On concentration dependence of arsenic diffusivity

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Abstract. An analysis of the equations used for modeling thermal arsenic diffusion in silicon has been carried out. It was shown that for arsenic diffusion governed by the vacancy-impurity pairs and the pairs formed due to interaction of impurity atoms with silicon self-interstitials in a neutral charge state, the doping process can be described by the Fick's second law equation with a single effective diffusion coefficient which takes into account two impurity flows arising due to interaction of arsenic atoms with vacancies and silicon self-interstitials, respectively.

Arsenic concentration profiles calculated with the use of the effective diffusivity agree well with experimental data if the maximal impurity concentration is near the intrinsic carrier concentration. On the other hand, for higher impurity concentrations a certain deviation in the local regions of arsenic distribution is observed. The difference from the experiment can occur due to the incorrect use of effective diffusivity for the description of two different impurity flows or due to the formation of nonuniform distributions of neutral vacancies and neutral self-interstitials in heavily doped silicon layers.

1 Introduction

Arsenic is the basic $n$-type impurity in the technology of manufacturing silicon semiconductor devices and integrated microcircuits. It is due to the small difference between the atomic radii of arsenic and silicon that results in a high value of arsenic solubility limit in silicon. At present, arsenic doped regions are formed by ion implantation with subsequent thermal annealing of implanted layers. The thermal treatment provides the electric activation of impurity atoms, recrystallization of amorphous layers, and annealing of radiation defects created by ion implantation. During annealing a transient enhanced diffusion of impurity atoms occurs that results in the increase in the doped region dimensions and, respectively, in the increase of the $p$-$n$ junction depth. On the other hand, due to the strong dependence of the arsenic diffusivity on impurity concentration, there occurs the formation of the specific impurity distribution of a “box-like” form. These impurity distributions are characterized by a practically constant arsenic concentration within the limits of the doped region and a very sharp fall of impurity concentration in the bulk of a semiconductor. Such kind of impurity atom distribution is very important in semiconductor manufacturing because it imparts high electrophysical characteristics to semiconductor devices. It follows from the presented analysis that knowing the concentration dependence of arsenic diffusivity is very important for solving the problems of doping process modeling in the semiconductor technology. Investigation of different concentration dependences of arsenic diffusivity is the goal of this research.
2 Model of diffusion of arsenic atoms

To investigate the concentration dependence of arsenic diffusivity, it is reasonable to consider the diffusion processes which are independent of the factors that complicate the diffusion description, such as arsenic clustering or precipitation, annealing of the defects created by ion implantation, oxidation of the surface of a semiconductor, etc. Therefore, let us consider thermal arsenic diffusion from a constant dopant source on a surface that ensures the maximal impurity concentration below a solubility limit of arsenic in silicon. Let us also assume that the distributions of neutral point defects responsible for impurity diffusion are approximately uniform within the diffusion zone [1] and the local charge neutrality is valid [2, 3, 4, 5]. Then, the system of equations for impurity diffusion due to the formation, migration, and dissociation of the “impurity atom — vacancy” and “impurity atom — silicon self-interstitial” pairs, being in a local thermodynamic equilibrium with the substitutionally dissolved impurity atoms and point defects participating in the pair formation [6], takes the following form:

\[
\frac{\partial C}{\partial t} = \nabla \{ [D^E(\chi) + D^F(\chi)] h (C, C^B) \nabla C \},
\]

\[
\chi = \frac{(C - C^B) + \sqrt{(C - C^B)^2 + 4n_i^2}}{2n_i},
\]

\[
D^{E,F}(\chi) = D^{E,F}_i D^{EC, FC}(\chi) = D^{E,F}_i 1 + \frac{\beta^{E,F}_1 \chi + \beta^{E,F}_2 \chi^2}{1 + \beta^{E,F}_1 + \beta^{E,F}_2},
\]

\[
h (C, C^B) = 1 + \frac{C}{\sqrt{(C - C^B)^2 + 4n_i^2}}.
\]

\[
D^{E,F}_i = D^{E,F - , F -}_i + D^{E,-, F -}_i + D^{E2-, F2-}_i,
\]

\[
\beta^{E,F}_1 = \frac{D^{E-, F -}_i}{D^{E-, F -}_i}, \quad \beta^{E,F}_2 = \frac{D^{E2-, F2-}_i}{D^{E2-, F2-}_i}.
\]

