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PROCESSES OF HEAT AND MASS TRANSFER IN SOLID BODIES

MODELING OF DIFFUSION MASS TRANSFER OF IMPLANTED DOPANTS IN SILICON. I. FORMULATION OF THE MODEL

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A generalized model of diffusion mass transfer of implanted dopant atoms (donors and acceptors) in crystalline silicon has been developed. It takes into account all possible charge states of diffusing species (vacancies, interstitial Si atoms, and "dopant atom–vacancy" and "dopant atom–interstitial silicon atom" pairs) and the difference between the diffusion coefficients of differently charged pairs. Expressions for the source/sink terms are derived which describe all bimolecular reactions between the species (generation and annihilation) in the course of diffusion with account for their charges.

Introduction. The main trend in the development of the technology of very large-scale integrated (VLSI) circuits is a further increase in the degree of integration, that is, an increase in the number of transistors per unit area and creation of multilayer heterostructures. This has led to the appearance of the so-called ultrashallow *p–n* junctions (USJ). The leading manufacturers of VLSI circuits are carrying out investigations directed at the reduction of the depth of USJ to $L \leq 10$ nm.

At the present time, a basic means of obtaining USJ is ion implantation of dopants (donors (As, P, Sb) or acceptors (B, Al)) into silicon at a relatively low energy and high dose of atoms with subsequent annealing to electrically activate them. In the case of high-temperature annealing there is diffusion of dopant atoms, which is accompanied by interaction with nonequilibrium point defects. The choice of the correct regime of annealing is needed to obtain the required profile of the concentration of donors or acceptors over the depth, which determines the properties of *p–n* junctions in VLSIC and the characteristics of the entire device. Therefore investigation of diffusion mass transfer of implanted atoms in silicon plays an important role in the technology of VLSI circuits (see reviews [1–3]), with mathematical stimulation being widely used for the purpose [4].

However, in the mathematical models developed to date [5–9, etc.] such important factors as the presence of different charge states of diffusing species and their interaction with one another (for example, annihilation/generation of point defects) in the course of homogenizing are not taken into account in full measure. In view of this, the aim of the present work is to formulate a generalized model of diffusion of implanted atoms in silicon with accounts for all possible charge states of both nonequilibrium point defects (vacancies and interstitial atoms) and diffusing complexes (vapor) of the type of "dopant atom–vacancy" and "dopant atom–interstitial atom of silicon," as well as interactions of dissimilar species during diffusion.

Physical Foundations of the Model. The physics of diffusion in silicon has been well studied [1–3]. In contrast to metals where "direct" mechanisms of diffusion operate (a vacancy mechanism for substitutional atoms and an interstitial one for interstitial atoms) [10, 11], in a covalent silicon crystal there are "indirect" mechanisms owing their origin to the interaction of dopant atoms with point defects (vacancies V and interstitial silicon atoms I). The following elementary reactions of the lattice dopant atom A with a point defect are possible: A + V $\leftrightarrow$ AV (formation of the A–vacancy pair); A + I $\leftrightarrow$ A_i (kick-out of the atom A by the interstitial atom Si leading to the formation of the

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interstitial dopant atom A_i); A + I ↔ AI (formation of the "atom A–interstitial atom Si" pair, which occupies one position in the crystal lattice — the so-called interstitialcy defect); A ↔ A_i + V (dissociation reaction). Since dopant atoms in the interstitial and interstitialcy positions are experimentally indistinguishable, diffusion of the AI complexes (pairs) is considered, where AI is understood to be both an interstitialcy and an interstitial atom A_i, which can be displaced only due to constant interaction with interstitial atoms of Si [2, 3]. Because of the presence of the binding energy between the dopant atom A and a vacancy located even at the position of the third nearest neighbor of this atom, the diffusion of AV pairs is considered, and the lattice atoms A are regarded as immobile [1–3].

Depending on the local configuration in the crystal lattice of silicon the point defects (vacancies and silicon self-interstitials) may have an electric charge ±1, ±2, or 0 [2]. The A atoms at the sites of the crystal lattice have a charge +1 (donors) or −1 (acceptors). They can form diffusing complexes $(AX)^{\alpha}$, $\alpha = 0, \pm 1$, with neutral X^0 and oppositely charged point defects: the donors pair with the X^- and $X^{=}$ species and the acceptors — with the X^+ and X^{++} defects, X ≡ V, I. The total diffusion flow of dopant atoms is composed of the flows of AX pairs located in different charge states. This is accompanied by the appearance of an internal electric field, which influences the diffusion of charged particles.

