INTERACTIONS OF POINT DEFECTS WITH BORON AND ARSENIC PRECIPITATES

Iuval Clejan and Scott T. Dunham
Department of Electrical, Computer and Systems Engineering
Boston University, Boston, MA 02215

Abstract

The Reduced Precipitation Model (RPM), a moment based approach to precipitation kinetics developed in previous work [1], is extended to include interactions of point defects with arsenic and boron deactivation. The model accounts for the effect of precipitation on point defect populations, as observed by Rousseau *et al.* [2], and conversely the effect of point defect populations on precipitation, as observed by Stolk *et al.* [3] and Cowern *et al.* [4]. In the model, point defect interactions with precipitates are assumed to be fast relative to the growth of the precipitates, so that the concentration of point defects affects the energetics of precipitation. The kinetics of precipitation are also affected through the influence of the point defect concentrations on the diffusivity of the dopant. The effect of precipitation on point defects is to incorporate or emit point defects, with a ratio of point defects per precipitate atoms in each cluster depending on the interstitial supersaturation.

INTRODUCTION

The Reduced Precipitation Model (RPM) was developed in a previous paper [1] in order to practically, yet realistically, model extended defect kinetics in VLSI structures. In order to be realistic under low thermal budget conditions, when kinetics are important, a model needs to keep track of the size distribution of extended defects. However, if a model keeps track of all relevant sizes of precipitates, it becomes impractical to incorporate it in a two or three dimensional diffusion solver, since size acts as an extra effective dimension. It was shown that the RPM is able to describe the size distribution of extended defects by keeping track of the evolution of only the first three moments of that distribution. These were m_0, the concentration of precipitates, m_1 the concentration of precipitated atoms, and m_2 which is related to the breadth of the distribution. The reduction in the number of variables was possible through the use of the closure assumption that the free energy of the system is minimized at each point during its evolution, given the first three moments of the distribution. There resulted three equations for the evolution of each moment [1]. The price for this reduction in the number of variables is that two nonlinear equations have to be solved in order to determine the size distribution, and this must be done at each point on the spatial lattice, and for each time during the evolution. To speed computation, prior to each set of simulations tables are computed for the quantities which depend on the distribution, in terms of m_1/m_0 and m_2/m_0, and the tables used for interpolation during a simulation.

The model was successfully applied to arsenic and phosphorus precipitation, under circumstances where the influence of the point defects on the precipitation and diffusion of the dopants was thought to be negligible [5].

In order to be able to describe situations which arise in VLSI processing, such as transient enhanced diffusion (TED) and transient activation [6], it is necessary to model how precipitates interact with point defects. Since point defects also interact with dopants, this is an indirect interaction between dopant diffusion and precipitates, which we have previously neglected. Not only must we take into account the effect of precipitates on point defect populations, but also the effect of point defect populations on precipitation and activation. For example, for boron it has been observed [7] that a shoulder at a concentration below the solid solubility forms after post-implant annealing. It has been suggested [3] that this shoulder is a result of interstitial induced clustering.

A previously studied phenomenon of interactions between interstitials and point defects is oxygen precipitation [8]. Oxygen precipitates need to emit interstitials in order to relieve the stress due to the volume mismatch between Si and SiO_2. As with oxygen precipitation, the dopant precipitates may require vacancies or interstitials in order to lower the stress that they produce in the silicon lattice.

POINT DEFECT-PRECIPITATE INTERACTIONS

In the following, we will carry out the analysis for precipitates with a smaller unstrained molar volume than Si (e.g., boron). These precipitates are assumed to incorporate interstitials and emit vacancies. The analysis is the same for precipitates with a larger molar volume than Si, except that quantities involving vacancies must be exchanged with quantities involving interstitials.

We will assume that precipitate interactions with point defects are fast and hence enter only in the energetics, not in the kinetics. We will also assume that precipitates are neutrally charged, and thus electrically inactive.

