

Atomic Scale Simulation of Extended Defects: Monte Carlo Approach

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Abstract

This paper reports Monte Carlo calculation of the bimolecular reaction of extended defects, which explicitly takes the time evolution of size density of extended defects into account in an effort to cover a broad range of behaviors. Our Monte Carlo calculation is in quantitative agreement with the experimental deactivation data and successfully reproduces the rapid deactivation at the beginning phase followed by slow deactivation thereafter. During the annealing step, the density of the dislocation loops decreases while their size increases. Furthermore, the dislocation loops suppress the injection of silicon interstitial, thereby retarding the enhancement of the marker layers at the start of annealing.

1. Introduction

Ion implantation of dopants into silicon introduces a damage in the form of an interstitial and a vacancy. If the concentration of a dopant exceeds its equilibrium value of active concentration, the subsequent heat treatment can cause the dopant to be inactive. The injection of silicon interstitial and the enhancement of the marker layers underneath the dopant layer usually accompany deactivation of a dopant. Several models such as clustering and precipitation have been proposed to explain the formation of electrically inactive dopants in silicon.

In clustering models, multiple dopant atoms are assumed to come close together to form a new defect, which is electrically inactive at room temperature. Recently, Sakamoto et al.[1] applied a set of point-defect diffusion model, which included the diffusion effects of the clustering of boron, phosphorous, and arsenic. In their model, a boron cluster was interpreted as the accumulation of boron-interstitial pairs, B_2I , and B_2I_2 (complex of boron atoms and interstitials). In addition, As_2V (complex of two arsenic atoms and a vacancy) and As_3 (compound of three arsenic atoms) components were assumed for arsenic clusters. In contrast, the precipitation model considers the formation of much larger structures that may contain thousands of dopant atom[2]. The precipitates may form at any size whereas clusters are assumed to have on the order of only a few atoms. The size distribution of precipitates depends on the initial super-saturation of dopant atoms, the time and the temperature of the annealing and other kinetic factors such as the diffusivity and the reaction rates.

In order to explain the bimolecular kinetics of extended defects, many numerical approaches have been undertaken. Since extended defects such as dislocation loops and oxygen precipitates may contain millions of atoms, it is impossible to solve a number of rate equations within a feasible time limit with today's computer technology. For this reason, many researchers have tried to reduce the number of rate equations to a reasonable number using appropriate numerical techniques. Since the accuracy of the solution strongly depends on the size of grid spacing, however, reduction schemes such as the linear rediscretization method and the logarithmic rediscretization technique can not provide an adequate solution for the behavior of extended defects. Therefore, in our work, we apply a Monte Carlo method to the bimolecular reaction of extended defects.

2. Bimolecular kinetics of extended defects and Monte Carlo simulation

The modeling of the precipitation process is complex because the precipitates have a wide range of size and shapes. In order to model the activation/deactivation process due to the precipitation, it is necessary to consider the full distribution of

precipitate sizes as a function of time $f_n(t)$. The size variation of precipitate is considered through a succession of simple bimolecular reactions between precipitate and single atom. In our model, therefore, the defects are assumed to grow or shrink by either gaining or losing one atom at a time.

Dopant precipitation is driven by the fact that above a certain level of doping concentration, forming a separate dopant-rich phase can reduce the free energy of the system. However, there is an energy barrier associated with the formation of the separate phase[3,4]. Therefore, the probabilities of the forward and reverse processes per unit time, represented as G and R , respectively, can be expressed as follows:

$$G = \nu \exp\left(-\frac{\Delta g_f}{kT}\right), \quad R = \nu \exp\left(-\frac{\Delta g_b}{kT}\right), \quad (1)$$

where ν is a the jump frequency; and Δg_f and Δg_b are the forward and reverse activation energies, respectively. According to bimolecular kinetics, the time evolution of the density of i -size is described by the following equation:

$$\frac{\partial f_i}{\partial t} = (\beta_{i-1}f_{i-1} - \alpha_i f_i) - (\beta_i f_i - \alpha_{i+1} f_{i+1}), \quad (2)$$

where f_i is the density of i -size defects and β_i and α_i are the forward and reverse reaction rates of i -size extended defects, respectively.

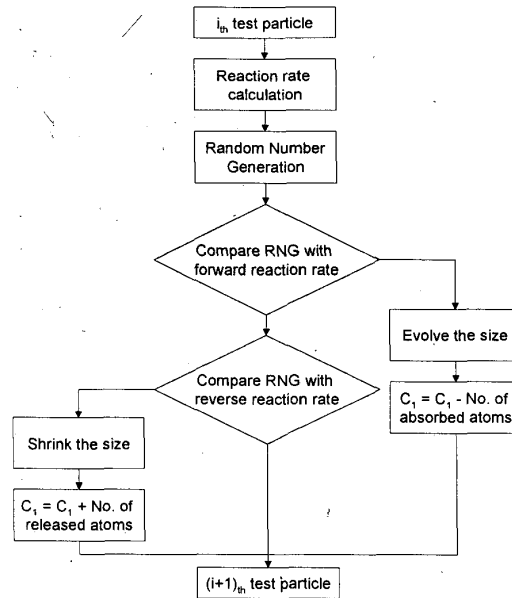


Figure 1: Monte Carlo algorithm for bimolecular reaction.

