

A New Dopant Diffusion Modeling Based on Point Defect Kinetics

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This study reports a new modeling of dopant diffusion in a silicon substrate, obtained by analyzing dopant diffusion phenomena under an extrinsic condition during oxidation. Iso-concentration techniques were employed in the experiment to determine the diffusion coefficients. The result revealed that a large amount of self-interstitials remained under an extrinsic condition, while vacancies were drastically reduced. A numerical calculation was explored to model the dopant diffusion experiments.

1. INTRODUCTION

An accurate modeling of dopant diffusion in a silicon substrate under an extrinsic condition, especially during oxidation, is indispensable for realizing a reliable process design of lower submicron devices. This modeling requires knowledge about various aspects of point defects, particularly about the generation and recombination phenomena both at the oxidizing interface and in the silicon bulk, and their charge state effect on dopant diffusion, because dopants diffuse via the point defect mechanisms.

An increase in interstitial concentration and an decrease in vacancy concentration during oxidation, caused by generation and recombination, have been reported from the analyses of oxidation enhanced and retarded diffusions (OED,ORD).¹⁻⁵⁾ However, in most of the early modelings for OED and ORD, the concentration of excess interstitials was not well controlled at the interfaces.

This report proposes a new model for point defect kinetics, based on the combined analysis of OED and ORD phenomena by controlling the interstitial generation. Since OED and ORD will be relatively reduced by the recombination of self-interstitials and vacancies, the amount of self-interstitials and its recombination rate will be deter-

mined through the simultaneous analyses of both OED and ORD. In this work, boron and antimony were chosen as typical species for OED and ORD, respectively. Furthermore, point defect kinetics was extended to a new modeling of dopant diffusion.

2. EXPERIMENTAL PROCEDURES

The iso-concentration technique was employed in sample preparation to maintain a constant vacancy concentration in the silicon bulk. Figure 1 shows a schematic illustration of initial impurity distributions. ¹⁰B and ¹¹B were subsequently used in the OED experiment, while As and Sb were used in the ORD experiment, respectively. Here, ¹⁰B and Sb were used as tracers to determine the diffusion coefficients, and ¹¹B and As were doped to control the amount of initial vacancies. An undoped silicon layer was additively formed by the epitaxial technique to maintain the generation/recombination rates of the point defects at the Si/SiO₂ interface. Then, the wafers were subjected to drive-in diffusion in a N₂ ambient and in a dry O₂ ambient at 950°C for 5-64 hours.

The depth profiles of the impurities were measured by SIMS using a Cameca IMS4F secondary ion microscope.

3. EXPERIMENTAL RESULTS

3-1. Boron OED under an extrinsic condition

The diffusion coefficient of boron was determined solely from the redistribution of ^{10}B . The diffusion coefficient in an oxidizing ambient has a slight oxidation time dependence. Therefore, the experimentally obtained diffusion coefficient for dry O_2 annealing was averaged over space and time.

Typical examples of ^{10}B diffusion profiles in the substrate measured after being subjected to drive-in diffusion both in a N_2 ambient and dry O_2 ambient at 950°C for 16 hours are shown in Fig.2. The comparison of boron profiles shown in Fig.2 shows that ^{10}B diffuses faster during dry O_2 annealing than during N_2 annealing. The result indicates that boron OED occurs even under an extrinsic condition. Figure 3 summarizes the diffusion coefficient as a function of ^{11}B concentration in bulk silicon. The diffusion coefficients were determined from the depth profiles subjected to 16 hours of drive-in diffusion. The ^{10}B diffusion coefficient during N_2 annealing, D_N , is extremely larger under an extrinsic condition compared with the values under an intrinsic condition. It is presumably due to the increased concentration of positively charged vacancies, which induce a vacancy diffusion of boron, by increasing the ^{11}B concentration. Furthermore, it can be seen that the diffusion coefficient during dry O_2 annealing, D_O , is far larger than D_N .

Although it has been believed that OED cannot occur under an extrinsic condition, OED can obviously be seen not only under an intrinsic condition but also under an extrinsic condition. Since OED is attributed to self-interstitials generated at the oxidizing interface, the resulting OED indicates that a large amount of self-interstitials survive even under an extrinsic condition.

3-2. Antimony ORD under an extrinsic condition

The relationship between the antimony diffusion coefficient and the arsenic concentration during N_2 annealing and dry O_2 annealing at 950°C are shown in Fig.4. The antimony diffusion