The free energy of a precipitate which has incorporated n dopant atoms and q interstitials, and emitted r vacancies is:

$$\begin{aligned} \Delta G_{n,q,r} &= \Delta G_n^{\text{surface}} + \Delta G_{n,q,r}^{\text{stress}} - nkT\log\left(C_A/C_{ss}\right) \\ &\quad - qkT\log\left(C_I/C_I^*\right) + rkT\log\left(C_V/C_V^*\right), \end{aligned} \tag{1}$$

where C_A is the active dopant concentration, C_I is the interstitial concentration, C_V is the vacancy concentration, C_I^* is the equilibrium interstitial concentration, C_V^* is the equilibrium vacancy concentration, and C_{ss} is the solid solubility of the dopant. We will assume that Frenkel pair recombination is fast, perhaps even assisted by the presence of the precipitates, so that $C_I C_V = C_I^* C_V^*$. In that case, the last two terms combine to give $-mkT \log(C_I/C_I^*)$, where $m = q + r$. As discussed in [5], we can approximate the surface energy by:

$$\Delta G_n^{\text{surface}} = \sum_i c_i n^{a_i}, \tag{2}$$

where $a_i < 1$ and c_i are fitting parameters. It was found sufficient to keep only one term in this sum in order to fit the data shown in this work.

We assume that the stress energy of a precipitate is a smooth function and for small deviations from its minimum can be approximated by the quadratic form:

$$\Delta G_{n,m}^{\text{stress}} = H_n + A_n(m - \gamma_n n)^2. \tag{3}$$

where H_n is the residual stress energy when the number m of point defects incorporated/emitted per precipitate for size n precipitates is at its equilibrium optimum value.

If only the stress energy had to be minimized, then its average value would always be H_n, with an optimal $m^* = \gamma_n n$. However, since interactions with point defects are present, it is the total free energy which needs to be minimized for each precipitate size, giving

$$m^* = \frac{kT}{2A_n} \log(C_I/C_I^*) + \gamma_n n \tag{4}$$

and

$$\Delta G_n = \Delta G_n^0 - \frac{(kT)^2}{4A_n} (\log(C_I/C_I^*))^2 - kT\gamma_n n \log(C_I/C_I^*), \tag{5}$$

where ΔG_n^0 is the precipitate free energy when the point defects are at their equilibrium concentrations. If the concentration of point defects is not at their equilibrium values, the stress energy will not be fully relieved, since the system may gain chemical free energy at the expense of stress energy.

It should be noted that m^* is an average over a population of size n precipitates, and hence does not have to be integral. We are assuming that the precipitate population at each n, m is well described by the average over m, that is that the width of the distribution does not make a difference in the final answer. Also, we are assuming that the average m can be found by minimizing the free energy of a size n precipitate.

To make further progress, we must determine γ_n and A_n. Lacking a better alternative, such as *ab-initio* calculations, we assume that their functional form is given by continuum elasticity theory, although the constants involved may differ from those of continuum elasticity at small cluster sizes. Using continuum elasticity and certain simplifying assumptions [8], $\gamma_n = \gamma$ is found to be a constant independent of n, $H_n = 0$ and $A_n = \alpha/n$, where the constants depend on the pressure and the mechanical properties of the precipitate and the Si lattice [8]. We do not expect that α and γ should be numerically equal to the values obtained from the elastic constants, since we will deal primarily with cases for which the precipitate sizes are small. We should also point out that even if H_n is more complicated than the value obtained from linear elasticity for small clusters we can include the effect of this term with our approach since we are fitting all the terms in the free energy which depend on n with a polynomial.

In contrast to the case when point defect interactions with precipitates are ignored, the size distribution of precipitates given by our free energy minimizing closure assumption is in general a function not only of m_1/m_0 and m_2/m_0, but also of C_I/C_I^*. This is because the free energy of the system depends on C_I/C_I^*. However, it can be easily seen that if $1/A_n$ contains only zeroth, first and second powers of n, as is assumed in our case, then the distribution is independent of C_I/C_I^*. Even if A_n had a more complicated form, or γ_n was not a constant, the problem could be handled by generating a more complicated table, involving more tabulated functions and another input dimension (C_I/C_I^*), making the table three dimensional.

