MODELING OF SILICON DIFFUSION IN GALLIUM ARSENIDE.
1. MICROSCOPIC MECHANISMS OF DIFFUSION AND A MODEL OF THE TRANSITIONS OF SILICON ATOMS BETWEEN CRYSTAL SUBLATTICES

O. I. Velichko, A. A. Egorov, and S. K. Fedoruk

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A model is developed and a study is performed for amphoteric diffusion of silicon in gallium arsenide. A comparison of predictions with experimental data indicated adequacy of the devised model and high efficiency of the numerical method for solving the diffusion equation.

Presently, microcircuits operating on gallium arsenide are used increasingly often as an element base of computing technology and SHF devices [1, 2]. This is due to a higher speed of response and better noise characteristics of the microcircuits than for instruments operating on silica [3, 4]. A further rise of the speed of response of the arsenide-gallium microcircuits is linked primarily with improvement of their manufacturing process, which is impossible without thoroughly analyzing the physics of alloying of complex semiconductors.

For local alloying of arsenide-gallium substrates in the production of integrated microcircuits, an ion implantation method with subsequent thermal treatments is employed. Post-implantation thermal treatments provide annealing of the radiation defects and electric activation of the implanted impurities [5]. Solid-phase diffusion occurring here forms the final distributions of defects and impurity atoms in semiconductor crystals.

In connection with the intricacy of the phenomena occurring and the high cost of the substrates in comparison with silica-based technology, development of methods for modeling the processes of solid-phase diffusion acquire exceptional significance in designing arsenide-gallium microcircuits [6]. Since silicon is the most important n-type impurity in the alloying of gallium arsenide, the aim of the current study is to investigate and develop methods for modeling the solid-phase diffusion of silicon atoms in arsenide-gallium substrates.

1.1. Regularities of Silicon Diffusion in Gallium Arsenide. Analysis of current literature reveals that there are many works [7, 8-16] dealing with the experimental study of Si diffusion in GaAs. Yet, a model of the diffusion processes occurring in this case is lacking. To a certain extent, this has to do with the amphoteric behavior of silicon. To develop a model of Si solid-phase diffusion in GaAs we summarize available experimental data. Analysis shows that the following phenomena occur.

1. Silicon in gallium arsenide is an amphoteric impurity, i.e., the silicon atoms take up a substitution position both in the gallium sublattice (the donor Si^{+}_{Ga}) and in the arsenic sublattice (the acceptor Si^{-}_{As}) [7, 8].

2. At high levels of silicon alloying, the concentration of moving charge carriers is appreciably smaller than that of impurity atoms.

3. The diffusion coefficient of silicon is a function of the concentration of impurity atoms, if the concentration is close to or exceeds the intrinsic concentration of charge carriers n_i [10, 11].

4. The diffusion rate of silicon depends on the presence of other impurities [12]. For example, in the presence of zinc (being located in the gallium sublattice, zinc is an acceptor Zn^{-}_{Ga}), Si diffusion slows down [12]. At the same time, the Si diffusion rate in n-type materials increases sharply [13].

5. The diffusion coefficient of silicon is a function of the partial pressures of gallium and arsenic vapors. For example, with a semiconductor enriched with gallium atoms, Si diffusion is retarded as compared with

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stoichiometric conditions [11]. At the same time, with increased arsenic pressure, the diffusion rate of silicon rises [11, 14], and here we have the relation [11]

$$D_{Si} \sim P_{As}^{1/4}.$$

6. In Si diffusion, there is no noticeable variation in the state of the vacancy subsystem of the crystal, i.e., the phenomena of "undersaturation" and "supersaturation" of the semiconductor volume with vacancies are not observable [10].

7. The concentration of moving charge carriers in silicon-alloyed GaAs layers rises with increasing density of dislocations in the crystal [15].

8. The electron concentration decreases sharply near the semiconductor surface, i.e. a spatial dependence of the concentration of moving charge carriers is observed [15, 16].