In order to construct a model it is first of all necessary to determine the relationship between the concentrations of diffusing species (V, I, AV, AI) in different charge states.

Concentration of Diffusing Species. In a semiconductor a simple relationship between the concentrations of electrons n, holes p, and "intrinsic" charge carriers n_i holds:

$$n_i^2 = np \quad \text{or} \quad \frac{n_i}{p} = \frac{n}{n_i}, \tag{1}$$

where the temperature dependence of n_i is known from the literature [2].

The concentration of vacancies $C_{V^{\alpha}}$ and interstitial silicon atoms $C_{I^{\alpha}}$ in a charge state α, $\alpha = \pm 1, \pm 2$, are connected with the concentrations of the corresponding neutral defects ($\alpha = 0$) by the relations [2]

$$C_{X^{\alpha}} = K_{X^{\alpha}} C_{X^0} \left(\frac{n}{n_i}\right)^{-\alpha}, \quad X \equiv V, I. \tag{2}$$

The coefficients $K_{X^{\alpha}}$ have the meaning of equilibrium constants of the reactions of interaction of the neutral defect X^0 (X ≡ V, I) with electrons:

$$X^0 + \alpha e^- \leftrightarrow X^{\alpha}, \quad K_{X^{\alpha}} = \frac{C^*_{X^{\lambda}}}{C^*_{X^0}} \left(\frac{n}{n_i}\right)^{-\alpha}, \quad \alpha = \pm 1, \pm 2. \tag{3}$$

It is clear that $K_{X^0} = 1$ for $\alpha = 0$. The values of K_{X^0}, X ≡ V, I, at different temperatures are known [12, 13]. Then the total concentration of the point defects $C_X = \sum_{\alpha} C_{X^{\alpha}}$, where $\alpha = 0, \pm 1, \pm 2$, is expressed in terms of the concentration of neutral defects:

$$C_X = C_{X^0} \psi_X, \quad \psi_X = \sum_{\alpha=-2}^{+2} K_{X^{\alpha}} \left(\frac{n}{n_i}\right)^{-\alpha}, \quad X \equiv V, I. \tag{4}$$

For an "intrinsic", i.e., defectless undoped semiconductor, when $n = p \equiv n_i$, the equilibrium concentrations of neutral defects are interrelated as

$$C^*_{X^0} = \frac{C^*_X}{\psi^*_X}, \quad \psi^*_X = \sum_{\alpha=-2}^{+2} K_{X^{\alpha}}, \quad X \equiv V, I. \tag{5}$$

We will express the coupling between the total concentration of the pairs $C_{(AX)} = \sum_{\alpha} C_{AX^{\alpha}}$, $\alpha = 0, \pm 1$, $X \equiv V, I$, and the quantities $C_{AX^{\alpha}}$, $\alpha = 0, \pm 1$, for acceptors and donors; to be specific, we take B^- and As^+. As a reference state we adopt the pairs formed in the course of the reaction of a dopant atom with a neutral defect X^0, i.e., $(BX)^-$ and $(AsX)^+$.

The boron atoms form the $(BX)^{\alpha}$ pairs in the reactions $B^- + X^{\alpha+1} \leftrightarrow (BX)^{\alpha}$, for which the equilibrium constants are expressed as

$$K_{B^-X^{\alpha+1}} = \frac{C^*_{(BX)^{\alpha}}}{C^*_{B^-} C^*_{X^{\alpha+1}}}, \quad \alpha = 0, \pm 1 . \tag{6}$$

For small departures from equilibrium we may write

$$C_{(BX)^{\alpha}} = B_{B^-X^{\alpha+1}} C_{B^-} C_{X^{\alpha+1}} . \tag{7}$$

Summing up (7) over the charge states α, subject to Eqs. (1) and (2), we obtain

$$C_{(BX)^{\alpha}} = \frac{C_{BX}}{\xi_X^{(a)}} K_{B^-X^{\alpha+1}} K_{X^{\alpha+1}} \left(\frac{p}{n_i}\right)^{\alpha+1}, \quad \alpha = 0, \pm 1 , \tag{8}$$

where

$$\xi_X^{(a)} = \sum_{\alpha=0}^{+2} K_{B^-X^{\alpha}} \left(\frac{p}{n_i}\right)^{\alpha}, \quad X \equiv V, I . \tag{9}$$

