AN EXTENDED FIVE-STREAM MODEL FOR DIFFUSION OF ION-IMPANTED DOPANTS IN MONOCRYSTALLINE SILICON

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Low-energy high-dose ion implantation of different dopants (P, Sb, As, B and others) into monocrystailine silicon with subsequent thermal annealing is used for the formation of ultra-shallow p-n junctions in modern VLSI circuit technology. During annealing, dopant activation and diffusion in silicon takes place. The experimentally observed phenomenon of transient enhanced diffusion (TED), which is typically ascribed to the interaction of diffusing species with non-equilibrium point defects accumulated in silicon due to ion damage, and formation of small clasters and extended defects, hinders further downscaling of p-n junctions in VLSI circuits. TED is currently a subject of extensive experimental and theoretical investigation in many binary and multicomponent systems. However, the state-of-the-art mathematical models of dopant diffusion, which are based on the so-called "five-stream" approach, and modern TCAD software packages such as SUPREM-4 (by Silvaco Data Systems, Ltd.) that implement these models encounter severe difficulties in describing TED. Solving the intricate problem of TED suppression and development of novel regimes of ion implantation and rapid thermal annealing is impossible without elaboration of new mathematical models and computer simulation of this complex phenomenon. In this work, an extended five-stream model for diffusion in silicon is developed which takes into account all possible charge states of point defects (vacancies and silicon self-interstitials) and diffusing pairs "dopant atom-vacancy" and "dopant atom-silicon self-interstitial". The model includes the drift terms for differently charged point defects and pairs in the internal electric field and the kinetics of interaction between unlike "species" (generation and annihilation of pairs and annihilation of point defects). Expressions for diffusion coefficients and numerous sink/source terms that appear in the non-linear, non-steady-state reaction-diffusion equations are derived for both donor and acceptor dopants accounting for multiple charge states of the diffusing species.

Introduction

According to the International Road Map in Semiconductors, decreasing the depth of ultra-shallow p-n junctions (USJ) to the nanometric size (<10 nm) is the main tendency in the modern VLSI circuit technology. The USJ are produced by low-energy high-dose ion implantation of different dopants (donors: P, Sb, As and acceptors: B, Al) into monocrystailine silicon with subsequent thermal annealing at a high temperature (1200-1600 K). The latter is supposed to activate the dopant atoms and insure their diffusion in silicon to produce a required concentration profile. During annealing, such phenomena as transient enhanced diffusion (TED), which includes uphill diffusion, and the formation of the so-called "small clasters" are observed. This hampers obtaining a desirable distribution of dopants and hence the characteristics of the device as a whole. TED is typically ascribed to the interaction of diffusing species with non-equilibrium point defects (vacancies and silicon self-interstitials), which were accumulated in silicon due to ion damage, and with small clasters and extended defects (dislocations and the so-called {311} interstitial defects). Since TED hinders further downscaling of p-n junctions in VLSI circuits, it is currently a subject of extensive experimental and theoretical investigation in many binary and multicomponent systems [1-3].

However, the state-of-the-art mathematical models of dopant diffusion and modern TCAD software packages implementing these models (such as SUPREM-4 by Silvaco Data Systems) encounter severe difficulties in describing TED [4]. Solving the intricate problem of TED suppression and developing novel regimes of ion implantation and rapid thermal annealing is impossible without the elaboration of new mathematical models and computer simulation of this complex phenomenon. The existing models, including those used in SUPREM-4, are based on the so-called "five-stream" approach, which typically takes into account only few of the possible multiple charge states of diffusing species (point defects and dopant-defect pairs) [5-7].

In connection with the above, the objective of this work is the development of an extended five-stream model for diffusion of implanted dopants in silicon taking into account all the possible charge states of the diffusing species. This factor will be included in expressions for both diffusion fluxes and sink/source terms describing interaction between unlike species (generation/annihilation of pairs and point defects).

Model Formulation

Physical Background

Diffusion mass transfer of implanted dopant atoms A in crystalline silicon proceeds via the known "indirect" mechanisms [8]: diffusion of pairs "dopant atom - vacancy" (AV) and "dopant atom - silicon self-interstitial" (AI). Also, the diffusion of point defects X≡V,I (vacancies V and silicon self-interstitials/ interstitialcies I), which can exist in multiple charge states X^{α} ($\alpha=0, \pm1$ and $+2$), takes place [8]. Dopant atoms A in substitutional positions are considered immovable [5-8]. Since the dopants have a charge +1 (donors) or -1 (acceptors), they can form diffusing pairs $(AX)^{\alpha}$ with point defects of an opposite charge and neutral ones, hence the pairs can exit in three charge states: $\alpha=0$ and $+1$. Besides, interaction between different diffusing species (their generation and annihilation) takes place during annealing.

