical value q_c, such as that required by the condition (10″). In this case, as is obvious from the foregoing discussion, an instability threshold necessarily exists.

We note that in all cases the instability of the uniform state is caused by the competition between the drift flux, which give rise to growth of fluctuations, and the diffusion flux, which dissipates the fluctuations. Quasichemical reactions also dissipate concentration fluctuations.

In the second case R_0 can be positive or negative. Therefore, for $R_0 > 0$ it is obvious from the condition (10) that P_0 must be negative, and hence the condition (10) is a necessary condition for growth of instability. As a result, the sufficient condition for growth of instability is once again a threshold condition. If $R_0 > 0$ holds, then in principle the instability can be threshold-free. This variant is possible, when we again have $P_0 < 0$, i.e., the condition (12) must be satisfied. But if in the case $R_0 < 0$ it is possible to have $P_0 > 0$, then

$$\frac{1}{kT}\left|k_I^{-1/2}\frac{\partial G_I}{\partial \tilde{C}_i}+k_I^{1/2}\frac{\partial G_i}{\partial \tilde{C}_I}\right|<1, \tag{13}$$

and once again the instability has a threshold.

For positive reciprocal-influence coefficients the physical situation with R_0—positive or negative—could be controlled by the ratio of the diffusion coefficients, the reciprocal-influence parameters, and the concentration levels. For example, setting $D_i = pD_I$ and $|m_{iI}| = p|m_{Ii}|$ we obtain

$$\frac{1+k_Ip}{1+p}>\frac{1}{kT}\left|\frac{\partial G_I}{\partial \tilde{C}_i}+k_I\frac{\partial G_i}{\partial \tilde{C}_I}\right|,\qquad R_0>0, \tag{14a}$$

$$\frac{1+k_Ip}{1+p}<\frac{1}{kT}\left|\frac{\partial G_I}{\partial \tilde{C}_i}+k_I\frac{\partial G_i}{\partial \tilde{C}_I}\right|,\qquad R_0<0. \tag{14b}$$

Satisfying both conditions simultaneously from the combinations (12) and (14a) as well as (13) and (14b) depends on the quantities p and k_I as well as T and the relative change in G_j with respect to the corresponding concentrations.

Obvious limits for q follow from the finiteness of the size L of the region and the existence of a smallest dimension a, the distance between point defects: $L^{-2} < q^2 < d^{-2}$.

Analysis of the formulas (14) shows that τ_n is a weak function of τ_0^{-1}, changing monotonically from the value

$$\tau_n(\tau_0^{-1}\to\infty)\approx\left(1+\frac{C_{i0}}{C_{I0}}\right)\left(M_{i0}+M_{I0}\frac{C_{i0}}{C_{I0}}-D_i\frac{C_{i0}}{C_{I0}}-D_I\right)^{-1}q^{-2}$$

to the value

$$\tau_n(\tau_0^{-1}\to 0)\approx(D_i+D_I)\,(M_{i0}M_{I0}-D_iD_I)^{-1}q^{-2}.$$

The fact that the limiting values of τ_n are independent of τ_0^{-1} stems from the fact that in Eq. (11) τ_0^{-1} is present in two terms, which have different meanings. The first term has the meaning of a recombination term, determining the vanishing of point defects of a given type according to the reaction (8) and therefore inhibiting the growth of concentration fluctuations. The second term determines the inflow of point defects of a given type in the fluctuations according to the same scheme, encouraging growth of these fluctuations. Simplifying τ_n further by setting $C_{i0}/C_{I0}\approx 1$ and $D_i\approx D_I=D$ in Eq. (11) we obtain

$$\tau_n\approx[Dq^2(S-1)]^{-1}, \tag{15}$$

where

$$S=\frac{\Delta}{kT},\qquad \Delta=\frac{\partial G_I}{\partial \tilde{C}_i}+\frac{\partial G_i}{\partial \tilde{C}_I}.$$

The growth time of nonuniform fluctuations with fixed q can be estimated for real values of the diffusion coefficients $D\sim 10^{-9}$ cm^{2}s^{-1} with $T=1000\,^\circ$C. For example, for $q^2\approx 10^6$–10^8 cm^{-2} the values of τ_n will be equal to 10–10^3 s.