For the donor (As) the following reactions of the formation of pairs are possible: $As^+ + X^{\alpha-1} \leftrightarrow (AsX)^{\alpha}$, $\alpha = 0, \pm 1$. By analogy with Eqs. (7)–(9) we obtain

$$C_{(AsX)^{\alpha}} = \frac{C_{AsX}}{\xi_X^{(d)}} K_{As^+X^{\alpha-1}} K_{X^{\alpha-1}} \left(\frac{n}{n_i}\right)^{1-\alpha}, \quad \alpha = 0, \pm 1 , \tag{10}$$

$$\xi_X^{(d)} = \sum_{\alpha=-2}^{0} K_{As^+X^{\alpha}} \left(\frac{n}{n_i}\right)^{-\alpha}, \quad X \equiv V, I . \tag{11}$$

Continuity Equations. As a basis the so-called five-stream model was taken, which is described schematically in [12, 14]. In simplified modifications such an approach was applied to analyze the diffusion of dopants in silicon under different conditions [15, 16]. Since diffusing in silicon are the vacancies V, interstitial atoms of Si, and mobile pairs (complexes) AV and AI which interact with one another while the dopant atoms A at the lattice sites are immobile, we must write five equations of reaction diffusion:

$$\frac{\partial C_I}{\partial t} = -\operatorname{div} J_I - \frac{1}{\omega} (R_{I-V} + R_{A-I} + R_{AV-I}) , \tag{12}$$

$$\frac{\partial C_V}{\partial t} = -\operatorname{div} J_V - \frac{1}{\omega} (R_{I-V} + R_{A-V} + R_{AI-V}) , \tag{13}$$

$$\frac{\partial C_{AV}}{\partial t} = -\operatorname{div} J_{AV} + \frac{1}{\omega}(R_{A-V} - R_{AV-I} - R_{AV-AI}), \tag{14}$$

$$\frac{\partial C_{AI}}{\partial t} = -\operatorname{div} J_{AI} + \frac{1}{\omega}(R_{A-I} - R_{AI-V} - R_{AV-AI}), \tag{15}$$

$$\frac{\partial C_{A}}{\partial t} = \frac{1}{\omega}(R_{AI-V} + R_{AV-I} + 2R_{AV-AI} - R_{A-I} - R_{A-V}). \tag{16}$$

Here C_A is the concentration of the lattice atoms A; J_Y denotes diffusion flows (Y ≡ V, I, AV, AI), R_{X-Y} are the sources/sinks having the meaning of the rates of reactions between the species of kind X and Y (X, Y ≡ A, V, I, AV, AI, X ≠ Y); $\omega = a_0^3$ is the volume of the lattice cell of silicon. In the present work, the sources/sinks associated with the formation and evolution of A_mX_n-type clusters and extended defects (e.g., dislocations and the so-called {311}-defects) are not taken into account; they are the subject of separate studies [17 etc.]. Equations (12)–(16) have been written for total concentrations diffusing species, i.e., they include all their charge states.

Since electrons and holes are much more mobile than the diffusing species V, I, AV, and AI, Eqs. (12)–(16) should be supplemented with the condition of electrical neutrality:

$$\sum_{\alpha=\pm1,\pm2} \alpha C_{X^\alpha} + \sum_{\beta=\pm1} \beta C_{(AX)^\beta} + \gamma C_{A^\gamma} + p - n = 0, \quad X \equiv V, I, \quad \gamma = 1 \text{ or } -1. \tag{17}$$

Next it is necessary to determine the diffusion flows J_Y with account for the drift of charged species in the internal electric field and the sources/sink terms R_{X-Y}.

Diffusion Flows. We will consider separately the diffusion flows of point defects (vacancies and interstitial atoms of silicon) and AV and AI pairs.

Diffusion of point defects. For a defect of the X type (X ≡ V, I) with a charge α the expression for the flow with account for the effect of internal electric field has the form [2, 18]

$$J_{X^\alpha} = -D_{X^\alpha} \nabla C_{X^\alpha} + \mu_{X^\alpha} \alpha q \varepsilon C_{X^\alpha}. \tag{18}$$

Here D_{X^α} is the diffusion coefficient of X^α species; μ_{X^α} is the mobility determined from Einstein's relation $\mu_{X^\alpha} = D_{X^\alpha}/(k_BT)$; $\varepsilon = -\nabla\varphi$. Using the Boltzmann distribution of charge carriers in an electric field $n = n_i \exp[q\varphi/(k_BT)]$, we obtain $\varepsilon = -(k_BT/q)(n_i/n)\nabla(n/n_i)$. With account for the foregoing, we transform (18) accepting the assumption that the diffusion coefficient of point defects is independent of their charge $D_{X^\alpha} = D_X$ and using relation (1):

$$J_{X^\alpha} = -D_X\left(\nabla C_{X^\alpha} - \alpha C_{X^\alpha} \nabla \ln \frac{p}{n_i}\right). \tag{19}$$