9. There is a spatial dependence of the diffusion coefficient of Si, which is markedly smaller near the semiconductor surface [10, 11].

10. In alloying, a near-surface concentration maximum of impurity atoms is formed [15], even with diffusion from a steady source [12].

1.2. Microscopic Mechanisms of Diffusion. The above list of diffusion regularities makes it possible to ascertain the basic microscopic mechanism of the transfer of Si atoms in GaSa. According to current views of solid state physics, the transfer of impurity atoms in semiconductor crystals is effected by intrinsic point defects (IPD). In our case, these are vacancies and interstitial atoms of gallium and arsenic.

One of the most important characteristics of an IPD is its charge state (CS). In conformity with available experimental data, the gallium vacancies V_{Ga} have the following charge state: $V_{Ga}^{\times}$ (neutral), V_{Ga}^{-} [8], V_{Ga}^{2-} [17], and V_{Ga}^{3-} [10]. In [10] it is assumed that, as opposed to vacancies, the interstitial atoms of gallium I_{Ga} have positive charge states I_{Ga}^{m+}, where m is most probably equal to 3.

We now consider the arsenic sublattice. Experimental data point to the existence of arsenic vacancies. From data of electron paramagnetic resonance in conjunction with measurement results for the volt-farad characteristics in GaAs irradiated with electrons we established the presence of a doubly positively charged arsenic vacancy V_{As}^{2+} [18]. In addition, it is presumed that the gallium arsenide substrates contain As precipitates, which, in the thermal treatment, act as sources of interstitial arsenic atoms I_{As} [19]. However, the CS of the latter are not known. It is also conjectured that the defect charge in the arsenic sublattice is smaller than that in the gallium sublattice [7].

From item 4 of Section 1.1 it follows that the diffusion rate of silicon decreases in p-type semiconductors and rises abruptly in n-type semiconductors. This implies that negatively charged defects participate in the transfer of impurity atoms, since their concentration decreases in p-type materials and rises in n-type ones. Hence, positively charged gallium interstitial atoms and arsenic vacancies are not involved in the basic microscopic mechanism of diffusion.

We now exclude interstitial arsenic atoms I_{As} from the diffusion mechanism. As follows from item 5 of Section 1.1, the diffusion coefficient of silicon increases at an elevated pressure of arsenic vapors, i.e., at supersaturation of the I_{As} volume. However, it follows from item 9 that the diffusion coefficient is smaller near the semiconductor surface, i.e., where the I_{As} concentration is maximal. This means that the arsenic interstitial atoms per se are most likely not involved in the basic microscopic mechanism of diffusion. However, the supersaturation of the I_{As} semiconductor at an increased partial pressure of arsenic leads at the same time to a decrease in the concentration of the gallium interstitial atoms I_{Ga}, which, in turn, results in a rise in the concentration of the gallium vacancies V_{Ga}, which can take part in the impurity transfer.

As is clear from the above analysis, the most suitable IPD that ensure the transfer of the bulk of impurity atoms are gallium vacancies in various CS. We consider this microscopic mechanism more closely. As is well known, as a vacancy approaches an impurity atom, a vacancy-impurity complex (VIC) is formed in the substitution position [20]. As a result of reorientation, these complexes migrate over the semiconductor volume to the point of

disintegration. Relying on the results of the analysis performed we can write the quasichemical reactions of VIC formation and disintegration:

$$\mathrm{Si}_{\mathrm{Ga}}^{+} + V^{\times} \rightleftarrows (\mathrm{Si}_{\mathrm{Ga}}^{+} V^{\times}), \quad (1)$$

$$\mathrm{Si}_{\mathrm{Ga}}^{+} + V^{-} \rightleftarrows (\mathrm{Si}_{\mathrm{Ga}}^{+} V^{-}), \quad (2)$$

$$\mathrm{Si}_{\mathrm{Ga}}^{+} + V^{-2} \rightleftarrows (\mathrm{Si}_{\mathrm{Ga}}^{+} V^{2-}), \quad (3)$$