In a semiconductor system with a large number of different types of point defects interacting by a more complicated interaction the conditions of realization and the parameters of instability of the initial impurity distributions accompanying a change in the temperature will naturally be different. As an example, consider a semiconductor with intrinsic point defects and impurity atoms of two different types. Suppose that the impurities significantly affect the mutual arrangement and distribution of defects in the lattice. Suppose that these impurities diffuse by the interstitial mechanism. We introduce the following notation: Let the index I denote intrinsic interstitial lattice atoms (IIA) and correspondingly let i and j denote the two types of impurities. In accordance with what we have said above, the diffusion equations will have the form

$$\begin{aligned}\partial_tC_I&=D_I\partial_{xx}{}^2C_I-\partial_x(C_Im_{Ii}\partial_xC_i)-\partial_x(C_Im_{Ij}\partial_xC_j),\\ \partial_tC_i&=D_i\partial_{xx}{}^2C_i-\partial_x(C_im_{iI}\partial_xC_I)-\partial_x(C_im_{ij}\partial_xC_j),\\ \partial_tC_j&=D_j\partial_{xx}{}^2C_j-\partial_x(C_jm_{jI}\partial_xC_I)-\partial_x(C_jm_{ji}\partial_xC_i).\end{aligned} \tag{16}$$

In some cases the IIA are more mobile than the impurity atoms. If we assume D_i, $D_j\ll D_I$, then because of the different rates of the diffusion of impurities and IIA we can introduce a characteristic relaxation time for the distribution of the concentration of IIA, estimated as $\tau_I\sim l^2/D_i$, where l is the characteristic distance between sinks of IIA.

According to the preceding assumption concerning the relaxation rate of the IIA concentration, the system of equations (16) can be divided into two subsystems, fast and slow.

The fast subsystem of equations ($t\ll\tau_I$) has the form

$$\begin{aligned}&\partial_tC_I=D_I\partial_{xx}{}^2C_I-\partial_x[C_I(m_{Ii}\partial_xC_i+m_{Ij}\partial_xC_j)]\\ &\qquad C_i(t)=\text{const},\\ &\qquad C_j(t)=\text{const}.\end{aligned} \tag{17a}$$

and the slower processes are described by the subsystem

$$\begin{aligned}\frac{C_I}{\tau_I}&=D_I\partial_{xx}{}^2C_I-\partial_x[C_I(m_{Ii}\partial_xC_i+m_{Ij}\partial_xC_j)],\\ \partial_tC_i&=D_i\partial_{xx}{}^2C_i-\partial_x[C_i(m_{iI}\partial_xC_I+m_{ij}\partial_xC_j)],\\ \partial_tC_j&=D_j\partial_{xx}{}^2C_j-\partial_x[C_j(m_{jI}\partial_xC_I+m_{ji}\partial_xC_i)].\end{aligned} \tag{17b}$$

Suppose that the changed thermal conditions are such that the interactions between the impurities are much stronger than the reciprocal influence of IIA and the impurities. Then the system (17) separates into two independent parts: an equation for IIA and a subsystem of diffusion equations for interacting impurities, which has the form

$$\begin{aligned}\partial_tC_i&=D_i\partial_{xx}{}^2C_i-\partial_x(C_im_{ij}\partial_xC_j),\\ \partial_tC_j&=D_j\partial_{xx}{}^2C_j-\partial_x(C_jm_{ji}\partial_xC_i).\end{aligned} \tag{18}$$

For $D_I\ll D_i$, D_j these equations, retaining their form (18), will determine the rapidly varying part of the general system (16).

It is useful to consider the problem of the impurity redistribution caused by changing physical conditions (thermal annealing). One can make a linear analysis of the stability of a given spatial distribution of impurities similarly to the case described in the preceding section, especially since the equations have a similar form (with the exception of the fact that the kick-out process is absent in the new kinetic equations).

Without giving the calculations, which are analogous to those done previously, we can see immediately that in this model of the reciprocal influence of impurities the development of growing mutually correlated fluctuations of the concentration of different types of impurities is possible only if

$$M_{ij}M_{ji}>D_iD_j, \tag{12''}$$

where $M_{ij}=m_{ij}C_{i0}$ and $M_{ji}=m_{ji}C_{j0}$. In this case the fluctuations corresponding to wave vectors $q>0$ will grow.