For defects of the X type the total diffusion flow is equal to $J_X = \sum_\alpha J_{X^\alpha}$. Then from Eq. (19) with the aid of relations (2) and (4) we obtain

$$J_X = -D_X\left(\nabla C_X - C_X \nu_X \nabla \ln \frac{p}{n_i}\right), \quad \nu_X = \frac{1}{\psi_X} \sum_{\alpha=-2}^{+2} \alpha K_{X^\alpha} \left(\frac{p}{n_i}\right)^\alpha, \quad X \equiv V, I. \tag{20}$$

The values of the diffusion coefficients of point defects D_X are known from the literature [2, 3, 19].

Diffusion of the AV and AI pairs. We will consider the diffusion flows of the AX pairs, X ≡ V, I, for the atoms of acceptors (B^-) and donors (As^+), since for them the connection between the concentrations of pairs in different charge states is expressed differently (see Eqs. (8)–(11)).

For the acceptor (B^-) the diffusion flow of the $(BX)^\alpha$ pairs, $\alpha = 0, \pm 1$, is described similarly to (19) with account for the difference between the diffusion coefficients for different charge states. Substituting (8) into (19) and performing transformations, we obtain

$$J_{(BX)^\alpha} = -D_{(BX)^\alpha} B_{B^-X^{\alpha+1}} K_{X^{\alpha+1}} \left(\frac{p}{n_i}\right)^{\alpha+1} \left(\nabla \frac{C_{BX}}{\xi_X^{(a)}} + \frac{C_{BX}}{\xi_X^{(a)}} \nabla \ln \frac{p}{n_i}\right). \tag{21}$$

The total flow is determined as a sum over charge states $J_{BX} = \sum_\alpha J_{(BX)^\alpha}$. Then from (21), having differentiated the term $C_{BX}/\xi_X^{(a)}$ subject to expression (9), we obtain

$$J_{BX} = -\frac{1}{\xi_X^{(a)}} \sum_{\alpha=-1}^{+1} D_{(BX)^\alpha} K_{B^-X^{\alpha+1}} K_{X^{\alpha+1}} \left(\frac{p}{n_i}\right)^{\alpha+1} \left(\nabla C_{BX} + C_{BX} \frac{\eta_X^{(a)}}{\xi_X^{(a)}} \nabla \ln \frac{p}{n_i}\right), \tag{22}$$

where for the acceptor dopant

$$\eta_X^{(a)} = K_{B^-X^0} - K_{B^-X^{++}} K_{X^{++}} \left(\frac{p}{n_i}\right)^2, \quad X \equiv V, I. \tag{23}$$

Equation (22) contains the diffusion coefficients of the $(BX)^\alpha$ pairs, $\alpha = 0, \pm 1$, which are not equal between themselves. Once their values can be evaluated on the basis of experimental data on diffusion, Eq. (22) can be used for modeling.

In order to reduce the number of diffusion coefficients the following approach is possible [12]. The difference between the activation energies of the migration of the $(BV)^-$ and $(BV)^0$ complexes is due to the difference in the binding energy E_b in them:

$$\frac{D_{(BX)^0}}{D_{(BX)^-}} = \rho_{BX}^- = \exp\left(-\frac{\Delta E_b}{k_B T}\right), \tag{24}$$

where $\Delta E_b = E_b(B^-/X^+) - E_b(B^-/X^0) = 0.3$ eV, and this difference is electrostatic in character [12]. Therefore for the diffusion coefficients of the $(BX)^+$ and $(BX)^0$ pairs we may write

$$\frac{D_{(BX)^+}}{D_{(BX)^0}} = \rho_{BX}^+ \tag{25}$$

and adopt that $\rho_{BX}^+ = \rho_{BX}^- \equiv \rho_{BX}$, X ≡ V, I. Then Eq. (22) will be rewritten in the form

$$J_{BX} = -D_{(BX)^0} \frac{\theta_X^{(a)}}{\xi_X^{(a)}} \left(\nabla C_{BX} + C_{BX} \frac{\eta_X^{(a)}}{\xi_X^{(a)}} \nabla \ln \frac{p}{n_i}\right), \tag{26}$$

$$\theta_X^{(a)} = \sum_{\alpha=0}^{+2} K_{B^-X^\alpha} K_{X^\alpha} (\rho_{BX})^{\alpha-1} \left(\frac{p}{n_i}\right)^\alpha, \quad X \equiv V, I. \tag{27}$$

