Change in the microscopic diffusion mechanisms of boron implanted into silicon with increase in the annealing temperature

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Abstract
A two stream model of boron diffusion in silicon has been developed. The model is intended for simulation of transient enhanced diffusion including redistribution of ion-implanted boron during low temperature annealing. The following mechanisms of boron diffusion were proposed, namely: the mechanism of a long-range migration of nonequilibrium boron interstitials and the mechanism due to the formation, migration, and dissolution of the “impurity atom – silicon self-interstitial” pairs. Based on the model, simulation of the redistribution of boron implanted into silicon substrates for annealing temperatures of 800 and 900 Celsius degrees was carried out. The calculated boron concentration profiles agree well with the experimental data. It was shown that for a temperature of 800 Celsius degrees the transport of impurity atoms occurred due to the long-range migration of nonequilibrium boron interstitials generated during cluster transformation or dissolution. On the other hand, it was found that at a temperature of 900 Celsius degrees the pair diffusion mechanism played a main role in the significant transient enhanced diffusion. A number of parameters describing the transport of nonequilibrium boron interstitials and transient enhanced diffusion of substitutionally dissolved boron atoms were determined. For example, it was found that at a temperature of 900 Celsius degrees the time-average enhancement of boron diffusion was approximately equal to 44 times. The results obtained are important for the development of methods of transient enhanced diffusion suppression keeping in mind the scaling of the dimensions of silicon integrated microcircuits.

Keywords: implantation; annealing; diffusion; silicon; boron; interstitial
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1 Introduction

At present the high-dose low-energy ion implantation is widely used for manufacturing silicon microcircuits with ultra-large-scale integration (ULSI). During annealing of ion-implanted layers, transient enhanced diffusion (TED) of dopant atoms occurs. The TED is one of the major factors that limits the device scaling and parameter improvement, especially for the active regions with the p-type of conductivity formed by B implanted into Si with doses providing dopant concentration above the solubility limit for the annealing temperature. To suppress the TED of boron atoms, various methods are used in the technology of ULSI, including dopant implantation into the preamorphized layer [1, 2].

In Fig. 1 the boron concentration profiles after annealing for 60 s at temperatures of 800 and 900 °C are presented. The experimental boron distributions measured by secondary ion mass spectroscopy (SIMS) are taken from Yeong et al. [2]. In [2] Czochralski grown (100) n-type silicon wafers were preamorphized by germanium (Ge) ion implantation at 15 keV to a dose of $1.5 \times 10^{15}$ cm$^{-2}$. Thereafter, boron implantation was conducted at 1 keV with the same dose. The thermal annealing was carried out under N$_2$ ambient, with ramp-up and ramp-down rates being equal to 60 °C/s and 45 °C/s, respectively.

It is seen from Fig. 1 that significant diffusion redistribution of the concentration profiles of ion-implanted boron occurs during rapid thermal annealing when part of impurity atoms is transferred into the undoped region located beneath the surface. Based on the experimental results of [2], it is possible to formulate the following features of ion-implanted boron redistribution:

(i). The main amount of boron atoms located in the region of high impurity concentration is immobile. Only negligible diffusion near the surface occurs that does not change the position of the peak of impurity concentration formed by ion implantation. (ii). Significant redistribution of boron is observed only in the region of concentrations below $10^8$ µm$^{-3}$. (iii). Boron redistribution in the low concentration region differs at temperatures of 800 and 900 °C, namely: a) at a temperature of 800 °C the boron concentration profile after annealing has an extended “tail”, and the shape of this ”tail” is a straight line if the axis of concentration is logarithmic; b) after annealing at a temperature of 900 °C the profile of boron distribution in the region of concentrations below $10^8$ µm$^{-3}$ rounded upward. It may be presumed that the different shape of boron concentration profiles for the temperatures of
Figure 1: Total boron concentration profiles calculated for temperatures of 800 and 900 °C on the basis of the long-range migration of boron interstitials. The experimental data (open and black circles) are taken from Yeong et al. [2].

800 and 900 °C is due to the change in the microscopic mechanism of boron diffusion on increase in the annealing temperature.

Thus, the analysis of the experimental data of [2] allows us to formulate the goal of the present work: to investigate the microscopic mechanisms of boron transport in the temperature range 800 – 900 °C when the change in the microscopic mechanisms occurs.

2 Microscopic mechanisms of boron diffusion

It was supposed in [3] that the formation of extended “tails” in the region of low impurity concentration during short low temperature thermal treatments of ion-implanted layers occurred due to migration of nonequilibrium impurity interstitials. Analysis of the analytical solutions [4, 5] obtained for the case
of continuous generation of nonequilibrium impurity interstitials within an implanted layer shows that there occurs the formation of a “tail” in the low-concentration region of impurity atoms during annealing. Moreover, the impurity concentration profile in this low concentration region represents a straight line if the axis of concentration is logarithmic. This conclusion is confirmed by the calculations made in [6].