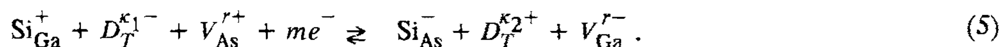
$$\mathrm{Si}_{\mathrm{Ga}}^{+} + V^{3-} \rightleftarrows (\mathrm{Si}_{\mathrm{Ga}}^{+} V^{3-}). \quad (4)$$

Thus, the main transfer of silicon atoms proceeds from the formation, migration, and disintegration of the complexes $(\mathrm{Si}_{\mathrm{Ga}}^{+} V_{\mathrm{Ga}}^{\times})$, $(\mathrm{Si}_{\mathrm{Ga}}^{+} V_{\mathrm{Ga}}^{-})$, $(\mathrm{Si}_{\mathrm{Ga}}^{+} V_{\mathrm{Ga}}^{2-})$, and $(\mathrm{Si}_{\mathrm{Ga}}^{+} V_{\mathrm{Ga}}^{3-})$. Apart from single gallium vacancies, VIC formation may also involve their clusters, e.g., divacancies. In this case, the CS of the defect that forms a complex can be higher than the CS of the vacancy V_{Ga}^{3-}.

It should be noted that a certain part of the impurity atoms can be transferred through other defects. For example, the transfer of silicon atoms in the arsenic sublattice $\mathrm{Si}_{\mathrm{As}}^{-}$ can involve V_{As} or the interstitial arsenic atoms I_{As}, if they are electrically neutral or in a positive CS. However, from Section 1.1 it follows that, with an ordinary thermal treatment, the contribution of these mechanisms to the diffusion is insignificant.

1.3. Model of Transitions of Silicon Atoms between Crystal Sublattices. As experimental data show, the portion of silicon atoms in the arsenic sublattice increases with a buildup of the impurity concentration and, at high levels of alloying, becomes comparable with the silicon concentration in the gallium sublattice [7, 8]. This implies that the description of the alloying process requires the development of a model of silicon atom transitions from the gallium sublattice to the arsenic sublattice and back.

We assume that the transition of $\mathrm{Si}_{\mathrm{Ga}}^{+}$ to the arsenic sublattice occurs as a result of capture of the vacancy V_{As}, and the reverse transition of $\mathrm{Si}_{\mathrm{As}}^{-}$ to the gallium sublattice is due to capture of the gallium vacancy V_{Ga}. We now consider this reaction in the most general form, taking into account the CS of defects. Because direct interaction of $\mathrm{Si}_{\mathrm{Ga}}^{+}$ with a positively charged arsenic vacancy, for example, V_{As}^{2+}, is impossible, we presume that the escape of $\mathrm{Si}_{\mathrm{Ga}}^{+}$ from a site of the gallium sublattice results from interaction with a certain point defect (PD). We will not specify the form of this defect. The escape of $\mathrm{Si}_{\mathrm{As}}^{-}$ from a site of the arsenic sublattice proceeds similarly. Then the quasichemical reaction of reversible transition can be represented as



$$\mathrm{Si}_{\mathrm{Ga}}^{+} + D_{T}^{\kappa_1 -} + V_{\mathrm{As}}^{r+} + me^{-} \rightleftarrows \mathrm{Si}_{\mathrm{As}}^{-} + D_{T}^{\kappa_2 +} + V_{\mathrm{Ga}}^{r-}. \quad (5)$$

Here m is the number of electrons involved in the reaction.