Using the analogy with Eqs. (19), (21), and (22) and taking into account Eqs. (10) and (11), for the donor dopant (atoms As^+) we obtain the following expression for the total diffusion flow of the AsX pairs in all of the charge states $\alpha = 0, \pm 1$:

$$J_{AsX} = -\frac{1}{\xi_X^{(d)}} \sum_{\alpha=-1}^{+1} D_{(AsX)^\alpha} K_{As^+X^{\alpha-1}} K_{X^{\alpha-1}} \left(\frac{n}{n_i}\right)^{1-\alpha} \left(\nabla C_{AsX} + C_{AsX} \frac{\eta_X^{(d)}}{\xi_X^{(d)}} \nabla \ln \frac{n}{n_i}\right), \tag{28}$$

$$\eta_X^{(d)} = K_{As^+X^0} - K_{As^+X^=} K_{X^=} \left(\frac{n}{n_i}\right)^2, \quad X \equiv V, I. \tag{29}$$

For the donors (atoms P^+) the difference between the energies of the interatomic bond in the $(PX)^-$ and $(PX)^0$ pairs is equal to $\Delta E_b = E_b((PX)^-) - E_b((PX)^0) = 0.3$ eV, which is the reason for the difference between the corresponding diffusion coefficients [20]. Using this value of ΔE_b for the atoms As^+, we introduce the following relations by analogy with Eqs. (24) and (25):

$$\frac{D_{(AsX)^-}}{D_{(AsX)^0}} = \rho_{AsX}^- = \exp\left(-\frac{\Delta E_b}{k_B T}\right), \quad \frac{D_{(AsX)^0}}{D_{(AsX)^+}} = \rho_{AsX}^+ \tag{30}$$

and assume that $\rho_{AsX}^+ = \rho_{AsX}^- \equiv \rho_{AsX}$, $X \equiv V, I$. Then Eq. (28) takes the form

$$J_{AsX} = -D_{(AsX)^0} \frac{\theta_X^{(d)}}{\xi_X^{(d)}} \left(\nabla C_{AsX} + C_{AsX} \frac{\eta_X^{(d)}}{\xi_X^{(d)}} \nabla \ln \frac{n}{n_i}\right), \tag{31}$$

$$\theta_X^{(d)} = \sum_{\alpha=-2}^{0} K_{As^+X^\alpha} K_{X^\alpha} (\rho_{AsX})^{-\alpha-1} \left(\frac{n}{n_i}\right)^{-\alpha}, \quad X \equiv V, I. \tag{32}$$

Thereby all the diffusion flows entering into Eqs. (12)–(15) have been determined.

Expressions for Sources/Sinks. In describing the rate of recombination of nonequilibrium point defects (the term R_{I-V} in Eqs. (12) and (13)), the assumption on a small departure from equilibrium is usually used and, without account for charge states, this rate is determined in the form

$$R_{I-V} = 4\pi r (D_I + D_V)(C_I C_V - C_I^* C_V^*), \tag{33}$$

where the radius of capture r is taken to be equal to the period of the silicon lattice: $r = a_0 = 0.235$ nm [2, 18, 21].

To take into account different charges of the interstitial silicon atoms Si and vacancies $C_I C_V - C_I^* C_V^*$ in (33) should be replaced by the sum over charge states $\sum_{\alpha,\beta} (C_{I^\alpha} C_{V^\beta}) - C_{I^\alpha}^* C_{V^\beta}^*$, $\alpha, \beta = 0, \pm 1, \pm 2$, since, as noted above, the diffusion coefficient of point defects is independent of their charge. To simplify the representation, we assume that the radius of interaction r is also independent of the charges of point defects and is equal to a_0 [2]. To reduce the number of possible variants, we will consider pair reactions of recombination of a charged defect of the same type (I or V) with a neutral defect of another type, i.e., the following nine pairs: $I^0 + V^0$, $I^- + V^0$, $I^= + V^0$, $I^+ + V^0$, $I^{++} + V^0$, $I^0 + V^-$, $I^0 + V^=$, $I^0 + V^+$, and $I^0 + V^{++}$. Then, using Eqs. (2), (4), and (5), we obtain

$$R_{I-V} = 4\pi a_0 (D_I + D_V)\, \varphi_{I-V} \left(\frac{C_I}{\psi_I}\frac{C_V}{\psi_V} - C_{I^0}^* C_{V^0}^*\right), \quad \varphi_{I-V} = \psi_I + \psi_V - 1. \tag{34}$$