Monte Carlo method has been applied to the bimolecular reaction between dopant and interstitial. Instead of solving rate equation of Eq. (2), our Monte Carlo algorithm, as depicted in Fig. 1, calculates the forward and reverse reaction rates for every test particle. After the reaction rates of i -th test particle have been calculated, a random number is generated and compared with the calculated reaction rates. If the probability of reaction is less than the forward reaction rate, the i -size precipitate evolves in size depending on the forward reaction rate. The excess energy (ΔG_n^{excess}) in the free energy equation typically becomes proportional to the precipitate surface area for large sizes. However, for small precipitates, the excess energy can be expected to deviate strongly from asymptotic behavior. Therefore, the following polynomial approximation can be used[3]:

$$\Delta G_n^{excess} = a_1 n^{m_1} + a_2 n^{m_2}. \quad (3)$$

The first term of Eq. (3) corresponds to the asymptotic behavior at large sizes, which is generally associated with the dependence of the active surface area on size, and the other term is the correction for the deviation of free energy from this asymptotic behavior at small sizes. Therefore, m_1 can be set to 2/3 for spherical defects and to 1/2 for planar ones. The interfacial energy coefficients, a_1 and a_2 , were fitted during the simulations and obtained 0.13 and 0.12, respectively.

3. Simulation results

A test structure with a relatively high-level value exceeding equilibrium concentration was generated by implanting a high dosage of arsenic atoms into silicon, followed by laser annealing to activate all dopants. The resulting doping profile is box-like, and thus we approximate the distribution of dopants by square profiles with depths as measured experimentally. Thereafter, the samples were subjected to thermal annealing[2].

To simulate the precipitation of the arsenic atoms, we changed the number of arsenic test particles from 1000 to 100000. These exemplary calculations take less than one minute of CPU time on a SUN Ultra 1 when the number of particles is 1000, and 10 minutes for 10000 particles. Furthermore, this calculation revealed that 10000 is appropriate to get a sufficiently accurate solution, wherein the estimated error does not exceed 17% when compared with the linear rediscrretization method. The linear rediscrretization method with 195 rate equations exhibits a percentage error of 35%. Furthermore, the logarithmic rediscrretization method with 20 - 90 equations demonstrates a percentage error of 20%. Figures 2(a) and 2(b) show a comparison of our Monte Carlo simulations of the bimolecular reaction with experimental arsenic deactivation data, taken from Dokumaci[2], obtained at 700°C thermal annealing for chemical concentration of $4.4 \times 10^{20} \text{ cm}^{-3}$ and $1 \times 10^{21} \text{ cm}^{-3}$, respectively. As shown in Figs. 2(a) and 2(b), a good agreement is obtained between simulation and experimental data. All of the simulations exhibit a very fast deactivation of arsenic at the beginning of thermal annealing process, which is due to the rapid formation of small clusters having relatively small formation energies. In Fig. 3 are shown the size distributions of precipitates in a sample with $1 \times 10^{21} \text{ cm}^{-3}$ after a heat treatment at 700°C for 5 minutes and 120 minutes, respectively. Figure 3 indicates that the distribution of precipitates broadens as the annealing time gets longer.

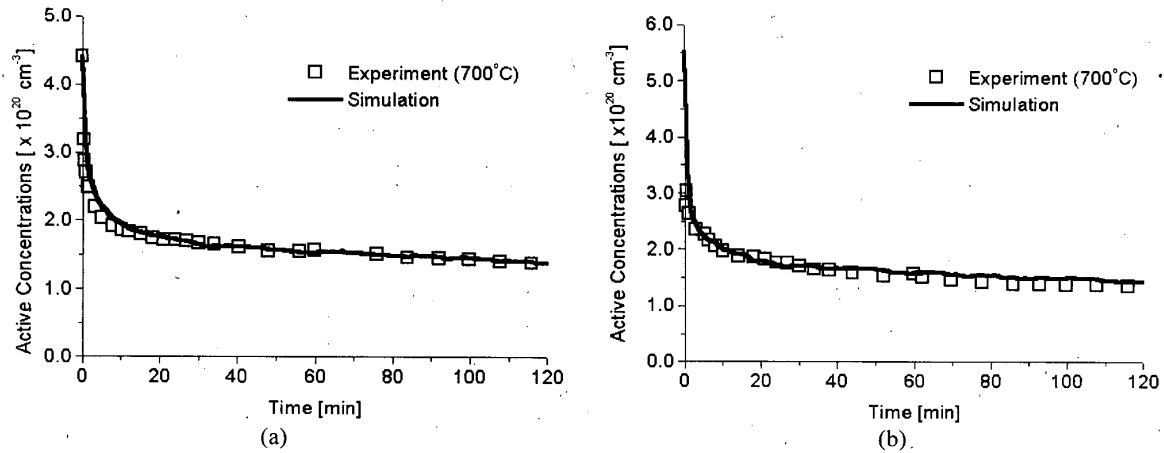


Figure 2: Comparison of simulation and experiment at 700°C at (a) a chemical arsenic concentration of $4.4 \times 10^{20} \text{ cm}^{-3}$, (b) a chemical arsenic concentration of $1 \times 10^{21} \text{ cm}^{-3}$ (experiment data from H. Dokumaci, Ph. D. Dissertation, University of Florida, 1997).

