

GENERALIZED DIFFUSION EQUATION FOR IMPURITY ATOMS
IN SEMICONDUCTOR CRYSTALS

V. A. Labunov and O. I. Velichko

UDC 53.01.072:681.3

A diffusion equation is obtained for impurity atoms migrating by means of the formation of equilibrium complexes with intrinsic point defects, the distribution of which is nonequilibrium and nonuniform.

Solid-phase diffusion of electrically active impurities is one of the major processes in fabricating discrete semiconductor devices and integrated microcircuits. This means that simulation of diffusion is the most important stage in the design and optimization of technological processes. The role of such simulation increased in particular after methods of ion implantation came into use; such methods can be used to create locally doped regions of micron and submicron dimensions, which are characterized by a strongly nonequilibrium state of the component of a system containing defects and impurities. The small size of the geometrical dimensions of the doped regions requires the development of an adequate description of the diffusion processes for ion-implanted impurities. With this in mind we consider diffusion mechanisms on a microscopic level together with the corresponding equations used in simulating the diffusion processes.

Since in elemental semiconductors impurities of elements of groups III and V are in the position of substitution, it was suggested that diffusive migration is realized via a simple vacancy mechanism as a result of exchanging sites between an impurity atom and an approaching vacancy [1, 2]. The diffusion equation for the given transport mechanism for impurity atoms has been obtained in [2] and assumes the following form:

$$C_t^S = \nabla [D(\chi) h \nabla C^S] - \nabla [D(\chi) h^B \nabla N^B], \quad (1)$$

$$\chi = [C^S - N^B + \sqrt{(C^S - N^B)^2 + 4n_{ie}^2}] / 2n_i, \quad (2)$$

$$h = 1 + h^B, \quad h^B = C^S / \sqrt{(C^S - N^B)^2 + 4n_{ie}^2}. \quad (3)$$

Equation (1) is of the type of the second Fick's law with the effective diffusion coefficient depending on the concentration of impurity atoms. When deriving the equation, account was taken of the drift of ionized impurity atoms due to the inner electric field, existence of different charge states of vacancies, and redistribution of vacancies under the action of the electric field, and also variation of the field in the presence of an impurity having the opposite type of conductivity. Nevertheless, the equation obtained in [2] does not represent an adequate description of the diffusion of impurities via a simple vacancy mechanism because, when it was derived, it did not take account of flows of impurity atoms emerging due to nonuniformity in vacancy distribution (so-called cross-effects of processes of particle transport [3]). Besides, Eq. (1) was obtained under the assumption that the distribution of neutral vacancies is in equilibrium and uniform, which is characteristic of purely thermal diffusion. In ion-implanted layers, or in layers subjected to ion irradiation, not only is the distribution of impurity atoms nonequilibrium, but the state of the defect subsystem of the crystal is also nonequilibrium; therefore the application of Eq. (1) for simulating modern technological processes is generally incorrect [4].

Both the nonequilibrium state and nonuniformity in the distribution of vacancies and also cross-effects of the transport in exchanging sites between the impurity atom and a vacancy are considered in the generalized diffusion equation [5]. However, [5] does not give explicit dependencies of effective transport coefficients on the concentration of impurity atoms. It is for this reason that when simulation programs are developed for diffusion processes [6], Eq. (1) is generally used.

We should note that the mechanism of diffusion via exchanging sites of impurity atoms and vacancies is not applicable for the description of a number of diffusion processes. Thus at present it is found experimentally in silicon that vacancy-impurity complexes are formed when impurity atoms of elements of groups III and V interact with vacancies [7]. Diffusion transport of impurity atoms is realized [7, 8] because of the migration and decay of these complexes. Experimental results suggest that vacancy-impurity complexes are formed not only in silicon but also in germanium [7]. The formation of these complexes is possible also in other semiconductors.