Here \(C\) and \(C^B\) are the concentrations of substitutionally dissolved arsenic atoms and background impurity of the opposite type of conductivity, respectively; \(\chi\) is the concentration of electrons \(n\), normalized to the intrinsic carrier concentration \(n_i\); \(h (C, C^B)\) is the factor describing the influence of built-in electric field on drift of charged pairs; \(D^{E,F}_i\), \(D^{E,-}_i\), and \(D^{E2-}_i\) are the partial intrinsic diffusivities of dopant atoms due to interaction with neutral, singly, and doubly charged vacancies, respectively; \(\beta^{E}_1\) and \(\beta^{E}_2\) are the empirical constants that describe the relative contribution of singly and doubly charged vacancies to the arsenic diffusion. Likewise, \(D^{F,F -}_i\), \(D^{F-, F -}_i\), and \(D^{F2-}_i\) are the partial intrinsic diffusivities of arsenic atoms due to interaction with neutral, singly, and doubly charged self-interstitials, respectively; \(\beta^{F}_1\) and \(\beta^{F}_2\) are the empirical constants that describe the relative contribution of singly and doubly charged self-interstitials to the impurity diffusion.
It follows from Eq. (7) and expressions (3), (4), (5), and (6) that to calculate the arsenic concentration distribution it is necessary to know the intrinsic diffusivities $D^E_i$ and $D^F_i$ that take into account the interaction of impurity atoms with vacancies and self-interstitials, respectively, and 4 values of the empirical constants $\beta_1^E$, $\beta_2^E$, $\beta_1^F$, $\beta_2^F$ that describe the relative contribution of the charged point defects. Unfortunately, it is very difficult to find these values because even the values of the relative contribution of the diffusion mechanism via self-interstitial to the total arsenic transport $f^I = \frac{D^F_i}{D^E_i + D^F_i}$ (7) are characterized by well-marked differences as follows from [7]. For example, $f^I = 0.09$ in the temperature range 975–1200 °C according to the data of [8], whereas $f^I = 0.35-0.55$ for a temperature of 1000 °C according to [9].

In view of the wide scatter of the values of $f^I$ and the complexity of separate determination of the parameters $\beta_1^E$, $\beta_2^E$, $\beta_1^F$, and $\beta_2^F$, a more simple diffusion equation:

$$\frac{\partial C}{\partial t} = \nabla \{ D(\chi) \ h (C, C^B) \ \nabla C \} ,$$

(8)

with the effective diffusivity

$$D(\chi) = D_i C(\chi) = D_i \frac{1 + \beta_1 \chi + \beta_2 \chi^2}{1 + \beta_1 + \beta_2}$$

(9)

is very often used for modeling arsenic diffusion. The empirical constants $\beta_1$ and $\beta_2$ in expression (9) are found from the best fit to experimental data. For example, in Ref. [10] a fitting routine based on different experimental data was used and temperature dependences of the arsenic partial diffusivities $D^\times_i$, $D^-_i$, $D^{2-}_i$ due to neutral, singly, and doubly charged intrinsic point defects were evaluated, which allows one to calculate the values of $D_i = D^\times_i + D^-_i + D^{2-}_i$, $\beta_1 = D^-_i/D^\times_i$ and $\beta_2 = D^{2-}_i/D^\times_i$ for different temperatures of thermal treatment.