We will describe the kinetics of the formation of the "dopant atom–point defect" pairs (the terms R_{A-I} and R_{A-V} in Eqs. (12)–(16)) for the atoms of the acceptor $A \equiv B^-$. For the reaction of the formation of the $(BX)^\alpha$ pair, $\alpha = 0, \pm1$, $X \equiv V, I$, the equilibrium constant (see Eq. (6)) has the meaning of the ratio of the constants of the rates of direct and reverse reactions: $K_{B^-X^{\alpha+1}} = k_f^\alpha / k_r^\alpha$. With a small departure from equilibrium for one charge state α we may write

$$R_{B-X}^\alpha = k_f^\alpha C_{B^-} C_{X^{\alpha+1}} - k_r^\alpha C_{(BX)^\alpha}, \quad k_f^\alpha = 4\pi r D_X, \tag{35}$$

where it is adopted that $r = a_0$ [2]. For all charge states the rate of formation of BX pairs will be determined as a sum over α, and from Eq. (35), subject to Eqs. (2), (4), and (8), we obtain

$$R_{B-X} = 4\pi a_0 D_X \varphi_X^{(a)} \left(\frac{C_{B^-} C_X}{\psi_X} - \frac{C_{BX}}{\xi_X^{(a)}} \right), \quad \varphi_X^{(a)} = \sum_{\alpha=0}^{+2} K_{X^\alpha} \left(\frac{p}{n_i} \right)^\alpha . \tag{36}$$

For he donor atoms (As^+) the expressions for the kinetics of formation of the $(AsX)^\alpha$ pairs, $\alpha = 0, \pm1$, $X \equiv V, I$, are derived similarly to Eq. (36) subject to Eq. (10):

$$R_{A-X} = 4\pi a_0 D_X \varphi_X^{(d)} \left(\frac{C_{As^+} C_X}{\psi_X} - \frac{C_{AsX}}{\xi_X^{(d)}} \right), \quad \varphi_X^{(d)} = \sum_{\alpha=-2}^{0} K_{X^\alpha} \left(\frac{n}{n_i} \right)^{-\alpha} . \tag{37}$$

We will consider the kinetics of the recombination of the $(BI)^\alpha$ and $(BV)^\alpha$ pairs, $\alpha = 0, \pm1$, with vacancies and interstitial atoms, respectively. According to [2], for such bimolecular reactions the role of Coulomb interaction is insignificant, therefore for the reaction $(BI)^\alpha + V \leftrightarrow B^-$ with one charge state α we may write

$$K_{(BI)^\alpha - V} = \frac{C_{B^-}^*}{C_{(BI)^\alpha}^* C_V^*} = \frac{k_f^\alpha}{k_r^\alpha}, \quad k_f^\alpha = 4\pi r \left(D_V + D_{(BI)^\alpha} \right) \tag{38}$$

and as a radius of interaction we can adopt the quantity a_0. Then from Eq. (38), summing over all charge states $\alpha = 0, \pm1$ and taking into account Eqs. (2), (6), (9), (24), (25), and (27), we obtain an expression for the recombination rate R_{BI-V}:

$$R_{BI-V} = 4\pi a_0 \left(D_V + D_{(BI)^0} \frac{\theta_I^{(a)}}{\xi_I^{(a)}} \right) \left(C_{BI} C_V - C_{B^-} C_V^* C_{I^0}^* \xi_I^{(a)} \right). \tag{39}$$

The source/sink term R_{BV-I} will be given in the same form:

$$R_{BV-I} = 4\pi a_0 \left(D_I + D_{(BV)^0} \frac{\theta_V^{(a)}}{\xi_V^{(a)}} \right) \left(C_{BV} C_I - C_{B^-} C_I^* C_{V^0}^* \xi_V^{(a)} \right). \tag{40}$$

By analogy with Eqs. (39) and (40) for the donor atoms (As^+) the kinetic parameters R_{AsI-V} and R_{AsV-I} will be written as

$$R_{AsI-V} = 4\pi a_0 \left(D_V + D_{(AsI)^0} \frac{\theta_I^{(d)}}{\xi_I^{(d)}} \right) \left(C_{AsI} C_V - C_{As^+} C_V^* C_{I^0}^* \xi_I^{(d)} \right), \tag{41}$$

$$R_{\mathrm{AsV-I}} = 4\pi a_0 \left(D_{\mathrm{I}} + D_{(\mathrm{AsV})^0} \frac{\theta_{\mathrm{V}}^{(\mathrm{d})}}{\xi_{\mathrm{V}}^{(\mathrm{d})}} \right) \left(C_{\mathrm{AsV}} C_{\mathrm{I}} - C_{\mathrm{As}^+} C_{\mathrm{I}}^* C_{\mathrm{V}^0}^* \xi_{\mathrm{V}}^{(\mathrm{d})} \right). \tag{42}$$