In addition to the vacancy mechanisms of diffusion, an important role in impurity transport processes is also played by internodal diffusion mechanisms in the presence of interaction among the impurity atoms and intrinsic internodal atoms [1, 9]. In silicon, such an interaction might result in the formation of complexes of impurity atoms and internodal atoms of silicon [7, 10]. A particular impurity atom passing into an internodal location as a result of interaction with an intrinsic internodal atom can also be considered as a degenerate complex consisting of a single atom [11].

The above analysis demonstrates the great importance of the mechanism of diffusion via moving complexes of impurity atoms and intrinsic point defects for crystalline semiconductors. We obtain the diffusion equation for an impurity in a semiconductor when its transport is realized via the given mechanism. When deriving the diffusion equation, we take account of the nonequilibrium state and nonuniformity of the distribution of intrinsic point defects in a way similar to [5], where the case of a nonuniform distribution of vacancies has been considered. In addition to the nonuniform distribution of intrinsic point defects we take account of the following effects: 1) the drift of complexes and of charged intrinsic point defects under the action of an inner electric field; 2) the existence of different charge states of the intrinsic point defects and different charge states of complexes; 3) the dependence of the inner electric field on concentration and distribution of the impurity under consideration and the impurity of the opposite type of conductivity; 4) processes of the formation of clusters; 5) the influence of the high level of doping on the intensity of the inner electric field and the rate of quasichemical reactions.

For this purpose we use the formalism of thermodynamics for nonequilibrium processes [3] and we write the diffusion equations and quasi-chemical reactions for all the kinds of particles under consideration [12, 13]:

$$C_i^\alpha = \nabla \left[D^\alpha \left(\omega^\alpha \nabla C^\alpha - \frac{z^\alpha e}{k_B T} \mathbf{E} C^\alpha \right) \right] + \sum_{i=1}^m v_i^\alpha v_i - S^\alpha + G^{T\alpha} + G^{R\alpha}, \quad (4)$$

$$\alpha = 1, 2, \dots, l, \quad \omega^\alpha = (C^\alpha / k_B T) \partial \mu^\alpha / \partial C^\alpha.$$

We find the quantities χ and \mathbf{E} from the condition of local electrical neutrality. In this case the functional dependence of the quantity χ is given by Eq. (2), and the quantity \mathbf{E} , calculated with account of the effects of the high level of doping, is determined by the expression [13]

$$\mathbf{E} = -z(k_B T / e) \omega^\chi \nabla \chi / \chi. \quad (5)$$

By using the law of mass action for equilibrium quasi-chemical reactions [14], we determine the concentrations of the intrinsic point defects in different charge states and the concentrations of complexes of impurity atoms and intrinsic point defects:

$$C^{hr} / (C^{h \times} \chi^{-zz^{hr}}) = h^{hr}(T, \chi), \quad (6)$$

$$C^{Shr} / (C^S C^{hr}) = H^{hr}(T, \chi). \quad (7)$$

We write Eqs. (4) for the impurity atoms in the substitutional position and for complexes of the impurity atoms and intrinsic point defects. By transforming the constructed system of equations with the help of Eqs. (2), (3), (5), (6), and (7), we obtain a generalized equation for the diffusion of impurity atoms:

$$C_i = \nabla \{ D^{Sh} [\nabla (\tilde{C}^{h \times} C^S) + \omega^\chi h^B \tilde{C}^{h \times} \nabla (C^S - N^B)] \} - \nabla [(\omega^\chi - 1)(\partial D^{Sh} / \partial \chi - P^{Sh}) \chi h^B \tilde{C}^{h \times} \nabla (C^S - N^B)] + \nabla [\omega^\chi Q^{Sh} \chi h^B \tilde{C}^{h \times} \nabla (C^S - N^B)], \quad (8)$$

$$\begin{aligned}
D^{Sh}(\chi) &= C_i^{h \times} \sum_r D^{Shr} H^{hr} h^{hr} \chi^{-zz^{hr}}, \\
P^{Sh}(\chi) &= C_i^{h \times} \sum_r (\partial D^{Shr} / \partial \chi) H^{hr} h^{hr} \chi^{-zz^{hr}}, \\
Q^{Sh}(\chi) &= C_i^{h \times} \sum_r D^{Shr} [\partial (H^{hr} h^{hr}) / \partial \chi] \chi^{-zz^{hr}}, \\
\tilde{C}^{h \times} &= C^{h \times} / C_i^{h \times}.
\end{aligned}$$