It maybe assumed that during the recrystallization of the amorphous layer at the initial stage of annealing the boron atoms occupy the substitutional position. These atoms are immobile within the implanted layer being displaced at the initial stage of annealing only for a short distance at a temperature near or below 800 °C to form clusters which incorporate boron atoms and self-interstitials. During the subsequent annealing, transformation and dissolution of these clusters occur. It is supposed that during these processes part of dopant atoms becomes interstitial and the other boron atoms return again to the substitutional position [7]. These substitutional atoms are immobile as before because the temperature is too low for the formation and migration of pairs, including point defect and dopant atom, whereas boron interstitials can migrate to the surface and into the bulk of the semiconductor. Migrating into the bulk, these boron interstitials form an extended “tail” in the low-concentration region which is characterized by a straight line if the logarithmic scale is used for impurity concentration.

At a temperature near 900 °C or above the substitutionally dissolved boron atoms become also mobile. Due to the high concentration of nonequilibrium self-interstitials, a significant transient enhanced diffusion occurs which provides the formation of a “tail” rounded upward. It is supposed that diffusion of substitutionally dissolved boron occurs due to the formation, migration, and dissolution of the “impurity atom — silicon self-interstitial” pairs [7, 8]. Note, that these pairs are in local equilibrium with the substitutionally dissolved boron atoms and nonequilibrium self-interstitials. We also suppose that on this stage of annealing the vacancy concentration is negligible, and one can neglect the diffusion flux occurring due to the boron pairing with vacancies.

3 Model of boron diffusion

The analysis of the microscopic mechanisms allows us to propose the following model of ion-implanted boron diffusion. It is seen from Fig.1 that irrespective
of the temperature, the main part of boron atoms in the region of high dopant concentration is immobile and forms clusters with silicon self-interstitials [9]. During transformation or dissolution of these clusters at a temperature near 900 °C or above one fraction of boron atoms becomes substitutional and can diffuse by the mechanism of the formation, migrations and dissolution of the “impurity atom – silicon self-interstitial” pairs, whereas the other fraction of previously clustered boron occupies the interstitial position and can migrate due to changing the interstitial sites in silicon lattice. Taking into account the transformation or dissolution of boron clusters, one can use the following systems of equations to describe these processes of boron diffusion:

1. **Expression for the total concentration of impurity atoms** $C_T$:

   $$C_T = C + C^{AI} + C^{AC} + C^{AD};$$  

2. **Conservation law for the impurity atoms incorporated into clusters [7]:**

   $$\frac{\partial C^{AC}}{\partial t} = S^{ACS} + S^{ACI} - G^{ACS} - G^{ACI};$$

3. **Conservation law for the impurity atoms bound to extended defects [7]:**

   $$\frac{\partial C^{AD}}{\partial t} = S^{ADS} + S^{ADI} - G^{ADS} - G^{ADI};$$

4. **Conservation law for all impurity atoms:**

   $$\frac{\partial C_T(x,t)}{\partial t} = \frac{\partial C}{\partial t} + S^{AS} + S^{AI} - G^{AS} - G^{AI};$$

5. **Equation describing the pair diffusion mechanisms [7]:**

   $$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left[ D_E \frac{\partial (\tilde{C} \times C)}{\partial x} + \frac{D_E \tilde{C} \times C}{\chi} \frac{\partial \chi}{\partial x} \right] + \frac{\partial}{\partial x} \left[ D_F \frac{\partial (\tilde{C} \times C)}{\partial x} + \frac{D_F \tilde{C} \times C}{\chi} \frac{\partial \chi}{\partial x} \right] + \frac{C^{AI}(x,t)}{\tau^{AI}} - S^{AS} + G^{AS};$$

5
6. Equation describing the long-range migration of nonequilibrium boron interstitials [6, 7]:

\[ \frac{\partial^2 C_{AI}}{\partial x^2} - \frac{C_{AI}}{l_{AI}^2} + \frac{S_{\tau}^{AI}}{l_{AI}^2} + \frac{G_{\tau}^{AI}}{l_{AI}^2} = 0, \]  

(6)

where

\[ S^{AI} = S^{ACI} + S^{ADI}, \quad G^{AI} = G^{ACI} + G^{ADI}, \]  

(7)

\[ S^{AS} = S^{ACS} + S^{ADS}, \quad G^{AS} = G^{ACS} + G^{ADS}, \]  

(8)

\[ l_{AI} = \sqrt{d_{AI} \tau_{AI}}, \]  