To determine the parameter $R_{\mathrm{BV-BI}}$, we will consider the bimolecular reaction BV + BI $\leftrightarrow$ $2\mathrm{B}^-$ assuming that the kinetics of recombination does not depend on the charges of the pairs:

$$K_{\mathrm{BV-BI}} = \frac{(C_{\mathrm{B}^-}^*)^2}{C_{\mathrm{BV}}^* C_{\mathrm{BI}}^*} = \frac{k_{\mathrm{f}}}{k_{\mathrm{r}}}. \tag{43}$$

Using the foregoing considerations, we obtain

$$R_{\mathrm{BV-BI}} = 4\pi a_0 \left(D_{(\mathrm{BV})^0} \frac{\theta_{\mathrm{V}}^{(\mathrm{a})}}{\xi_{\mathrm{V}}^{(\mathrm{a})}} + D_{(\mathrm{BI})^0} \frac{\theta_{\mathrm{I}}^{(\mathrm{a})}}{\xi_{\mathrm{I}}^{(\mathrm{a})}} \right) \left(C_{\mathrm{BV}} C_{\mathrm{BI}} - C_{\mathrm{B}^-}^2 C_{\mathrm{I}^0}^* C_{\mathrm{V}^0}^* \xi_{\mathrm{I}}^{(\mathrm{a})} \xi_{\mathrm{V}}^{(\mathrm{a})} \right), \tag{44}$$

and for the donor dopant (As^+)

$$R_{\mathrm{AsV-AsI}} = 4\pi a_0 \left(D_{(\mathrm{AsV})^0} \frac{\theta_{\mathrm{V}}^{(\mathrm{d})}}{\xi_{\mathrm{V}}^{(\mathrm{d})}} + D_{(\mathrm{AsI})^0} \frac{\theta_{\mathrm{I}}^{(\mathrm{d})}}{\xi_{\mathrm{I}}^{(\mathrm{d})}} \right) \left(C_{\mathrm{AsV}} C_{\mathrm{AsI}} - C_{\mathrm{As}^+}^2 C_{\mathrm{I}^0}^* C_{\mathrm{V}^0}^* \xi_{\mathrm{I}}^{(\mathrm{d})} \xi_{\mathrm{V}}^{(\mathrm{d})} \right). \tag{45}$$

The values of the concentrations of diffusing species C_{I}, C_{V}, C_{AI}, and C_{AV}, which are contained in the equations for the source/sink terms (34), (36), (39), (40), and (44), are determined from the solution of the system of equations (12)–(16), whereas the concentration of free electrons/holes in the expressions for the parameters $\theta_{\mathrm{X}}^{(\mathrm{a,d})}$, $\xi_{\mathrm{X}}^{(\mathrm{a,d})}$, $\varphi_{\mathrm{X}}^{(\mathrm{a,d})}$, and ψ_{X}, X $\equiv$ V, I, are determined from the condition of electric neutrality (17). The equilibrium concentrations of the point defects C_{X}^* and $C_{\mathrm{X}^0}^*$ in silicon are known from the literature [2, 22].

Thus, all the sources/sinks that enter into continuity equations (12)–(16) have been determined. Since the problem of the diffusion of the implanted dopant in silicon is substantially nonlinear, it can be solved only numerically.

Diffusion Coefficients under Nonequilibrium Conditions. Experimental data on the coefficients of diffusion in silicon were obtained under "intrinsic" conditions, when the content of a dopant is small and the concentrations of point defects are close to equilibrium ones: $C_{\mathrm{X}} = C_{\mathrm{X}}^*$, X $\equiv$ V, I. These quantities have the meaning of coefficients of self-diffusion of the dopant D_{A}^* (in the terminology of the theory of diffusion in metals [10, 11]). The relative contribution of the AI pairs to the diffusion mass transfer of A atoms is characterized by the formal parameter f_{I} [2, 3, 23]:

$$f_{\mathrm{I}} = \frac{D_{\mathrm{AI}}^*}{D_{\mathrm{AI}}^* + D_{\mathrm{AV}}^*} = \frac{D_{\mathrm{AI}}^*}{D_{\mathrm{A}}^*}, \tag{46}$$