In the case of the ideal state of an electron (hole) gas ($\omega^X \equiv 1$) and weak dependence of the equilibrium constants H^{kr} and h^{kr} on the level of doping, Eq. (8) assumes the form

$$C_i = \nabla \{ D^{Sh} [\nabla (\tilde{C}^{h \times} C^S) + h^B \tilde{C}^{h \times} \nabla (C^S - N^B)] \}, \quad (9)$$

and in the case of a low level of doping it is converted into the form

$$C_i^S = D_i \Delta (\tilde{C}^{h \times} C^S). \quad (10)$$

From diffusion equations (8)-(10) it is clear that they differ considerably from equations of the type of the second Fick's law. Thus, from the equations obtained it follows that the flow of impurity atoms is determined not only by their concentration gradient but also by the gradient of the product of the concentration of intrinsic point defects in a neutral charge state and the concentration of the impurity atoms. This means that Eqs. (8)-(10) describe not only smoothing processes for distributions of impurities in the course of diffusion, but also segregation processes for impurity atoms in the case of a nonuniform distribution of neutral intrinsic point defects in the course of heat treatment. Only for a uniform distribution of intrinsic point defects in a neutral charge state is Eq. (9) converted into an equation of the type of the second Fick's law (1).

As an example characterizing the differences of the equations obtained as compared to the equations of the type of the second Fick's law (1), computations are displayed in Fig. 1 for the doping of silicon with bombardment by ions from a gas-discharge plasma containing phosphorus, while Fig. 2 shows the process of redistribution of arsenic implanted in silicon in the course of rapid thermal annealing.

Computation of distribution profiles for the concentration of impurity was realized by numerically solving diffusion equation (10). The distribution of intrinsic point defects in a neutral charge state required for computation has been determined by solving analytically the diffusion equation for intrinsic point defects [17]. The analytical computations of distribution profiles for neutral intrinsic point defects shown in Figs. 1 and 2 correspond to the two opposite cases of redistribution of defects in the crystal. When doping silicon from a plasma, bombardment by low-energy ions leads to the generation of intrinsic point defects near the surface of the semiconductor. While diffusing into the bulk, these nonequilibrium defects are absorbed in drains, which results in the formation of a nonuniform distribution of intrinsic point defects. A significant excess of the concentration of intrinsic point defects above the thermal equilibrium values of concentration leads to the radiation-stimulated diffusion of impurity atoms, which enter silicon from the gas-discharge plasma. For rapid thermal annealing, a thin imperfect layer remains on the semiconductor surface after the solid-phase recrystallization of silicon doped with arsenic. This near-surface layer serves as an effective drain for point defects. The diffusion of defects to the surface and their subsequent absorption also result in the formation of a nonuniform distribution of intrinsic point defects.

For a quantitative characteristic of diffusion processes for point defects and impurity atoms, the following parameters were used: the mean length of the diffusion path of the intrinsic point defect ℓ^X and the mean length of the diffusion path of the impurity $L = \sqrt{D_i C_m^X t}$. The values ℓ^X and L were determined from the condition of matching between calculated and experimental data.