From the previous analyses we obtain:

$$\Delta G_{n,m}^{stress} = \frac{\alpha}{n}(m - \gamma n)^2 \tag{6}$$

The concentration of captured interstitials minus emitted vacancies is

$$C_I^c - C_V^e = \left(\gamma + \frac{kT}{2\alpha}\log\left(C_I/C_I^*\right)\right) m_1, \tag{7}$$

where m_1 is the concentration of precipitated atoms, and one of the dynamical variables in the RPM.

The effective point defect interaction ratio is thus

$$\left(\frac{m}{n}\right)^* = \gamma + \frac{kT}{2\alpha}\log\left(C_I/C_I^*\right). \tag{8}$$

The effective solubility can be found by setting the term in the free energy which is proportional to n equal to zero. The result is

$$C_s^{\text{eff}} = C_{ss}\left[\frac{C_I^*}{C_I}\right]^{\gamma} \exp\left[\frac{-kT}{4\alpha}\left\{\log(C_I/C_I^*)\right\}^2\right]. \tag{9}$$

There are many experiments that can be performed to study the effects of vacancies and interstitials on the activation of boron and arsenic, and conversely the effects of (de)activation on vacancies and interstitials. Before we quantify the model, we can see that at least the model predictions agree qualitatively with the experiments that have been performed so far. For boron, the model predicts a decrease in the effective solubility in the presence of an interstitial supersaturation, as is found in many post implant annealing experiments, e.g. [3, 4, 7]. For arsenic, the model predicts interstitial injection upon deactivation from a point defect equilibrium initial condition, as was deduced in [2] from the enhanced diffusion of a buried boron marker layer. Interstitial injection (e.g., from an oxide film) is predicted to lower the effective solubility, whereas vacancy injection (e.g., from a silicide film) is predicted to raise the effective solubility, as observed experimentally [6].

COMPARISON OF RPM TO EXPERIMENT

As an initial test, we looked at experiments performed by Rousseau *et al.* [2] on arsenic deactivation. These experiments were chosen because the initial conditions are clear: full activation due to laser anneal, and the injection of point defects due to diffusion and dissolution of As/V and As/I pairs is negligible due to the low temperature. Also, electrical measurements were taken in addition to SIMS, which places an extra constraint on the simulations. The effect of the point defects was observed experimentally by measuring the broadening of a boron marker layer, and with the simulation by monitoring C_I/C_I^*. As can be seen in Figure 1, the RPM reproduces the deactivation and diffusivity enhancement after 2 hours. However, the diffusivity enhancement after 15 seconds was found to be about half the value reported by Rousseau *et al.* [2]. A possible explanation is that the initial enhancement is prone to large measurement errors [2]. A good fit to the arsenic data was found with $\gamma \approx 0.1$ and $\alpha \approx 4.9$. At small times after the deactivation begins and the interstitial saturation is large ($C_I/C_I^* \sim 10^4$), the effective interaction ratio is about 0.01 according to Equation 8. After two hours ($C_I/C_I^* \sim 100$) and the effective interaction ratio is about 0.05.

We were also able to match data for anneals of boron implants. In order to match the data, it was necessary to model the fast initial transient period during which the interstitial concentration drops from a high value (as predicted by "+1" model) [9] to a lower value near equilibrium with {311} defects. During this transient, interstitials can also get incorporated in the boron-interstitial clusters (BICS) since (as shown in Figure 2) there is no energy barrier to the formation of BICS at the beginning of the process, due to the large interstitial supersaturation. Those BICS which grew past a critical size are able to keep growing at the lower interstitial supersaturation established by the {311} defects after the transient, lowering the concentration at the shoulder until either the effective solubility of Equation 9 is reached, or the interstitials diffuse away and diffusion stops. Throughout the process, the smaller clusters dissolve and keep nourishing the large ones. Due to the finite defect size, the shoulder remains above the effective solid solubility, which is calculated for an infinitely large precipitate.

The effect of {311} defects was modeled with a simple model that considered the evolution of both free interstitials and interstitials in {311} defects. It was assumed that the concentration of {311} defects was fixed at a value consistent with experimental observations [10]. After the initial transient, the {311} defects maintain the interstitial concentration at a value $C_I^{\max}$ around the peak of the implant. The value for $C_I^{\max}$ was chosen such that the magnitude and duration of the TED were consistent with experiment. It was found that $\gamma = 0.4$ and $\alpha = 4.8$ gave a good fit to the data. According to Equation 8, the interaction ratio is about 0.5 for the high interstitial supersaturation present during the TED, consistent with the presence of $B_{2x}I_x$ clusters.