We can derive the following simplified form the growth time τ_n of spatially nonuniform fluctuations in the approximation $4|C_0'|/B_0'^2\ll 1$, which means that the deviation of the relative magnitudes of the products of the drift fluxes from the purely diffusion fluxes is small:

$$\tau_n\approx\frac{D_i+D_j}{q^2[M_{ij}M_{ji}-D_iD_j]}. \tag{19}$$

According to this expression, as expected, a long time is required for nonuniformities to develop on large scales, if the concentration-dependent interaction is not too strong, which in this model means that the product of the drift fluxes of impurities is not much greater than the product of the purely diffusion fluxes of the impurities. This time decreases as the concentration-dependent interaction of different types of point defects increases.

The necessary and sufficient condition (12″) is equivalent to the inequality (10) with the stipulation that there is no threshold for impurity stratification.

In Ref. 68 a gettering effect is reported for Au in P-doped n-Si with rapid thermal annealing. The investigations performed in Ref. 68 showed that the uniform preannealing profile of the distribution of the acceptor Au becomes nonuniform after rapid thermal annealing and separates into regions of high and low concentration. A complete explanation of the appearance of such variations is not given in Ref. 68.

Using the experimental values for the annealing temperature $T = 1000\,^{\circ}\mathrm{C}$ and the diffusion coefficient of the impurity $D = 7.5\cdot 10^{-6}$ cm²/s, we find that in order for concentration stratification to occur over average distances $\sim 75\,\mu$m, according to our formula (15), a time $\tau_n \approx 10$ s is required for $\Delta \approx 0.06$ eV, i.e., the results of Ref. 68 can be interpreted on the basis of the proposed cooperative interaction of defects of different types. With rapid thermal annealing this mechanism for the interaction of point defects can be activated between the defects Au–P or Au–V–P or Au–O.

Thus, generalizing the results of this section, we note that when temperature-induced concentration-dependent reciprocal influence of migrating IIA and impurities are present the spatially uniform state of these defects can become unstable with respect to concentration fluctuations. Depending on the values of the parameters of the problem, the growth of the fluctuations can have a threshold with respect to the wave vectors or it may be threshold-free. The stratification of a given distribution of impurities is all the more effective the stronger the concentration-dependent reciprocal influence is. The growth time for a periodic impurity distribution—regions of low and high concentration—with dimensions of, for example, 10^{-5} cm, is estimated to be of order of several seconds.

In the case of cooperative effects between IIA and an interstitial impurity, in the specific formulation of the problem with rapid transition to a new annealing temperature, rapid relaxation of the concentration of intrinsic point defects to equilibrium for the new annealing temperature can inhibit the manifestation of reciprocal influence of point defects of different types. Stratification will be possible if the growth time of the instability is shorter than the time required for the concentration of intrinsic point defects to relax to the equilibrium concentration. Since the absorption lifetime of excess IIA is approximately $\tau_I \approx l^2/D_I$, for $l \approx 10^{-2}$ cm and $D_I \approx 10^{-9}$ cm²/s we have $\tau_I \approx 10^5$ s, i.e., $\tau_I > \tau_n$.

We note that stratification of the spatially uniform state still does not mean that the decomposition of the solid solution of impurity or other point defects has started. Such a redistribution of impurities can result in effective binding of impurities in pairs and formation of impurity-defect complexes, which will affect the physical and electrophysical properties of the semiconductor. But in order to study the kinetics of pairs and complexes we must study the corresponding kinetic equations for these formations together with the system of kinetic-diffusion equations presented above for the impurities.

3. RESTRUCTURING IMPURITY-DEFECT COMPLEXES AND PHOTOCONDUCTIVITY IN SEMICONDUCTORS

A defect complex is usually associated with some impurity, and it is the impurity that mainly determines the electronic properties of the complex, so that we assume below that the multistable impurity is a restructuring defect complex. Restructuring of the complex means that the impurity moves from one spatial position in the lattice to another. In the model of configurational coordinates, as is well known, to each stable position of a point defect in the potential diagram there is associated a definite configurational coordinate Q. The energy of the transition from one stable configuration to another is determined by the height of the potential barrier separating these positions.