It is worth noting that impurity diffusion due to the “impurity atom — silicon self-interstitial” pairs can occur basically via interaction with self-interstitials in the neutral charge state. Then, the description of impurity diffusion by Eq. (8) and concentration dependence of diffusivity (9) is identical to the use of the initial equation (11) and concentration dependence (3). Really, it is possible in this case to present the concentration dependence (9) as a sum of concentration dependencies (3) written for diffusion due to the vacancy-impurity pairs and for diffusion via the “impurity atom — silicon self-interstitial” pairs:

$$D_i \frac{1 + \beta_1 \chi + \beta_2 \chi^2}{1 + \beta_1 + \beta_2} = D_i^E \frac{1 + \beta_1^E \chi + \beta_2^E \chi^2}{1 + \beta_1^E + \beta_2^E} + D_i^{F\times} .$$

(10)

It follows from Eq. (10) that

$$D_i = D_i^{E\times} + D_i^{F\times} + D_i^{E^-} + D_i^{E^{2-}} ,$$

(11)
\[ \beta_1 = \frac{D_i^{E-}}{(D_i^{E-} + D_i^{F-})}, \quad \beta_2 = \frac{D_i^{E2-}}{(D_i^{E-} + D_i^{F-})}. \]  

(12)

3 Simulation of arsenic diffusion in silicon

In Fig. 1 the arsenic concentration profile calculated for the case of thermal diffusion from a constant source on the surface of a semiconductor is presented. The experimental data obtained in [11] are used for comparison. In Ref. [11], arsenic diffusion was carried out at a temperature of 1108 °C for 120 min. The arsenic concentration profile was measured by neutron activation analysis.

The analytical solution for the constant value of arsenic diffusivity, i.e., without taking account of the concentration dependence \( D = D(\chi) \) and the drift of charged pairs in built-in electric field, is

\[ C(x, t) = C_S \text{erfc} \left( \frac{x}{L} \right) \]

(13)

which is also presented by the dotted curve in Fig. 1. Here \( C_S = \text{const} \) is the arsenic concentration on the surface of a semiconductor, \( L = 2 \sqrt{D_i t} \) is the characteristic length of impurity diffusion and \( \text{erfc}(x) = 1 - \text{erf}(x) \) is the additional error function.

![Figure 1: Arsenic concentration profiles formed by thermal diffusion from a constant source on the silicon surface. The dotted and solid curves represent the arsenic concentration profiles calculated from analytical solution (13) and obtained by numerical solution of the diffusion equation that takes account of the concentration dependence of arsenic diffusivity and drift of the charged species in the built-in electric field. Diffusion temperature is 1108 °C for 120 min. Filled circles are the experimental data of [11].](image)

The intrinsic diffusivity \( D_i = 2.55 \times 10^{-6} \ \mu m^2/s \) and the parameters \( \beta_1 = 611 \) and \( \beta_2 = 44.94 \) that prescribe a concentration dependence of impurity diffusivity [9] at a temperature of 1108 °C have been obtained from the expression of [10].
\[
D_{\text{As}}(\chi) = 4.95 \times 10^{-4} \exp \left(-\frac{1.4 \text{ eV}}{k_B T}\right) + 6.103 \times 10^8 \exp \left(-\frac{3.95 \text{ eV}}{k_B T}\right) \chi + 7.76 \times 10^{11} \exp \left(-\frac{5.1 \text{ eV}}{k_B T}\right) \chi^2 \quad \text{[\(\mu m^2/s\)]} \quad (14)
\]

It is clearly seen from Fig. [1] that the account of the drift of charged pairs \((\text{As}^+D^\times)\) and \((\text{As}^+D^2^-)\) and also the account of the concentration dependence of arsenic diffusivity due to the increased concentrations of charged defects \(D^-\) and \(D^2^-\) in the region with higher impurity concentration results in a good agreement of the calculated profile with experimental data. It is worth noting that the analytical solution gives smaller concentration values and, respectively, smaller depth of the \(p-n\) junction in comparison with the experiment.

Based on the good agreement of numerical calculations with experimental data [11], one can carry out modeling of arsenic diffusion for higher impurity concentration at the surface of a semiconductor \(C_S = 2.0 \times 10^8 \mu m^{-3}\). It follows from Ref. [12] that the maximal value of equilibrium electron concentration \(n_e\) that can be obtained in arsenic doped silicon at a temperature of 1108 °C is equal to 4.24\(\times 10^8 \mu m^{-3}\). A further increase of electron concentration is limited by the clustering of impurity atoms. Taking into account these data on \(n_e\), it might be expected that for \(C_S = 2.0 \times 10^8 \mu m^{-3}\) the arsenic clustering is negligible and can be excluded in diffusion modeling. The arsenic concentration profile after thermal treatment for 30 min calculated under these assumptions is presented in Fig. [2].