In Fig. 1, computations are presented for doping silicon from the plasma of a gas discharge. As in [15], it was assumed that impurity atoms from the plasma incorporate themselves into the lattice of the semiconductor, with their concentration on the surface being independent of the duration of the treatment. As is seen from Fig. 1, by using the proposed equation we can explain the phenomenon of the formation of a lengthy "plateau" with the constant value of the concentration of impurity atoms on the distribution profile of the impur-

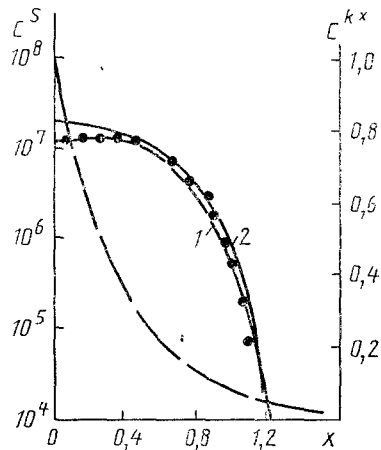


Fig. 1

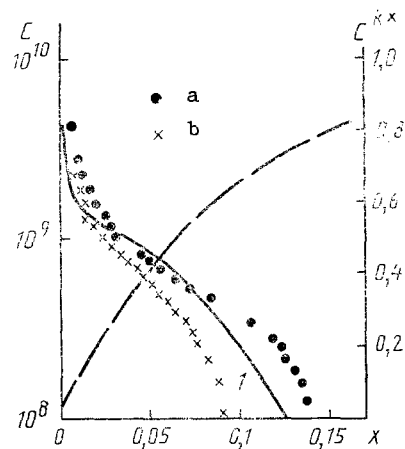


Fig. 2

Fig. 1. Distribution of phosphorus in doping from the plasma of a gas discharge: curve 1, calculated distribution of the impurity for $L = 0.51 \mu\text{m}$ and $\ell^x = 0.4 \mu\text{m}$; curve 2, calculation for $\ell^x = 0.3 \mu\text{m}$, conducted in [15] with the use of the equation of the second Fick's law; a dashed curve, distribution of neutral intrinsic point defects for $\ell^x = 0.4 \mu\text{m}$ (points represent experimental data [15]). C^S , μm^{-3} ; C^{kx} , relative units; x , μm .

Fig. 2. Distribution of implanted arsenic after a rapid thermal annealing: curve 1, calculated distribution of the impurity after annealing for $L = 0.043 \mu\text{m}$ and $\ell^x = 0.1 \mu\text{m}$; a dashed curve, distribution of neutral intrinsic point defects; experimental data [16]: a) thermal treatment for 10 s at a temperature of 1100 °C; b) two-stage thermal treatment, which includes preliminary heating up to 550 °C during 30 min.

ity. For the case of an impurity entering through the surface of the semiconductor it is impossible to describe the appearance of such a "plateau" in the framework of the equation of the second Fick's law, even if additional parameters are introduced in the diffusion coefficient of impurity atoms. This is supported by the computation of the process of radiation-stimulated diffusion when silicon is doped from plasma, as in [15]. In that work it was assumed that the diffusion coefficient of the impurity was proportional to the concentration of vacancies. As an adjusting parameter describing nonuniformity of distribution of nonequilibrium vacancies generated on the surface of the semiconductor, there also was used the mean length of the diffusion path of point defects ℓ^x . As is seen from Fig. 1, the obtained solution of the equation of the second Fick's law is characterized by a monotonic drop in the impurity concentration toward the interior of the semiconductor.

It should be noted that with the help of the generalized equation that was obtained, we can readily describe also the phenomenon of clearly expressed "ascending" diffusion in a region of silicon near the surface if we take account of the fact that the surface can serve as an effective drain for intrinsic point defects. Results of these computations are shown in Fig. 2.

The examples presented show that the obtained equation describes adequate diffusion processes for nonequilibrium and nonuniform distribution of intrinsic point defects and allows us to simulate processes of doping, the computations of which are impossible to perform within the framework of Eq. (1).