For definiteness, we consider an impurity of the donor type. Let this impurity have two stable positions, characterized by the configurational coordinates Q_s and Q_i. We denote the electronic states of the impurity in these positions by D_s^q and D_i^q, respectively. Here q determines the charge state of the impurity. In addition, in the neutral state the configuration Q_s is energetically favored, while in the positively charged state the configuration Q_i is favored (Fig. 1). The first position of the impurity corresponds to a deep electronic level in the forbidden band and the second position corresponds to a shallow level lying close to the conduction band (Fig. 2): For simplicity we assume that it is in fact located in the conduction band.[9] These arguments are plausible.[70,71]

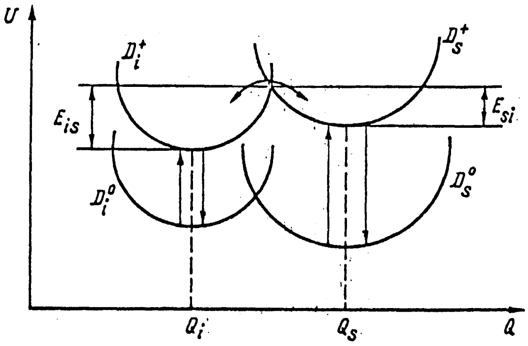

FIG. 1.

Assuming, in addition, in order to simplify the analysis, that the concentration of shallow acceptors N_a is lower than the total concentration of the donor impurity N_d ($N_a \leqslant N_d$), we obtain a situation when in equilibrium all shallow donors are in the state D_i^+. It is then obvious that at zero temperature $N_i^+ = N_a^-$ impurities remain in the shallow charge state; in the deep neutral state we have $N_s^0 = N_a - N_a^-$, and correspondingly, $N_s^+ \approx 0$ in the state D_s^+. Of course, the lifetime of the electrons with respect to recombination through the level $D_s \tau_n \approx (\gamma_n N_s^+)^{-1}$ will be infinite on the centers D_s^+ while the lifetime of the holes

$$\tau_p = (\gamma_p N_s^0)^{-1} = (\gamma_p (N_d - N_a))^{-1}$$

will be small because of the relatively large assumed concentration

$$N_s^0 \approx 10^{14} - 10^{16}\ \mathrm{cm}^{-3},$$

and the usual values of the recombination coefficient for trap-

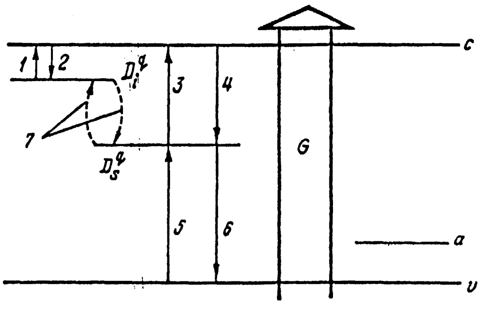

FIG. 2. Kinetic proceses in the model studied: *1*, *3*, *5* and *2*, *4*, *6* are generational recombination processes between the levels D_i^q and D_s^q from the valence band (v) and the conduction band (c); *7*—configurational transitions; *8*—photoproduction of nonequilibrium electron-hole pairs.

ping on a neutral center $\gamma_r^0 \approx 10^{-8}\ \mathrm{cm^3 \cdot s^{-1}}$ (Refs. 72, 73). As the temperature increases the transitions $D_i^+ \to D_s^+$ should start with probability (see, for example, Ref. 71)

$$W_{is} \sim \exp(-E_{is}/(kT)),$$

where E_{is} is the height of the energy barrier between the configurations Q_i and Q_s. It is obvious that the reverse transitions will also occur with probability W_{si} determined by the potential barrier of a different height E_{si}. For example, for not too large changes in the concentrations of shallow charged impurities $N_i^+ \approx N_a^-$, the concentration of centers under equilibrium conditions can be determined from the equation of detailed balance for impurity transitions: $N_i^+ = KN_s^+$, i.e., $N_s^+ \approx N_a^-/K$. From what we have said above it is obvious that

$$K = \exp(\Delta E/(kT)),$$

where $\Delta E = E_{is} - E_{si}$. The appearance of centers N_s^+ in turn results in an increase of the recombination processes for electrons through the state D_s^+. Correspondingly, the lifetime τ_n of the electrons decreases, i.e., recombination processes through these deep centers can become the principal processes not only for holes but also for electrons.

The changes in the recombination processes, analogous to the changes occurring when the temperature is varied in the scheme described above, can also be produced by external illumination. We note that changing the conditions of compensation with respect to the impurities ($N_a > N_d$) shuts down the recombination channel not only for electrons through the D_s^+ state but also for holes through the D_s^0 state at zero temperature. However, constant external illumination can once again open these recombination channels.