Continuity Equations

The "five-stream" model [5-7] includes four continuity equations (for pairs AX and point defects X), a mass balance equation for substitutional dopant atoms, and a condition of local electroneutrality (because electrons and holes are much more mobile than the diffusing species). These equations look as:

$$\partial C_I/\partial t = -\mathrm{div}\, J_I - (R_{I-V} + R_{A-I} + R_{AV-I})/\omega, \qquad (1)$$

$$\partial C_V/\partial t = -\mathrm{div}\, J_V - (R_{I-V} + R_{A-V} + R_{AI-V})/\omega, \qquad (2)$$

$$\partial C_{AV}/\partial t = -\mathrm{div}\, J_{AV} + (R_{A-V} - R_{AV-I} - R_{AV-AI})/\omega, \qquad (3)$$

$$C_{AI}/\partial t = -\mathrm{div}\, J_{AI} + (R_{A-I} - R_{AI-V} - R_{AV-AI})/\omega, \qquad (4)$$

$$\partial C_A/\partial t = (R_{AI-V} + R_{AV-I} + 2R_{AV-AI} - R_{A-I} - R_{A-V})/\omega, \qquad (5)$$

$$\sum_{\alpha=\pm1,\pm2} \alpha C_{X^\alpha} + \sum_{\beta=\pm1} \beta C_{(AX)^\beta} + \gamma C_{A^\gamma} + p - n = 0. \qquad (6)$$

Here J_k is the diffusion flux of k-th species, which includes a drift term in the internal electric field, C_k is their volumetric concentration, $R_{l\text{-}j}$ is the sink/source term describing interaction between l-th and j-th species, $\omega=a_0^3$ is the unit cell volume, a_0 is the lattice period of silicon, p and n are the concentrations of holes and electrons ($np = n_i^2$), α, β and γ are charge states, $\gamma=+1$ for donors and -1 for acceptors.

Diffusion Fluxes

The expression for diffusion flux of point defects X^α for one charge state α looks as

$$J_{X^\alpha} = -D_{X^\alpha} \nabla C_{X^\alpha} + \mu_{X^\alpha} \alpha e \vec{\varepsilon} C_{X^\alpha}, \qquad (7)$$

where D_{X^α} is the diffusion coefficient of species X^α, e is the charge of an electron, $\vec{\varepsilon} = -\nabla\phi$ is the electric field strength, ϕ is the electric potential, μ_{X^α} is the mobility coefficient defined by Einstein's formula $\mu_{X^\alpha} = D_{X^\alpha}/(k_B T)$, k_B is the Boltzmann constant.

Using the Boltzmann distribution of charged species in the electric field and summarizing over the charge states implying that diffusion coefficient D_X (X≡V,I) does not depend on α [8], from Eq.(7) the total diffusion flux of point defects is obtained

$$J_X = -D_X[\nabla C_X - C_X \chi_X \nabla \ln(p/n_i)],$$

$$\chi_X = (1/\psi_X)\sum_{\alpha=-2}^{+2} \alpha K_{X^\alpha}(p/n_i)^\alpha,$$

$$\psi_X = \sum_{\alpha=-2}^{+2} K_{X^\alpha}(n/n_i)^{-\alpha}, \qquad (8)$$

where K_{X^α} are the equilibrium constants for ionization reactions $X^0 + \alpha e^- \leftrightarrow X^\alpha$, which are known in literature for a wide temperature range.