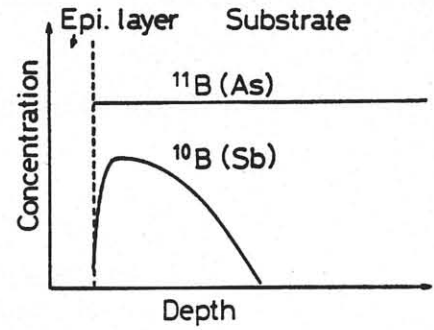


Fig.1 Schematic illustration of initial dopant distribution profiles

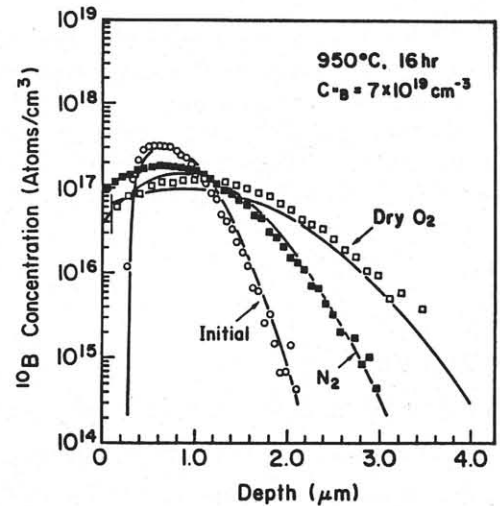


Fig.2 Redistribution profiles of ^{10}B after N_2 annealing and after dry O_2 annealing at 950°C for 16 hours in the substrate, where ^{11}B was flatly concentrated at about $7 \times 10^{19} \text{cm}^{-3}$. The depth was plotted from the original surface before being subjected to drive-in diffusion.

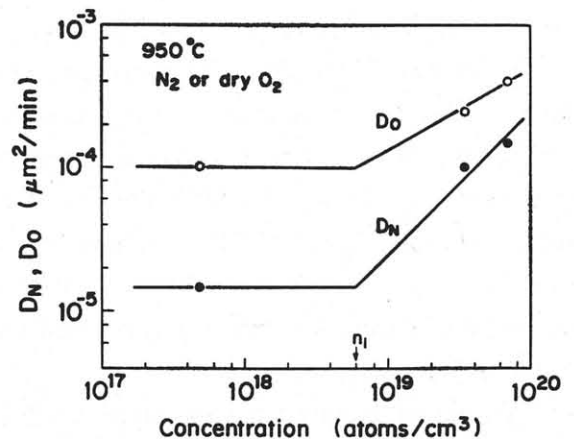


Fig.3 Relationship between boron diffusion coefficient and ^{11}B concentration at 950°C . D_N means boron diffusion coefficient in N_2 ambient, and D_O means that in dry O_2 ambient, respectively. D_N and D_O were determined from redistribution profiles of ^{10}B after annealing for 16 hours.

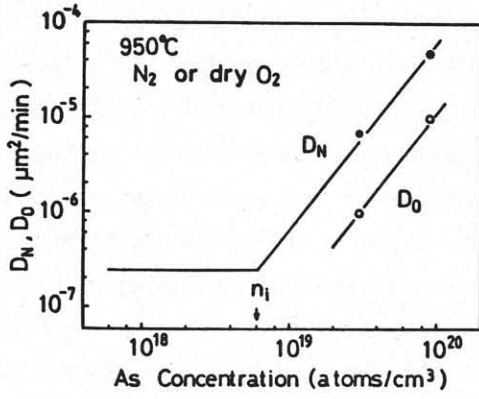


Fig.4 Relationship between antimony diffusion coefficient and arsenic concentration at 950°C. D_N and D_0 were determined from redistribution profiles after dry O_2 annealing for 16 hours.

coefficients were determined from the redistribution profiles after annealing for 16 hours. As shown in Fig.4, D_N under an extrinsic condition is much larger than the value under an intrinsic condition. It is presumably due to an increase in negatively charged vacancies, V^- and $V^{\cdot-}$, by increasing the arsenic concentration. Furthermore, it can be seen that antimony ORD obviously occurs at a relatively low temperature, 950°C. Since antimony diffuses mainly via the vacancy mechanism,⁵⁾ the result indicates that the recombination of point defects occurs, and that the concentration of vacancy decreases, at least, to about 20% of the initial vacancy concentration after oxidation for 16 hours.

These OED and ORD phenomena have led to the conclusion that the concentration decrease by recombination is relatively small for self-interstitials, and on the contrary, relatively large for vacancies.

4. NUMERICAL ANALYSIS

To investigate the experimental results in more detail, the diffusion equations for dopants and point defects were solved, taking account of the interaction of these point defects. These equations for interstitials and vacancies are given by

$$\frac{\partial C_I}{\partial t} = D_I \frac{\partial^2 C_I}{\partial x^2} - k_R (C_V C_I - C_V^{\text{eq}} C_I^{\text{eq}}),$$

$$\frac{\partial C_V}{\partial t} = D_V \frac{\partial^2 C_V}{\partial x^2} - k_R (C_V C_I - C_V^{\text{eq}} C_I^{\text{eq}}).$$

where C_I and C_V are the concentrations of the interstitial and vacancy, respectively. D_I and D_V are the diffusion coefficients, k_R the bulk recombination rate constant, and C^{eq} the concentration at thermal equilibrium.