Figure 2: Arsenic concentration profiles formed by thermal diffusion from a constant source on the silicon surface. The dotted and solid curves represent the arsenic concentration profiles calculated from analytical solution (13) and obtained by numerical solution of the diffusion equation that takes account of the concentration dependence of arsenic diffusivity and drift of the charged species in the built-in electric field. Diffusion temperature is 1108 °C for 30 min.

It can be seen from Fig. [2] that the form of arsenic profile differs substantially from the distribution presented in Fig. [1] and from analytical solution (13). Indeed, due to the significant increase in arsenic diffusion in the high concentration region, the impurity distribution in this part of the profile becomes flat.
and differs substantially from the erfc-function. On the other hand, the arsenic profile becomes abruptly falling in the bulk of a semiconductor and it is characterized by a significant concentration gradient. It means that using a strong nonlinear dependence of arsenic diffusivity on impurity concentration, it is possible to form concentration profiles of electrically active arsenic atoms with an ideal “box-like” form.

Let us compare now the calculations of diffusion process characterized by a strong nonlinear concentration dependence of diffusivity with experimental data. Figure 3 presents the arsenic concentration profile calculated for the treatment temperature of 1050 °C and duration of 60 minutes. The parameters of arsenic diffusivity $D_i = 5.8134 \times 10^{-7} \, \mu m^2/s$; $\beta_1 = 238.9$; and $\beta_2 = 12.7$ were taken from [10]. The value of the impurity concentration at the surface of a semiconductor $C_S$ has been chosen equal to $2.3 \times 10^8 \, \mu m^{-3}$. This value is below the maximal equilibrium electron concentration value $n_e = 3.566 \times 10^8 \, \mu m^{-3}$ for the annealing temperature under consideration [12]. Therefore, it is possible to assume that arsenic clustering does not play an important role in diffusion.

![Figure 3: Arsenic concentration profiles formed by thermal diffusion from a constant source on the silicon surface. The dotted and solid curves represent the arsenic concentration profiles calculated from analytical solution (13) and obtained by numerical solution of the diffusion equation that takes account of the concentration dependence of arsenic diffusivity and drift of the charged species in the built-in electric field. Diffusion temperature is 1050 °C for 60 min. Filled circles are the experimental data of [11].](image)

It can be seen from Fig. 3 that the calculated arsenic concentration profile agrees well with experimental data both in the region of the high impurity concentration and in the region of the low concentration of impurity atoms including the region of p-n junction. On the other hand, some difference between the calculated and experimental profiles is observed in the region where a strong decrease in the impurity concentration begins. For comparison, in Fig. 4 the results of simulation of arsenic diffusion based on the model of [13] are presented. It is supposed in this model that doubly charged point defects do not significantly contribute to arsenic diffusion. The following parameters that describe arsenic diffusion have been used in simulation: $D_i = 5.537 \times 10^{-7} \, \mu m^2/s$, $\beta_1 = 100$, and $\beta_2 = 0$ [13]. The impurity concentration
at the surface $C_S$ has been chosen equal to $2.9 \times 10^8 \, \mu m^{-3}$.

Figure 4: Arsenic concentration profiles formed by thermal diffusion from a constant source on the silicon surface. The dotted and solid curves represent the arsenic concentration profiles calculated from analytical solution (15) and obtained by numerical solution of the diffusion equation. Diffusion temperature is 1050 $^\circ$C for 60 min. Filled circles are the experimental data of [11].