Figures 3 and 4 show comparisons of the model to data by Stolk *et al.* [3], and Cowern *et al.* [4]. A more accurate model for the precipitate free energy as a function of size may improve the fit, and may be necessary in order to fit a larger set of data.

CONCLUSIONS

The RPM has been extended to include interactions of precipitates with point defects. Two new physical parameters are introduced which describe the optimum number of point defects absorbed or emitted per precipitated atom under equilibrium and non-equilibrium point defect concentrations respectively. These two parameters also control the effect of the point defect concentrations on the effective solubility of the solute. The model is able to match both boron post-implant annealed profiles with a shoulder due to precipitation and a tail due to TED, and interstitial supersaturations during arsenic deactivation, with a consistent set of parameters.

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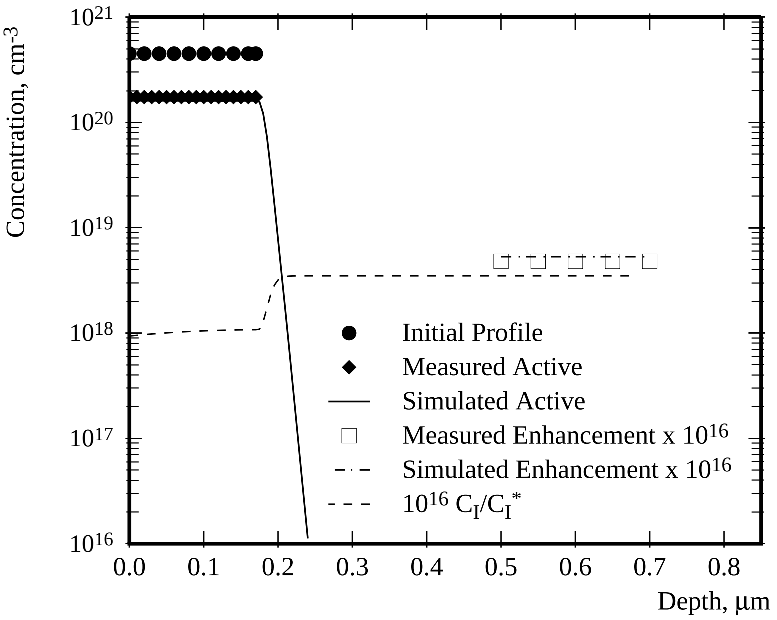

Fig. 1: Active arsenic concentrations and enhanced marker layer diffusion before and after a 2h 750°C anneal of a laser-annealed profile and comparisons to model. Data from Rousseau *et al.* [2].

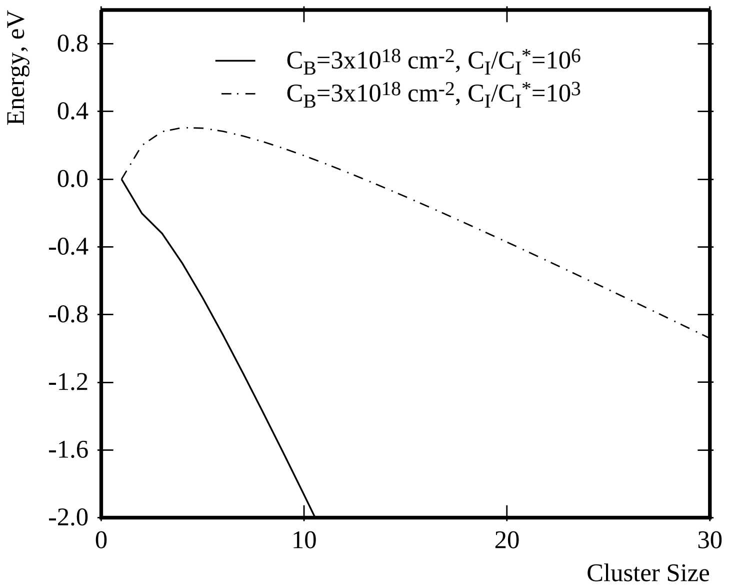

Fig. 2: Free energy of clusters as function of size at 790°C for initial high interstitial concentration and once {311} defects have formed. The boron concentration is just below the shoulder concentration.