The effects on the diffusion constant of point defect populations in their different charge states have been taken into account, on the assumption that the total concentration of charged point defects is not affected by dopant concentration. The energy required to change the charge states (less than 1eV) is much smaller than the formation energies of a point defect ($\approx 5\text{eV}$). Furthermore, athermal migration requires the defect charge state to change alternatively during site to site migration.⁶⁻⁷⁾ The population will be, therefore, determined mostly by the difference between the Fermi level and the defect levels. The relative populations of an interstitial C_{I_Y} and a vacancy C_{V_Y} in charge state Y are given by

$$C_{I_Y} = C_I \int_{E_{I_{YZ}}}^{E_{I_{XY}}} f(E) dx,$$

$$C_{V_Y} = C_V \int_{E_{V_{YZ}}}^{E_{V_{XY}}} f(E) dx.$$

where $f(E)$ is the Fermi distribution function, $E_{I_{XY}}$ and $E_{V_{XY}}$, and $E_{I_{YZ}}$ and $E_{V_{YZ}}$ are the energy threshold level between the charge state X and Y, and Y and Z, respectively. The difference of point defect levels and Fermi levels are determined by solving the Poisson equation simultaneously.

For the simulation of dopant concentration, the dopant diffusion coefficient can be expressed as a function of the linear combination of point defect concentrations, i.e., C_V^- , $C_V^{\cdot-}$, C_V^0 , C_V^+ , C_V^{++} , C_I^- , C_I^0 , C_I^+ , and C_I^{++} , to agree with the experimental results in Figs.3 and 4, by using their "affinity" constant for the dopant.

The bulk recombination rate was determined to agree with the Sb ORD experiments in Fig.4.

Furthermore, the diffusion coefficients of point defects followed the reported values.⁸⁾

The simulated concentration profiles of the dopants and point defects, corresponding to the OED experiment, are shown in Fig.5(a) and (b). As shown in Fig.5(a), the simulated dopant diffusion profile agrees well with the experimental result in Fig.2. At the initial stage of oxidation, as shown in Fig.5(b), the concentration of a self-interstitial near the surface drastically increases by surface generation. On the contrary, the concentration of a vacancy shows a relatively small change within 1 hour or so. Therefore,

the local equilibrium condition of the point defects was not achieved, and the product, $C_V C_I$, became extremely larger than the value of $C_V^{eq} C_I^{eq}$. This tendency of point defect concentrations was nearly the same, even under a wide range of diffusion coefficients. A few hours later, however, the concentration of a self-interstitial approaches a peak value near the surface due to a decrease in the surface generation rate. On the other hand, the concentration of vacancy gradually decreases, and approaches a value less than a tenth of the equilibrium concentration after oxidation for 16 hours.

5. CONCLUSION

The dopant diffusion phenomena under an extrinsic condition during oxidation were investigated at 950°C, using the iso-concentration technique. From the OED experiment, it was revealed that a large amount of self-interstitials remained under an extrinsic condition. On the other hand, it was indicated from the antimony ORD experiment that the vacancy concentration decreases at least to 20% of the initial vacancy concentration. Furthermore, a new dopant diffusion modeling based on these analyses was proposed.

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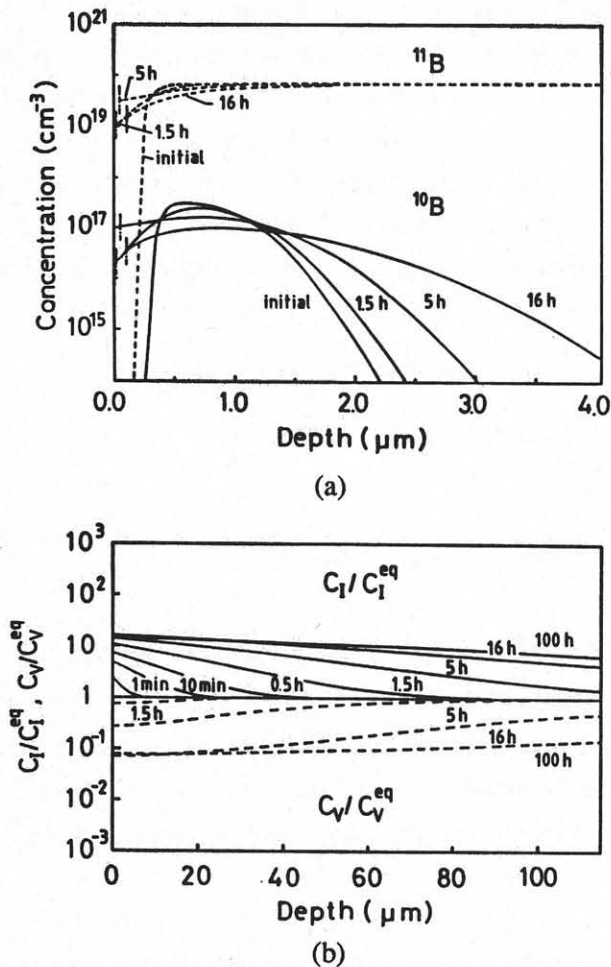


Fig.5(a) Simulated dopant diffusion profiles during dry O₂ annealing at 950°C. (b) Simulated concentration profiles of point defect during dry O₂ annealing at 950°C.