For pairs "atom - point defect" $(AX)^\alpha$, an equation for the diffusion flux for one charge state α is similar to Eq.(7). Summarizing over all charge states and taking into account a difference in partial diffusion coefficients of differently charged pairs, for acceptor dopants A^- (e.g., boron) the total flux is described as

$$J_{AX} = -\frac{1}{\pi_X}\sum_{\alpha=-1}^{+1} D_{(AX)^\alpha} K_{A^-X^{\alpha+1}} K_{A^{\alpha+1}} \left(\frac{p}{n_i}\right)^{\alpha+1} \times \left(\nabla C_{AX} + C_{AX}\frac{\eta_X}{\pi_X}\nabla \ln\frac{p}{n_i}\right), \qquad (9)$$

where

$$\eta_X = K_{A^-X^0} - K_{A^-X^{++}} K_{X^{++}} (p/n_i)^2,$$

$$\pi_X = \sum_{\alpha=0}^{+2} K_{A^-X^\alpha}(p/n_i)^\alpha, \qquad (10)$$

and $K_{A^-X^{\alpha+1}}$ is the equilibrium constant for pairing reaction $A^- + X^{\alpha+1} \leftrightarrow (AX)^\alpha$, $\alpha=0,\pm1$.

To reduce the number of diffusion coefficients $D_{(AX)^\alpha}$ in Eq.(9), which are difficult to determine from experimental data, the following way can be used [7]. The difference in the activation energy for migration of pairs $(AX)^-$ and $(AX)^0$, as well as for that of pairs $(AX)^+$ and $(AX)^0$ is due to the difference in the corresponding binding energy ΔE_b; for boron ΔE_b=0.3 eV [7]. Thus it is possible to write

$$D_{(AX)^0}/D_{(AX)^-} = \rho_{AX}^- = \exp[-\Delta E_b/(k_B T)],$$

$$D_{(AX)^+}/D_{(AX)^0} = \rho_{AX}^+, \qquad (11)$$

and assume $\rho_{AX}^+ = \rho_{AX}^- = \rho_{AX}$, X≡V,I. Then Eq.(9) for the total diffusion flux of pairs AX is simplified to give

$$J_{AX} = -D_{(AX)^0}\frac{\theta_X}{\pi_X}\left(\nabla C_{AX} + C_{AX}\frac{\eta_X}{\pi_X}\nabla \ln\frac{p}{n_i}\right), \qquad (12)$$

$$\theta_X = \sum_{\alpha=0}^{+2} K_{A^-X^\alpha} K_{X^\alpha} (\rho_{AX})^{\alpha-1}(p/n_i)^\alpha. \qquad (13)$$

For donors A^+ (e.g., As), a formula for the total diffusion flux of pairs AX is derived similarly to Eqs.(9)-(13), but it should be borne in mind that pairing reactions look as $A^+ + X^{\alpha-1} \leftrightarrow (AX)^\alpha$, hence expressions (10), (11) and (13) will acquire a different form.

Sink/Source Terms

Typically, for describing the recombination rate of non-equilibrium vacancies and silicon self-interstitials $R_{I\text{-}V}$, an assumption of small deviation from local equilibrium is used, and without considering the multiple charge states the expression is written as

$$R_{I-V} = 4\pi r(D_I + D_V)(C_I C_V - C_I^* C_V^*), \qquad (14)$$

where C_X^* is the equilibrium concentration of point defects (X≡V,I), which is known in literature, r is the so-called capture radius, which is close to a_0.

To take into account the existence of multiple charge states of point defects, it is necessary to include in Eq.(14) the sum over all states $\sum_{\alpha,\beta}(C_{I^\alpha} C_{V^\beta} - C_{I^\alpha}^* C_{V^\beta}^*)$, α,β = 0, ±1, ±2 instead of term $(C_I C_V - C_I^* C_V^*)$. For simplicity, the capture radius is assumed independent of the charge, $r=a_0$, and the following nine binary annihilation reactions are considered: $I^0 + V^0$, $I^- + V^0$, $I^- + V^0$, $I^+ + V^0$, $I^{++} + V^0$, $I^0 + V^-$, $I^0 + V^=$, $I^0 + V^+$. $I^0 + V^{++}$. Then the following expression is obtained:

$$R_{I-V} = 4\pi a_0(D_I + D_V)\varphi_{I-V} \times [(C_I/\psi_I)(C_V/\psi_V) - C_{I^0}^* C_{V^0}^*], \quad \varphi_{I-V} = \psi_I + \psi_V - 1, \qquad (15)$$

where ψ_X is defined by Eq.(8) and the concentration of neutral point defects $C_{X^0}^*$ is calculated as

$$C^*_{X^0} = C^*_X / \psi^*_X, \quad \psi^*_X = \sum_{\alpha=-2}^{+2} K_{X^\alpha}. \tag{16}$$