NOTATION

C , total concentration of atoms of diffusible impurity; C^S , concentration of atoms of diffusible impurity in the position of substitution; N^B , concentration of ionized impurity atoms of the opposite type of conductivity; $D(\chi)$, effective coefficient of diffusion; χ ,

electron concentration reduced to n_i in the case of diffusion of a donor impurity, and hole concentration in the case of diffusion of an acceptor impurity; n_i and n_{ie} , concentration of intrinsic charge carriers and its effective value at high levels of doping; k_B , Boltzmann constant; α , type of particle under consideration; C^α , D^α , μ^α , z^α , concentration, diffusion coefficient, chemical potential, and the particle charge of the type α , respectively; v_i^α , quantity of particles of the type α formed in the course of a quasi-chemical reaction of the type i ; v_i , rate of this reaction; S^α , rate of absorption of particles of the type α with fixed imperfections of a crystal lattice; $G^{T\alpha}$ and $G^{R\alpha}$, rate of thermal generation of these particles and rate of their generation due to external radiation; E , intensity of internal electric field; z , charge of ion of diffusible impurity; ω^λ , function describing deviation of the state of the electron (hole) gas from the ideal gas for high levels of doping; C^{kr} and C^{kx} , concentration of intrinsic point defects of the type k in the charge state r and in a neutral charge state; z^{kr} , charge of intrinsic point defects of the type k in the charge state r ; C^{Skr} , concentration of complexes formed by the impurity atom in the position of substitution with the intrinsic point defect of the type k in the charge state r ; h^{kr} and H^{kr} , equilibrium constants of transfer reactions for intrinsic point defects from the neutral charge state in the charge state r and reactions of the formation of complexes; D^{Skr} , diffusion coefficient for the complex formed by the impurity atom and the intrinsic point defect of the type k in the charge state r ; C_i^{kr} , value of thermal equilibrium concentration of these intrinsic point defects in the bulk of the semiconductor; D_i , intrinsic diffusion coefficient of the impurity; t , duration of thermal treatment.

LITERATURE CITED

1. D. Shaw (ed.), Atomic Diffusion in Semiconductors, Plenum Publ., New York (1973).
2. S. M. Hu and S. Schmidt, J. Appl. Phys., 39, No. 9, 7272-4283 (1968).
3. S. R. de Groot and P. Mazur, Nonequilibrium Thermodynamics, American Elsevier, New York (1962).
4. O. I. Velichko, Izv. Vuzov. Radioelektron., 29, No. 12, 76-78 (1986).
5. R. Sh. Malkovich, Solid State Physics, 24, No. 2, 463-465 (1982).
6. S. M. Sze (ed.), VLSI Technology, 112-182; McGraw-Hill, New York (1983), pp. 112-182.
7. V. V. Emtsev and T. V. Mashovets, Impurities and Point Defects in Semiconductors [in Russian], Moscow (1981).
8. M. Yoshida, Jpn. J. Appl. Phys., 19, No. 12, 2427-2440 (1980).
9. S. M. Sze (ed.), VLSI Technology, McGraw-Hill, New York (1983).
10. S. M. Hu, J. Vac. Sci. Technol., 14, No. 1, 17-31 (1977).
11. Sh. Lyuka et al., Ion Implantation in Semiconductors and Other Materials [Russian translation], Moscow (1980), pp. 174-183.
12. O. I. Velichko and V. A. Labunov, Mikroelektronika, 14, No. 6, 542-547 (1985).
13. O. I. Velichko, Radiotekhnika i Elektronika, Republican Interdepartmental Collection of Papers, No. 14, 91-94 (1985).
14. V. N. Chebotin, Solid State Physical Chemistry [in Russian], Moscow (1982).
15. H. Strak, J. Appl. Phys., 34, No. 8, 2405-2408 (1963).
16. F. R. Fair, J. J. Wortman, and J. Liu, J. Electrochem. Soc., 131, No. 10, 2387-2394 (1984).
17. O. I. Velichko, Computer Simulation of Structure Sensitive Properties of Crystalline Materials [in Russian], Leningrad (1986), pp. 25-26.