where D_{AX}^* is the diffusion coefficient of the AX pairs, X $\equiv$ V, I, in all charge states under quasi-equilibrium conditions. Then, under nonequilibrium conditions, i.e., in the presence of excessive point defects, the effective diffusion coefficient D_{A} is related to the experimentally measured quantity D_{A}^* as [2, 3, 23]

$$D_{\mathrm{A}} = D_{\mathrm{A}}^* \left(f_{\mathrm{I}} \frac{C_{\mathrm{AI}}}{C_{\mathrm{AI}}^*} + (1 - f_{\mathrm{I}}) \frac{C_{\mathrm{AV}}}{C_{\mathrm{AV}}^*} \right) = D_{\mathrm{A}}^* \left(f_{\mathrm{I}} \frac{C_{\mathrm{I}}}{C_{\mathrm{I}}^*} + (1 - f_{\mathrm{I}}) \frac{C_{\mathrm{V}}}{C_{\mathrm{V}}^*} \right). \tag{47}$$

It is adopted here that $C_{\mathrm{AX}}/C_{\mathrm{AX}}^* = C_{\mathrm{X}}/C_{\mathrm{X}}^*$, X $\equiv$ V, I, [2, 23]. Equations (46) and (47) yield the relationship between the diffusion coefficients of the AX pairs under quasi-equilibrium conditions D_{AX}^* and the quantity D_{AX} for nonequilibrium conditions, X $\equiv$ V, I:

$$D_{AI} = D^*_{AI} \frac{C_I}{C^*_I}, \quad D_{AV} = D^*_{AV} \frac{C_V}{C^*_V}, \tag{48}$$

where $D^*_{AI}/D^*_A f_I$; $D^*_{AV} = D^*_A(1 - f_I)$. It is clear that under nonequilibrium conditions the diffusion coefficients of the AX pairs increase substantially, since at the early stages of annealing after implantation $C_X >> C^*_X$, X ≡ V, I.

Similarly to (48), for the diffusion coefficients of the $(AX)^\alpha$ pairs in different charge states, $\alpha = 0, \pm 1$, assuming that $C_{(AX)^\alpha}/C^*_{(AX)^\alpha} = C_{X^\beta}/C^*_{X^\beta}$, X ≡ V, I, we obtain

$$D_{(AX)^\alpha} = D^*_{(AX)^\alpha} \frac{C_{X^\beta}}{C^*_{X^\beta}}, \tag{49}$$

where for the atoms of the acceptor (B^-) $\beta = \alpha + 1$ and for those of the donor (As^+) $\beta = \alpha - 1$.

The values of f_I and D^*_A for various dopants are given in the literature [2, 3, 19, 23, etc.]. Therefore the model suggested can be used for numerical investigation of the diffusion of the implanted atoms of donors and acceptors in silicon.

Conclusions. Thus, a more general (than those available in the literature) mathematical model of diffusion of implanted atoms (of both donors and acceptors) in silicon has been formulated which takes into account all possible charge states of both point defects (vacancies and interstitial atoms of Si) and diffusing complexes (pairs) AI, AV. In deriving expressions for diffusion flows the difference between the diffusion coefficients of the AI and AV pairs in different charge states was taken into account. In the framework of the five-stream model, generalized expressions were obtained for the rates of all possible pair reactions of interaction of dissimilar diffusing species (point defects and AI, AV pairs) having different electric charges. The method for estimating the diffusion coefficients of the AI, AV pairs under nonequilibrium conditions from experimental values of the self-diffusion coefficient has been described.

The results of numerical simulation of the diffusion of an implanted dopant in silicon will be presented in the second part of the article.

NOTATION

a_0, period of the crystal lattice, m; C, concentration, m^{-3}; D, diffusion coefficient, m^2/sec; E, energy, eV; ΔE, difference of energies, eV; J, diffusion flow, m/sec; K, reaction equilibrium constant; k, reaction rate constant, sec^{-1}; k_B, Boltzmann constant; L, depth, m; n, concentration of free electrons, m^{-3}; p, concentration of holes, m^{-3}; q, electron charge, C; R, source/sink strength, m^3/sec; r, radius of interaction, m; T, temperature, K; t, time, sec; α, charge state; ε, electric field strength, V/m; μ, mobility, $m^2/(J{\cdot}sec)$; ρ, ratio of diffusion coefficients; φ, electric potential, V; ω, volume of an elementary crystal cell, m^3; ξ, ψ, η, ν, θ, and φ, dimensionless complexes. Subscripts: b, bond; i, internal; f, forward reaction; r, reverse reaction. Superscripts: *, equilibrium value; a, acceptor; d, donor.

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