Let's derive expression for kinetic terms R_{A-I} and R_{A-V}, which appear in Eqs.(1)-(5), for acceptors A^-. For one charge state of point defect X^α, assuming small deviation from local thermodynamic equilibrium and implying $r=a_0$, we can write

$$R^\alpha_{A-X} = k^\alpha_f C_{A^-} C_{X^{\alpha+1}} - k^\alpha_r C_{(AX)^\alpha}, \quad k^\alpha_f = 4\pi r D_X, \tag{17}$$

where k_f^α and k_r^α are the rates of forward ($A^+ + X^{\alpha-1} \to (AX)^\alpha$) and reverse ($(AX)^\alpha \to A^+ + X^{\alpha-1}$) reactions, whose ratio is equal to the equilibrium constant $K_{A^-X^{\alpha+1}} = k^\alpha_f / k^\alpha_r$. Then, summarizing over all charge states of point defects, we have

$$R_{A-X} = 4\pi a_0 D_X \varphi_X (C_{A^-} C_X / \psi_X - C_{BX} / \pi_X), \tag{18}$$

$$\varphi_X = \sum_{\alpha=0}^{+2} K_{X^\alpha} (p/n_i)^\alpha. \tag{19}$$

A formula similar to Eq.(18) can be derived for donor dopants A^+, but in this case the expressions for terms π_X (Eq.(10)) and φ_X (Eq.(19)) will be different.

In bimolecular recombination reactions of pairs $(AI)^\alpha$ and $(AV)^\alpha$ with vacancies and silicon self-interstitials, correspondingly, the role of coulomb interaction is insignificant [8]. For acceptors, at one charge state for reaction $(AI)^\alpha + V \leftrightarrow A^-$ we can write

$$K_{(AI)^\alpha-V} = C^*_{A^-} / (C^*_{(AI)^\alpha} C^*_V) = k^\alpha_f / k^\alpha_r,$$
$$k^\alpha_f = 4\pi r (D_V + D_{(AI)^\alpha}), \tag{20}$$

where $K_{(AI)^\alpha-V}$ is the equilibrium reaction constant. Summarizing over all the charge states of pairs and point defects, from Eq.(20) the expressions for kinetic terms R_{AI-V} and R_{AV-I} are obtained:

$$R_{AI-V} = 4\pi a_0 (D_V + D_{(AI)^0} \theta_I / \pi_I) \times$$
$$(C_{AI} C_V - C_{A^-} C^*_V C^*_{I^0} \pi_I), \tag{21}$$

$$R_{AV-I} = 4\pi a_0 (D_I + D_{(AV)^0} \theta_V / \pi_V) \times$$
$$(C_{AV} C_I - C_{A^-} C^*_I C^*_{V^0} \pi_V), \tag{22}$$

where term θ_X is defined by Eq.(13). Similar formulas can be derived for donors A^+, but the expressions for terms θ_X and π_X will have a different form.

To determine term R_{AV-AI} for acceptor dopants, let's consider bimolecular reaction $AV + AI \leftrightarrow 2A^-$ assuming that its kinetics is independent of the charge state of pairs AX. The equilibrium constant of this reaction is defined as

$$K_{AV-AI} = (C^*_{A^-})^2 / (C^*_{AV} C^*_{AI}) = k_f / k_r, \tag{23}$$

where k_f and k_r are the rate constants for the forward and reverse reaction. Employing the method similar to that used in deriving Eqs.(21) and (22), we obtain the following expression:

$$R_{AV-AI} = 4\pi a_0 (D_{(AV)^0} \theta_V / \pi_V + D_{(AI)^0} \theta_I / \pi_I) \times$$
$$(C_{AV} C_{AI} - C^2_{A^-} C^*_{I^0} C^*_{V^0} \pi_I \pi_V). \tag{24}$$

An formula similar to Eq. (24) can be derived for donor dopants A^+. Thus, all the kinetic terms that appear in continuity equations (1)-(5) are defined, and hence the model is complete.

Conclusion

In this research, an extended five-stream model for diffusion of implanted dopants in monocrystalline silicon during thermal annealing is formulated. Unlike previously known papers [1-7], the model takes into account all the possible charge states of the diffusing species. This important physical factor is included in the expressions for both diffusion fluxes J_k and sink/source terms R_{i-j}, which appear in the mass conservation equations (1)-(5). Further work will be focused on the development of a numerical method, elaboration and debugging of a computer program and performing numerical simulation of TED in particular systems.

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