It can be seen from Fig. 4 that both the arsenic concentration profiles obtained by analytical solution and those by numerical calculation agree well with experimental data excluding the region of a low impurity concentration. It is worth noting that here the approximate analytical solution of the diffusion equation (8) for $\beta_2 = 0$ obtained in [14] was used:

$$C(x, t) = C_S \left[ 1.00 - 0.87 \left( \frac{u}{u_0} \right) - 0.45 \left( \frac{u}{u_0} \right)^2 \right], \quad (15)$$

where

$$u = \frac{x}{\sqrt{t}}, \quad u_0 = 2 \sqrt{\frac{2D_i C_S}{n_i}}. \quad (16)$$

It was assumed in [14] that the concentration dependence of effective diffusivity is described by the following expression:

$$D^C(\chi) \ h(C, C^B) = 2 \left( \frac{C}{n_i} \right)^q. \quad (17)$$
4 Analysis of the results obtained by simulation of impurity diffusion with different concentration dependencies of arsenic diffusivity

The arsenic concentration profile presented in Fig. 1 shows that the concentration dependence of arsenic diffusivity obtained in [10] provides excellent agreement with experimental data on impurity concentration closed to the value of $n_i$. On the other hand, if the arsenic concentration $C >> n_i$ and the concentration profile of electrically active arsenic gets a “box-like” form (see Fig. 3), a difference from the experimental data is observed in the local region where a strong decrease in the impurity concentration begins. Therefore, for solving the problems arising in modeling silicon doping with arsenic it seems more convenient to use the concentration dependence proposed in [13] which is characterized by neglecting the interaction of impurity atoms with doubly charged point defects. Indeed, in this case, a good agreement with experiment is observed in the whole region of high impurity concentration and only a small difference takes place in the region of low arsenic concentration which is less important for subsequent calculations of electrophysical parameters. Taking into account the results of [16], one can suppose that this difference appears due to the overlooked possibility of direct migration of arsenic interstitial atoms.

Incomplete agreement of the calculated arsenic profile with the experimental ones can also be due to a certain inadequacy of using Eq. (8) in a heavily doped region $C >> n_i$, instead of a more exact equation (1). Indeed, with increase in the impurity concentration, the concentration of electrons becomes greater than $n_i$. As a result, the concentrations of negatively charged silicon interstitials are also increasing. If these defects play an important role in the impurity transport, the description of diffusion based on Eq. (8) becomes incomplete and it is necessary to use more exact equation (1). However, there can exist another explanation of the difference between numerical calculations and experimental data. Indeed, increase in the concentration of substitutionally dissolved impurity atoms as well as increase in the electron concentration can result in the formation of nonuniform distributions of neutral vacancies and silicon self-interstitials [15]. In this case, both Eq. (8) and Eq. (1) give inadequate description of the impurity diffusion. The solution of this problem requires further investigations.

5 Conclusions

The analysis of the equations used for modeling thermal arsenic diffusion in silicon has been carried out. With this purpose, different concentration dependencies of impurity diffusivity that are used for modeling arsenic transports processes have been analyzed. It is supposed that diffusion is carried out due to the formation, migration, and dissociation of “impurity atom — vacancy” and “impurity atom — silicon self-interstitial” pairs which are being in a local thermodynamic equilibrium with substitutionally dissolved impurity atoms and point defects participating in pair formation. It is shown that for arsenic diffusion governed by the vacancy–impurity pairs and by the pairs formed due to the interaction of impurity atoms
with silicon self-interstitials in a neutral charge state, the doping process can be described by the Fick’s second law equation with a single effective diffusion coefficient which takes into account two impurity flows arising as a result of the interaction of arsenic atoms with vacancies and silicon interstitials, respectively.

Arsenic concentration profiles calculated with the use of the effective diffusivity taking into account two different impurity flows agree well with experimental data if the maximal impurity concentration is close to the intrinsic carrier concentration $n_i$. On the other hand, similar calculations for impurity concentrations above $n_i$ are characterized by a certain deviation from experimental data in local regions of arsenic distribution. So, the use of a diffusion model that takes account of the significant contribution of doubly negatively charged point defects leads to the deviation in the region where a significant decrease in the impurity concentration begins. On the other hand, the neglect of the contribution of these defects leads to a difference in the region of a low impurity concentration. This difference can be due to the incorrectness which arises if a single effective diffusivity is used for the description of two different impurity flows. On the other hand, the origin of these small differences can be the formation of nonuniform distributions of neutral vacancies and neutral silicon self-interstitials in heavily doped layers.

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