If the electron recombination processes are determined by the states D_s^+ and D_s^0, as described above, then in the presence of photoexcitation the concentrations of the excess free carriers are determined not only by the recombination parameters τ_n and τ_p, but also by the parameters of the transition of the impurity from the state Q_i into the state Q_s and vice versa.

We shall write out, according to the chosen model (Fig. 2), the kinetic equations for the electron density (n), the hole density (p), the density of defects in different configurational and charge states ($N_i^{0/+}$ and $N_s^{0/+}$), as well as the conditions of electric neutrality and conservation of the total number of defects of the donor type. But, in accordance with our assumptions, the lifetime of free electrons with respect to the level D_i^0 is very short, so that all shallow donors are ionized: $N_i^0 = 0$. In addition, not all equations of the system will be independent. For this reason, retaining only the independent equations, we have

$$\partial_t N_s^+ = N_i^+ w_{is} - N_s^+ w_{si} - N_s^+ n\gamma_{ns} + N_s^0 p\gamma_{ps} + \alpha_{ns} N_s^0 - \alpha_{ps} N_s^+, \tag{20}$$

$$\partial_t N_i^+ = -N_i^+ w_{is} + N_s^+ w_{si}, \tag{21}$$

$$\partial_t n = G - N_s^+ n\gamma_{ns} + \alpha_{ns} N_s^0, \tag{22}$$

$$N_i^+ + N_s^+ + p = n + N_a^-, \tag{23}$$

$$N_d = N_i^+ + N_s^0 + N_s^+, \tag{24}$$

where γ_{ns} and γ_{ps} are the coefficients for capture of electrons and holes on the level D_s; α_{ns} and α_{ps} are the coefficients of thermionic emission of electrons and holes from the level D_s; w_{is} and w_{si} are the probabilities for transitions of the impurity between the configurations Q_i and Q_s; and G is the rate of photoproduction of free charge carriers.

When there is no illumination the stationary (equilibrium) solutions for the desired concentrations have the form

$$N_{i0}^+ = KN_{s0}^+; \qquad N_{s0}^0 = N_{s0}^+ \frac{n_0}{n_t}; \qquad p_0 = \frac{n_t p_t}{n_0};$$
$$N_{s0}^+ = \frac{n_0 - n_t p_t/n_0 + N_a^-}{K+1}, \tag{25}$$

where n_0 is determined from the equation

$$n_0^3 + n_0^2 [n_t (K+1) + N_a^-] - n_0 n_t [(N_d - N_a^-) \times (K+1) + p_t] - n_t^2 p_t (k+1) = 0. \tag{26}$$

Here we have introduced the following notation

$$n_t = \frac{\alpha_{ns}}{\gamma_{ns}}, \qquad p_t = \frac{\alpha_{ps}}{\gamma_{ps}}, \qquad K = \frac{w_{si}}{w_{is}}.$$

For the case of a nondegenerate semiconductor and nondegenerate levels it is well known that[74]

$$n_t = N_c \exp(-e_t/kT),$$

where e_t is the depth of the electronic level $D_s^{+/0}$; N_c is the electron density of states in the conduction band.

In the absence of thermionic emission of holes from the level D_s^0 ($p_t \approx 0$) the equilibrium electron density in the band is determined by the formula

$$n_0^2 + n_0 [n_t (K+1) - N_a^-] - n_t (K+1)(N_d - N_a^-) = 0.$$

If $N_d \gg n_t (K+1)$ holds, then for $N_d \gtrsim N_a$ we have

$$n_0 \approx [(N_d - N_a^-)/N_a^-] n_t (K+1), \tag{27}$$

and for $N_d \gg N_a^-$ we have

$$n_0 \approx (N_d n_t (K+1))^{1/2}, \tag{28}$$

i.e., as expected, the electron density in the band depends strongly on the degree of compensation of the semiconductor.

When the charge carriers are excited with light whose intensity varies in time, for example, harmonically, the carrier density (and therefore also the photocurrent in the sample) follows the change in the intensity of the light, but with some delay, i.e., a phase shift appears between the photoexcitation and the photocurrent. The phase shifts depend on both the volume lifetime of the charge carriers and the probability of hops of the impurity into different configurational positions. As the frequency of modulation of the light increases the photocurrent begins to exhibit a frequency dependence. The amplitude of the photocurrent, just as the phase angle, depend on the quantities mentioned.