(9)

\[ S_{\tau}^{AI} = S^{AI} \tau_{AI}, \quad G_{\tau}^{AI} = G^{AI} \tau_{AI}. \]  

(10)

Here \( C \) and \( C_{AI} \) are the concentrations of substitutionally dissolved impurity atoms and nonequilibrium dopant interstitials, respectively; \( C^{AC} \) and \( C^{AD} \) are the concentrations of impurity atoms incorporated into clusters and bound to the extended defects, respectively; \( S^{ACS} \) and \( S^{ACI} \) are respectively the rates of absorption of substitutionally dissolved impurity atoms and impurity interstitials due to the cluster formation; \( S^{ADS} \) and \( S^{ADI} \) are respectively the rates of absorption of substitutionally dissolved impurity atoms and impurity interstitials by extended defects; \( G^{ACS} \) and \( G^{ACI} \) are respectively the rates of generation of separate substitutionally dissolved impurity atoms and impurity interstitials during cluster transformation or dissolution; \( G^{ADS} \) and \( G^{ADI} \) are respectively the rates of generation of separate substitutionally dissolved impurity atoms and impurity interstitials during extended defect annealing; \( C^{V_x} \) and \( C^{I_x} \) are the concentrations of vacancies and self-interstitials in the neutral charge state normalized to the equilibrium concentrations \( C_{eq}^{V_x} \) and \( C_{eq}^{I_x} \), respectively; \( D^E (\chi) \) is the effective diffusivity of impurity atoms due to the vacancy—impurity pair mechanism; \( D^F (\chi) \) is the effective diffusivity of impurity atoms due to migration of the “impurity atom—self-interstitials” pairs; \( \chi \) is the concentration of charge carriers normalized to the intrinsic carrier concentration \( n_i \); \( C^B \) is the concentration of impurity with the opposite-type conductivity; \( d^{AI} \) is the diffusivity of nonequilibrium impurity interstitials; \( \tau^{AI} \) is the average lifetime of impurity interstitials mediated by recombination with vacancies and kickout of silicon.
atoms from the lattice sites. We note that the concentration dependencies $D^E(\chi)$ and $D^F(\chi)$ are described in [10].

4 Results of numerical calculations

In this section we use the developed model of boron diffusion for simulation of the experimental data of Yeong et al. [2]. It is worth to note that the experimental boron profiles measured in [2] for annealing temperatures of 800 and 900 °C are characterized, in contrast to the work of Hamilton et al. [1], by the absence of a local peak of boron concentration in the region of EOR defects. Therefore, we neglect all the processes mediated by the extended defects. We also suppose that after the initial stage of annealing only transformation or dissolution of the boron clusters occurs, and the absorption of boron atoms by the clusters is negligible.

To describe the spatial distribution of impurity atoms after solid phase recrystallization $C_0(x)$ and the spatial distribution of the generation rate for boron interstitials $G^{AI}(x,t)$, the Pearson-IV distribution $f^P(x,R_p,\Delta R_p,S_k)$ [11] is used:

$$C_0(x) = C_m f^P(x,R_p,\Delta R_p,S_k),$$

$$G^{AI}(x,t) = g_m f^P(x,R_p,\Delta R_p,S_k),$$

where

$$C_m = \frac{Q}{\sqrt{2\pi\Delta R_p}} \times 10^{-8}. \quad (13)$$

Here $C_m$ is the maximal concentration of boron atoms after implantation; $g_m$ is the maximal value of the generation rate of boron interstitials per unit volume; $Q [cm^{-2}]$ is the dose of ion implantation; $R_p$ and $\Delta R_p [\mu m]$ are the average projective range of boron ions and straggling of the projective range, respectively; $S_k$ is the skewness of the impurity profile.

In Fig. 1 the boron concentration profiles calculated for the diffusion occurring only due to the long-range migration of nonequilibrium boron interstitials are shown. As can be seen from Fig. 1, the calculated boron profile is in good agreement with the experimental data for an annealing temperature of 800 °C. The following values of the model parameters were used to provide
the best fit of the calculated boron concentration profile to the experimental one:

**Parameters prescribing the initial distribution of implanted boron:**

\(Q = 1.5 \times 10^{15} \text{ cm}^{-2}\); \(R_p = 0.0044 \mu\text{m}\); \(\Delta R_p = 0.0036 \mu\text{m}\); \(S_k = 0.24\).

**Parameters specifying the process of interstitial diffusion:** the duration of annealing \(\tau_p = 60 \text{ s}\); the annealing temperature \(T_C = 800 \degree \text{C}\); the maximum value of the generation rate of nonequilibrium impurity interstitials \(g_m = 2.4 \times 10^6 \mu\text{m}^{-3} \text{s}^{-1}\); the average migration length of boron interstitials \(l^{AI} = 11 \text{ nm}\); the effective escape velocity of interstitial impurity atoms \(v_{eff}^S = 0\); the concentration of boron interstitials on the right boundary \(C_{B}^{AI} = 0\); the position of the right boundary \(x_B = 0.5 \mu\text{m}\). It is also supposed that the average lifetime of nonequilibrium impurity interstitials \(\tau^{AI}\) is significantly shorter than the duration of annealing.