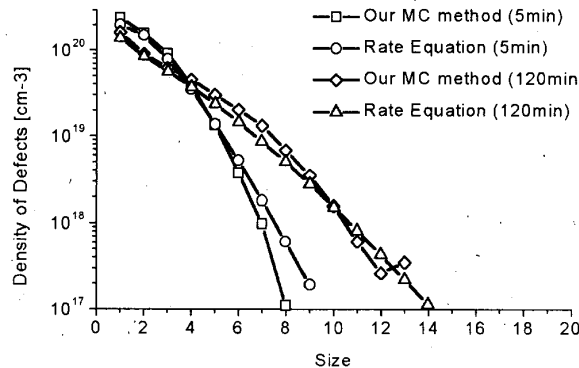


Figure 3: Precipitate size distributions for the concentration of $1 \times 10^{21} \text{ cm}^{-3}$ after 5 minutes and 120 minutes.

The Monte Carlo simulation of dislocation loops was implemented in a similar manner to the method employed for precipitation. The driving force for the loop coarsening process, as in the case of precipitation, is based on the minimization of the total interfacial energy. Interstitials, and show a faster reaction rate than that of precipitation displace test particles in the Monte Carlo method. Figure 4 shows the time evolution of the density and size of the loop during annealing process at 700°C. As depicted in Fig. 4, the density of dislocation loops decreases while their size increases during the annealing process. At the very beginning of the annealing process, the equilibrium condition between point defects and extended defects is not yet reached. Consequently, the loop growth is maintained until the interstitials are no longer supersaturated and the critical radius has caught up with the mean loop size, which causes coarsening of the dislocation loops. As time progresses, however, the concentration of interstitials around the dislocation loop is decreased, which causes the interstitials captured by dislocation loop to be released. These released interstitials contribute to the diffusion of the impurities.

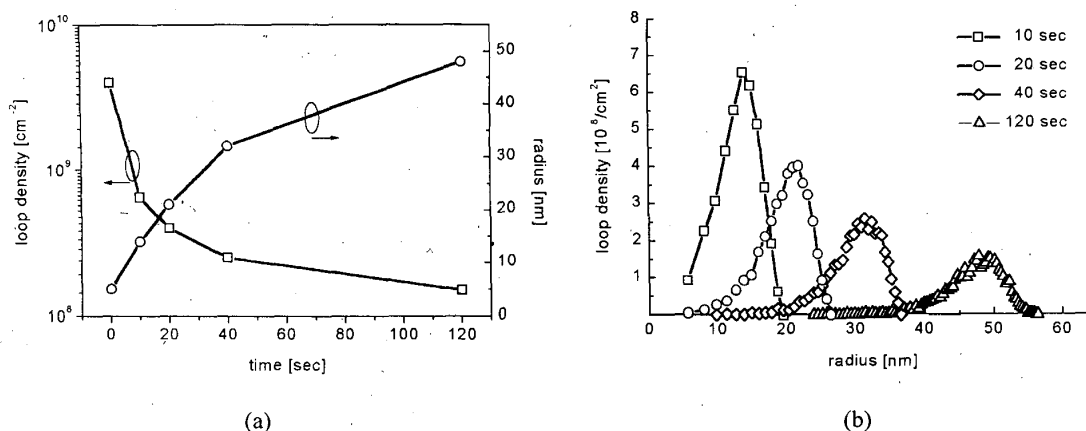


Figure 4: (a) Time evolution of loop density and size during anneal at 700°C, and (b) time-varying distribution of density and radius of dislocation loop.

4. Conclusions

The implantation of high-dose dopants exceeding equilibrium active concentration not only induces the precipitation of dopants but also induces damage in the form of dislocation loops underneath the a/c interface. In this study, bimolecular reaction kinetics of the precipitation and the formation of dislocation loops were investigated by a Monte Carlo method. A relatively good agreement between Monte Carlo simulations and experimental data was observed. This simulation of precipitation exhibited a very fast deactivation of arsenic at the beginning of the thermal annealing process, which is due to the rapid formation of small clusters. The density of the end-of-range loops decreases while their size increases during the annealing process. Since the end-of-range loops suppress the injection of silicon interstitial, the enhancement of the marker layer is retarded at the beginning of annealing process.

References

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