Since the lifetime of free holes, which is determined by the level D_s^0, is quite short and the lifetime of the free electrons, which is determined by the level D_s^+, remains quite long with low levels of illumination, it can be assumed that $\delta n \gg \delta p$. Then we can write the following equations for determining the desired nonequilibrium particle densities under the conditions of a weak harmonic band perturbation $\delta G = G_0 \exp(i\omega t)$ with frequency ω:

$$i\omega \delta N_{i0}^+ = -\delta N_{i0}^+ \tau_{is}^{-1} + \delta N_{s0}^+ \tau_{si}^{-1}, \tag{29}$$

$$i\omega \delta n_0 = G_0 - \delta N_{s0}^+ \tau_{nN}^{-1} - \delta n_0 \tau_n^{-1} + \delta N_{s0}^0 n_t \gamma_{ns}, \tag{30}$$

$$\delta N_{i0}{}^{+}+\delta N_{s0}{}^{+}\approx\delta n_0, \tag{31}$$

$$\delta N_{s0}{}^{+}+\delta N_{s0}{}^{0}+\delta N_{i0}{}^{+}=0, \tag{32}$$

where $\tau_{is\langle si\rangle}^{-1}=w_{is\langle si\rangle}$ and $\tau_{nN}^{-1}=\gamma_{ns}n_0$ is the probability that the center D_s^+ vanishes due to capture of an electron by the center. From the system (29)–(32) we can determine the density of the majority charge carriers

$$\delta n=\delta G \Big/ \left\{\frac{1}{\tau_n^*}+\frac{1}{\tau_{nN}}\frac{1+K+z^2}{(1+K)^2+z^2}+i\left(\frac{z}{\tau_{nN}}\frac{K}{(1+K)^2+z^2}+\omega\right)\right\},$$

where $z=\omega\tau_{is}$ and τ_n^* is the average lifetime of electrons in the band:

$$\tau_n^*=[\gamma_{ns}(N_s{}^{0+}+n_t)]^{-1}.$$

We represent δn in the form

$$\delta n=\delta n_0\exp[i(\omega t-\varphi(\omega))], \tag{33}$$

where the real amplitude of the density of nonequilibrium carriers is given by

$$\delta n_0=G_0\tau_n^* \Big/ \left\{\left[1+\frac{\tau_n^*}{\tau_{nN}}\frac{1+K+z^2}{(1+K)^2+z^2}\right]^2+(\tau_n^*z)^2\left[\frac{1}{\tau_{nN}}\frac{K}{(1+K)^2+z^2}+\frac{1}{\tau_{is}}\right]^2\right\}^{1/2}, \tag{34}$$

and the tangent of the phase shift angle $\varphi(\omega)$ in the majority carrier density—electrons (or photocurrent)—relative to the phase of the irradiating light has the form

$$\mathrm{tg}\,\varphi(\omega)=z\left\{\frac{\tau_n^*}{\tau_{is}}+\frac{\tau_n^*}{\tau_{nN}}\frac{K}{(1+K)^2+z^2}\right\}\Big/\left\{1+\frac{\tau_n^*}{\tau_{nN}}\frac{1+K+z^2}{(1+K)^2+z^2}\right\}. \tag{35}$$

Measurements of the phase relations of signals can now be easily performed experimentally with high accuracy, in particular, in connection with the development of photoacoustic methods of investigation,[75] so that we shall focus our attention on the phase relation (35) and the information which can be extracted from it.

It is obvious from the expression (35) that for both low frequencies ($z\ll 1$) and high frequencies $\tan(\varphi(\omega))$ asymptotically approaches linear functions of frequency with different slopes (see Fig. 3); also, the slope at low frequencies is larger than at high frequencies.

If the ratio of the probabilities is such that $\tau_{nN}^{-1}\ll(\tau_n^*)^{-1}$ holds, then for high frequencies ($z\gg 1+K$) the slope is equal to the lifetime of the electrons τ_n^*, as in the usual case.[76] We note that if the ratio of the probabilities is reversed, then the slope is equal to the time τ_{nN}. This situation is possible when $N_d/N_a^-\gg 1$, and therefore the electron density in the band in the corresponding temperature interval is determined by the formula (23) while the density of holes in the level corresponding to the state D_s^+ is

$$N_{s0}{}^{+}\approx n_0/(1+K),$$

which is greater than n_t.