For the quasichemical reaction (5) there is a corresponding condition of conservation of electric charge

$$1 - \kappa_1 + r_{\mathrm{As}} - m = -1 + \kappa_2 - r_{\mathrm{Ga}}. \quad (6)$$

Local thermodynamic equilibrium (LTE) is assumed to exist between silicon atoms in the arsenic sublattice and in the gallium sublattice. Let k_1 and k_2 be the rates of the direct and reverse reactions (5). Then the for the reaction (5) the law of active masses [7, 21] has the form:

$$k_1 \, C C_{D}^{\kappa_1 -} \, C_{\mathrm{As}}^{Vr+} \, \chi^{m} = k_2 \, C^{A} \, C_{D}^{\kappa_2 +} + C_{\mathrm{Ga}}^{Vr-}. \quad (7)$$

We take into consideration that there is LTE between vacancies in various CS, and their concentrations are related by the formulas [22]

$$\tilde{C}_{Ga}^{Vr-} = \tilde{C}_{Ga}^{V\times} \chi^{r_{Ga}} h_{Ga}^{r-} (T) , \tag{8}$$

$$\tilde{C}_{As}^{Vr+} = \tilde{C}_{Ga}^{V\times} \chi^{-r_{As}} h_{As}^{r+} (T) , \tag{9}$$

where $\tilde{C}_{Ga}^{V\times} = C_{Ga}^{V\times}/C_{Ga_i}^{V\times}$ and $\tilde{C}_{As}^{V\times} = C_{As}^{V\times}/C_{As_i}^{V\times}$. Here χ is the electron concentration reduced to n_i [22]:

$$\chi = \frac{C - C^A - N + \sqrt{(C - C^A - N)^2 + 4n_{ie}^2}}{2n_i} , \tag{10}$$

Similar functional relations also hold for concentrations of the PD D_T in various CS:

$$C_D^{\kappa_1 -} = C_D^{\times} \chi^{\kappa_1} h_D^{\kappa_1 -} (T) , \tag{11}$$

$$C_D^{\kappa_2 +} = C_D^{\times} \chi^{-\kappa_2} h_D^{\kappa_2 +} (T) . \tag{12}$$

Substituting Eqs. (6) and (8)-(12) into Eq. (7) yields

$$C^A = A\chi^2 C , \quad A = A^0 A^V , \tag{13}$$

$$A^0 = (k_1 h_D^{\kappa_1 -} h_{As}^{r+})/(k_2 h_D^{\kappa_2 +} h_{Ga}^{r-}) , \tag{14}$$

$$A^V = \tilde{C}_{As}^{V\times} / \tilde{C}_{Ga}^{V\times} . \tag{15}$$

Expression (13) in combination with expression (10) defines the functional relation C^A vs C.

To determine the quantity A we employ experimental data [9]. In [9], both the total concentration of the impurity C^T and the electron concentration n were measured. For alloying of gallium arsenide, silicon diffusion from a steady source was carried out at a temperateure of 815°C over 10 h. Since semiconductor alloying was effected by high-temperature diffusion from a steady source, the vacancy subsystems of the two sublattices are in a state of thermodynamic equilibrium. To obtain the value of A we use the results of measurements taken at a depth of 0.6 μm in order to eliminate near-surface effects. The measured values of $C_{0.6}^T$ and $n_{0.6}$ are $2.64 \cdot 10^7$ and $2.78 \cdot 10^6$ μm^{-3}, respectively.

Since the value of n_i for 815°C is $0.8788 \cdot 10^5$ μm^{-3}, the relation $n >> n_i$ is fulfilled. Then from Eq. (10) it follows that C-C^A-$N >> n_i$ and

$$n \approx C - C^A - N . \tag{6}$$

Considering that

$$C^T = C + C^A , \tag{7}$$

from expressions (10) and (13) we derive the equation for the quantity A:

$$A = \frac{C^T - n - N}{(C^T + n + N)\,(n/n_i)^2} . \tag{18}$$

The value of A thus determined is $3.069 \cdot 10^{-4}$.