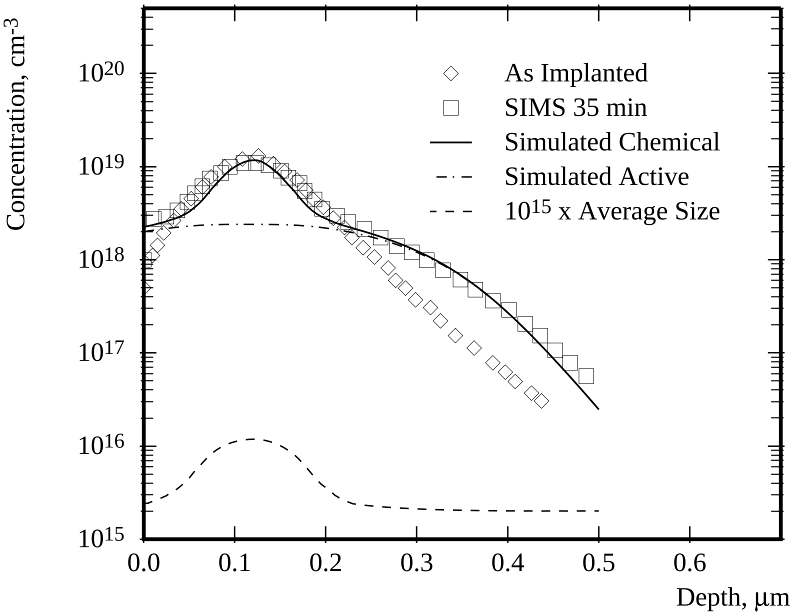

Fig. 3: Active and total boron concentrations after a 35min 790°C anneal of a 1.5×10^{14} cm^{-2} 30 keV boron implant. Also shown is the average number of B atoms in precipitates. Data from Stolk *et al.* [3].

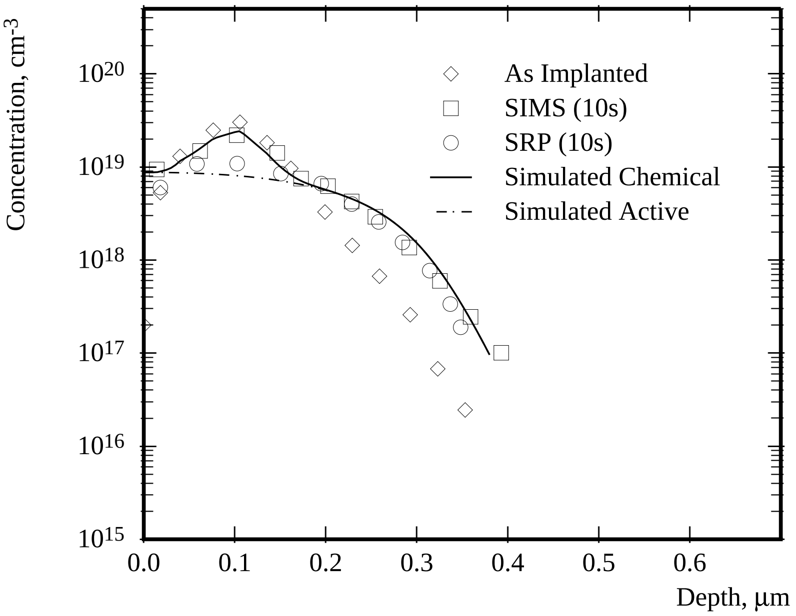

Fig. 4: Active and total boron concentrations after a 10s RTA at 900°C of a 3×10^{14} cm^{-2} boron implant. Data from Cowern *et al.* [4].

KEYWORDS

point defects, precipitation, clustering, boron interstitial clusters, activation, diffusion, arsenic, boron, solubility, size distribution.