At low frequencies we obtain under the same conditions

$$\mathrm{tg}\,\varphi(\omega)\approx\omega\tau_{is}(1/4-1/2),$$

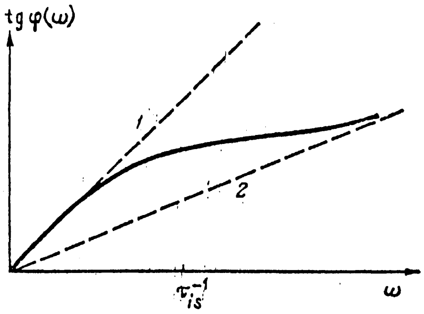

FIG. 3. Qualitative frequency dependence of the tangent of the phase shift angle (the case $\tau_{is}\gg\tau_n^*$). The slope of the straight line *1* is equal to $(1/2-1/4)\tau_{is}$ and the slope of the straight line *2* is equal to τ_n^*.

i.e., a possibility opens up for determining directly the parameter τ_{is} of the transition of the impurity.

If, however, $N_d/N_a^-\gg 1$ holds, then the density $n_0(T)$ has the same form and $\tan(\varphi(\omega))$ contains, aside from τ_{is}, the ratio

$$Kn_0/[(N_{s0}{}^{+}+n_t)(1+K)^2].$$

For this reason, in this case additional information is required about the value of the energy e_t, the concentration of acceptors N_a and donors N_d, and the quantity K. For low frequencies it is assumed that the sum of the probabilities ($w_{is}+w_{si}$) of the transitions $D_i^+\leftrightarrow D_s^+$ is much lower than the probability of annihilation of the center D_s^+ as a result of capture of an electron:

$$(\tau_{is}{}^{-1}+\tau_{si}{}^{-1})\ll\gamma_{ns}n_0.$$

This assumption makes it possible to estimate the energy difference

$$\Delta E=E_{is}-e_t\gtrsim kT\ln\left|\frac{10\nu_0}{\gamma_{ns}N_c(N_d-N_a^-)/N_a^-}\right|$$

where ν_0 is the oscillation frequency of the atom in the lattice.

For example, for the characteristic times in Si, $m_n\approx 0.5m_e$, $\gamma_{ns}\approx 10^{-3}\ \mathrm{cm^3\cdot s^{-1}}$, $\nu_0\approx 10^{13}\ \mathrm{s^{-1}}$, and degree of compensation $(N_d-N_a)/N_a\approx 0.1$ at room temperature $kT\approx 0.026$ eV, we obtain the completely satisfactory estimates $\Delta E=E_{is}-e_t\gtrsim 0.045$ eV.

Thus when the configurational transition of impurities is taken into account a characteristic functional dependence $\tan(\varphi(\omega))$ appears. By measuring the phase shift in the entire frequency range of interest, both τ_n^* and τ_{is} can be determined by analyzing the functional dependences. The height of the energy barrier E_{is} can be determined, in principle, by supplementing frequency measurements with temperature measurements.

Thus the proposed cooperative interaction between point defects of different types in semiconductors can be significant if the concentration of defects is sufficiently low (10^{14}–$10^{17}\ \mathrm{cm^{-3}}$). The temperature-induced cooperative interaction can result in stratification of the spatially uniform distribution of point defects into regions of high and low density. The conditions for instability of the initial distribution of point defects relative to the wave vectors of the concentration fluctuations and the growth time of the concentration nonuniformities depend on the lattice temperature, the diffusion coefficients, the concentration levels, and the concentration-induced change in the formation energy of defects.

The redistribution of defects due to cooperative interaction can result in the formation of an impurity-defect complex with bound-electron levels of variable depth. For this reason methods for measuring the electronic properties of such complexes and theoretical analysis of different models become important. Investigation of photoconductivity is found to be an effective method for these purposes. The characteristic electronic properties of these complexes can be determined from the frequency dependences of the phase shift of the photoconductivity. By supplementing frequency measurements with temperature measurements it is possible to determine the height of the energy barrier separating stable positions of a complex in the lattice. The appearance of a complicated frequency dependence of the tangent of the phase shift angle can be used as a test for observing bistable impurity-defect complexes.

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