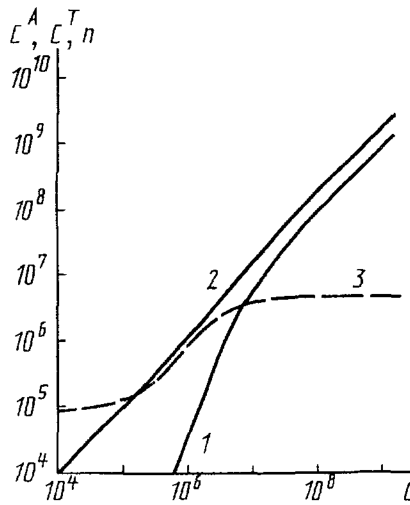


Fig. 1. Concentration of silicon atoms in the arsenic sublattice vs silicon concentration in the gallium sublattice: 1) silicon concentration in the arsenic sublattice; 2) total concentration of the impurity; and 3) electron concentration. C^A, C^T, C, n, μm^{-3}.

Drawing on the obtained value of A we can calculate the functional dependences of C^A, n, and C^T on C. Determining C^A requires that nonlinear algebraic equation (13) be solved. The solution was performed using the Newton method.

As is evident from Fig. 1, the silicon concentration in the arsenic sublattice is $C^A << C$ for $C < 10^6\ \mu\text{m}^{-3}$; however, the impurity portion in this sublattice increases sharply for $C \geq 10^6\ \mu\text{m}^{-3}$, and, when $C \geq 10^7\ \mu\text{m}^{-3}$, C^A approaches C. As a consequence of the indicated phenomenon, the concentration of the charge carriers rises only up to a certain limiting value n^C equal to $5 \cdot 10^6\ \mu\text{m}^{-3}$. As allows from Eq. (13), this value is determined by the product of A^0 and A^V. It is seen from expressions (14) and (15) that A^0 depends on the treatment temperature, whereas A^V is governed by the state of the vacancy subsystems of the two sublattices. As follows from Eqs. (13)-(15), the maximal attainable concentration of electrons at a specified temperature can be raised by increasing the concentration of the gallium vacancies or decreasing that of the arsenic vacancies. It is known from the physics of solid-phase diffusion that the required effect can be achieved by introducing special impurities or defects into the silicon-alloyed regions. This conclusion is supported by experimental data [16]. Thus, in [16] it is demonstrated that implantation of phosphorus in gallium arsenide causes an increase in the electron concentration in the silicon-alloyed layers.

NOTATION

n_i, n_{ie}, concentration of intrinsic charge carriers and its effective value at high levels of alloying; P_{As}, partial pressure of arsenic vapor; V_{Ga}^{r-}, gallium vacancy in the charge state r_{Ga}^-; V_{As}^{r+}, arsenic vacancy in the charge state r_{As}^+; C_{Ga}^{Vr-}, C_{As}^{Vr+}, concentrations of these particles; $\times$, sign of the neutral charge state; $C_{\text{Ga}_i}^{V\times}$, $C_{\text{As}_i}^{V\times}$, thermally equilibrium concentrations of gallium and arsenic vacancies in the neutral charge state; I_{Ga}^{m+}, interstitial atom of gallium in the charge state $m+$; I_{As}, interstitial atom of arsenic; $D_T^{\kappa 1-}$, $D_T^{\kappa 2+}$, point defects in the charge states κ_1- and κ_2+, respectively; $C_D^{\kappa 1-}$, $C_D^{\kappa 2+}$, concentrations of these particles; e^-, electron; C, C^A, atomic concentrations at the sites of the gallium and arsenic sublattices, respectively; C^T, total concentration of silicon atoms; N, concentration of ionized atoms of another impurity of the opposite type of conductivity; e, electron charge; k_{B}, Boltzmann constant; T, temperature; t, time of thermal treatment; h_{Ga}^{r-}, h_{As}^{r+}, constants of the local thermodynamic equilibrium for the reactions of transition of gallium and arsenic vacancies from the neutral state to the charge states $r-$ and $r+$, respectively; $h_D^{\kappa 1-}$, $h_D^{\kappa 2+}$, constants of the local thermodynamic equilibrium for the reactions of transition of the point defect D_T from the neutral state to the charge states κ_1- and κ_2+, respectively; χ, reduced electron concentration.

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