The boron concentration profile presented in Fig. 1 for a temperature of \(T_C = 800 \degree \text{C}\) was calculated on the assumption that approximately 6.9% of the implanted boron atoms are being transferred to the transient interstitial positions and then become immobile again occupying the substitutional sites. Migration of these nonequilibrium interstitial atoms results in the formation of an extended “tail” on the boron concentration profile.

A similar simulation was also performed for a temperature of \(T_C = 900 \degree \text{C}\). The following parameters specifying the process of interstitial diffusion were used: \(g_m = 9.0 \times 10^6 \mu\text{m}^{-3} \text{s}^{-1}\); \(l^{AI} = 10 \text{ nm}\). It can be seen from Fig. 1 that the calculated boron profile disagrees with the experimental one. The quantitative difference of the shape of the experimental boron concentration profile points to the fact that boron diffusion at a temperature of \(T_C = 900 \degree \text{C}\) cannot be attributed to the mechanism of the log–range migration of nonequilibrium impurity interstitials. Therefore, we carried out a new simulation taking into account two independent fluxes of boron atoms.

Figure 2 presents the profiles of the total boron concentration and concentration of substitutionally dissolved boron atoms after annealing at 900 \degree \text{C} calculated within the framework of the full two stream diffusion model. It is supposed that the pair diffusion mechanism play an important role at a temperature of 900 \degree \text{C} in addition to the long-range migration of boron interstitials. The value of boron diffusivity obtained from the best fit to the experimental data is equal to \(2.7 \times 10^{-6} \mu\text{m}^2/\text{s}\) that approximately 46 times exceeds the thermal equilibrium value of diffusivity equal to \(6.11 \times 10^{-8} \mu\text{m}^2/\text{s}\). It means that a significant transient enhanced diffusion occurs. The extracted value of the empirical coefficient \(\beta_1^F\) which describes the contribu-
The average migration length of boron interstitials is equal to 12 nm.

Figure 2: Substitutionally dissolved boron concentration profile calculated for a temperatures of 900 °C on the basis of the model considering two mechanisms of boron diffusion. The experimental data for total boron concentration (black circles) are taken from Yeong et al. [2]. Dashed curve — boron solubility limit in silicon. The dashed-dotted curve — concentration of intrinsic carriers.

The good agreement of the calculated boron concentration profile with the experimental data in contrast to Fig. 1 allows one to make a conclusion that at 900 °C the basic mechanism of the boron transient enhanced diffusion is the mechanism of formation, diffusion, and dissolution of the “substitutionally dissolved boron atom — silicon self-interstitial” pairs, whereas at a temperature of 800 °C the impurity transport is due only to the long-range migration of nonequilibrium boron interstitials.
5 Conclusions

The model of boron diffusion in silicon has been developed. The model is intended for simulation of transient enhanced diffusion including the redistribution of ion-implanted boron during low temperature annealing. Two possible mechanisms of boron diffusion are taken into account, namely: the mechanism of the long-range migration of nonequilibrium boron interstitials and the mechanism of the formation, migration, and dissolution of the “impurity atom – silicon self-interstitial” pairs. Based on the model simulation of the redistribution of boron implanted in silicon substrates with a low energy and a high dose was carried out. The case of rapid thermal annealing (60 s) was investigated for two characteristic temperatures of 800 and 900 °C. The calculated boron concentration profiles agree well with the experimental data of [2]. It is shown that for a temperature of 800 °C the boron atoms substitutionally dissolved in the silicon lattice are immobile and the transport of impurity atoms occurred due to the long-range migration of nonequilibrium boron interstitials formed during cluster transformation or dissolution. On the other hand, it is shown that at an annealing temperature of 900 °C the mechanism of formation, diffusion, and dissolution of the “substitutionally dissolved boron atom — silicon self-interstitial” pairs plays the main role in the significant transient enhanced diffusion. A number of parameters describing the transport of nonequilibrium boron interstitials and transient enhanced diffusion of substitutionally dissolved boron atoms have been determined. For example, it is found that the average migration length of nonequilibrium boron interstitials is equal to 11 nm at a temperature of 800 °C. At a temperature of 900 °C the time-average boron diffusion enhances approximately 44 times. The results obtained are important for the development of the methods of transient enhanced diffusion suppression keeping in mind the scaling of the dimensions of silicon integrated microcircuits.

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