Diffusion-limited interaction of dislocation loops and interstitials during dry oxidation in silicon

Heemyong Park
Florida Integrated Research in Silicon Technology, Department of Electrical Engineering, University of Florida, Gainesville, Florida 32611

Heyward Robinson and Kevin S. Jones
Florida Integrated Research in Silicon Technology, Department of Materials Science and Engineering, University of Florida, Gainesville, Florida 32611

Mark E. Law
Florida Integrated Research in Silicon Technology, Department of Electrical Engineering, University of Florida, Gainesville, Florida 32611

(Received 26 January 1994; accepted for publication 12 May 1994)

The interaction of implantation-induced dislocation loops and interstitials in silicon is studied. Experiments under dry oxidation conditions consistently show a significant reduction of OED (oxidation enhanced diffusion) of boron in a buried layer due to very efficient interstitial capturing action of dislocation loops, suggesting diffusion-limited dislocation loop growth. Simple analytic solution of interstitial supersaturation and analysis of the data in terms of time dependence of the OED suppression demonstrate that the interaction of dislocation loops and interstitials is not a reaction-limited but a diffusion-limited process. Simulations incorporating the model for the interaction mechanism agree with both secondary ion mass spectroscopy and transmission electron spectroscopy data.

Crystal damage in silicon has been considered as a crucial constraint in the fabrication processes of modern scaled-down devices. To explain evolution and suppression of the implantation-induced damage, it is necessary to study the mechanism of interaction between extended defects and point defects in association with transient dopant diffusion. This work studies the quantitative evolution process of dislocation loops through capturing interstitials.

The authors have presented a model for the dislocation loop evolution[1–3] by accounting for the established dislocation theory and by comparison with a series of oxidation-enhanced diffusion (OED) experiments by Meng *et al.*[4,5] The experiments strongly suggested that the dislocation loops work as very efficient sink for interstitials by strong interaction with them during dry oxidation. Other researchers recently presented experimental data and a model for reduced diffusion of boron due to dislocation loops during wet oxidation.[6] They argued that the loop growth is a reaction-limited process, based on their simulation with SUPREM-IV matching the secondary ion mass spectroscopy (SIMS) profiles of boron. Their experiment is performed in a different injection realm than Meng's, since wet oxidation creates a larger interstitial supersaturation.

If the interaction is mostly governed by the diffusive flux of the interstitials reaching the core boundary of the loops from outside, it is called a diffusion-limited process. In this case, the free interstitial concentration around the loop layer boundary should quickly decrease nearly to the equilibrium concentration, and the loop growth should be fairly rapid, since most of the fast-diffusion interstitials will be efficiently captured by the loops. On the other hand, if the loop growth is determined by the intrinsic reaction of the extra layer of silicon atoms, then it will be called a reaction-limited process. If this is the case, the interstitial concentration around the loop layer boundary would not decrease rapidly, since the interaction would not depend directly on the concentration of interstitials outside the core. These two cases are the limiting cases, and it should be noted that it is also possible that both cases are important, i.e., a mixed interaction. Assessment of their relative importance is an important matter, since it directly represents the efficiency of dislocation loops as sink of interstitials.

The letter re-examines the data by Meng *et al.*[4,5] by a simple analysis, and attempts to determine the nature of dislocation loop reaction. In the prior work,[4] evolution of dislocation loops during dry oxidation was studied through transmission electron microscopy (TEM). During oxidation, the size of dislocation loops increase while the density decreases. However, TEM alone is not enough to quantify the interaction of loops and point defects. In a follow-up experiment,[5] the interstitial capture efficiency of the loops was measured by monitoring the reduction in OED of a buried boron layer. In the second experiment, a thin (<500 Å) boron marker layer was grown epitaxially on Si wafers, followed by epitaxial growth on an overlayer of 6000 Å of undoped silicon. As-grown boron profiles were obtained by SIMS. The dislocation loops were introduced into some of the samples by a 2×10^{15} cm^{-2} Si implant at 50 keV, which is the same condition as in the first experiment.[4] The samples implanted with Si were preannealed at 900 °C for 10 min in nitrogen ambient prior to oxidation so as to form the dislocation loops and to anneal out excess point defects. All the samples were then annealed at 900 °C from 10 min to 4 h in either N_2 or dry O_2 ambient. SIMS measurements of boron profiles revealed the time dependence of OED. The depth locations of the dislocation loops layer and of the boron buried layer are at about 0.15 and 0.6 μm from the surface, respectively. TEM pictures showed that the dislocation loop morphology was the same as in the experiment by Meng *et al.*[4] without the boron layer.

 0003-6951/94/65(4)/436/3/$6.00

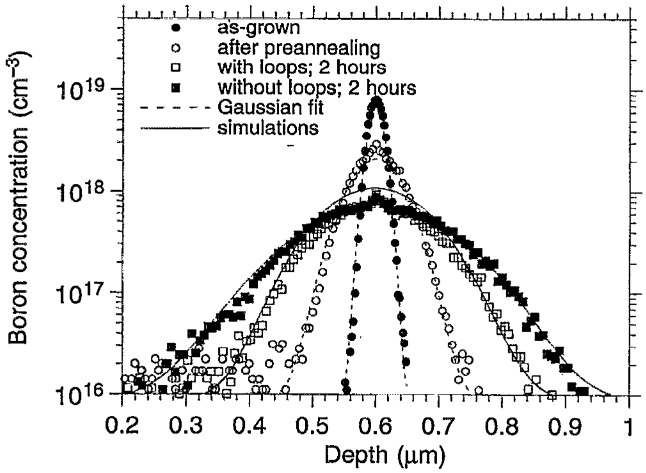

FIG. 1. SIMS data (Ref. 5) and FLOOPS simulation of B diffusion with and without dislocation loops during the dry oxidation at 900 °C for 2 h.

In Fig. 1, the SIMS profiles show the reduced OED of boron due to the suppressed interstitial supersaturation at 2 h of dry oxidation. For the case with the loops, the equivalent 2 h diffusion starts from the B profile obtained after the preannealing step required for loop formation. The result confirms the role of dislocation loops as an efficient sink of interstitials, capturing most interstitials injected from the surface. The significant reduction in OED suggests the diffusion-limited process of dislocation loop growth.

Based on the TEM data and the SIMS boron profiles, we developed the model for dislocation loop evolution.[1–3] The model accounts for the distribution of pressure inherent to dislocation loops as well as the statistical distribution of loop size and density, and their variation during oxidation. In Fig. 1, the simulations (solid lines) were performed with the model, which computes the interstitial distribution below the loop layer where boron buried layer exists. Spatial variation in the interstitial concentration near the buried layer is not significant, since the large diffusivity of interstitials results in flat distribution very quickly. Temporal change in the interstitial distribution is the key to understanding the nature of loop-interstitial interaction.

This can be clarified by investigating the time dependence of OED in the two limiting cases. We can obtain an analytic solution of interstitial continuity equations under simplifying but meaningful approximations. The increase in interstitial concentration C_I near the surface has a nearly monotonous pattern when it is solely due to the injection at the oxidizing surface without dislocation loops. By examining simulations of the normal OED, we can effectively approximate C_I just below the loop layer as an exponential function of time t within a range of interest:

$$C_I \cong (C_I^f - C_I^*)(1 - e^{-k_g t}) + C_I^*, \tag{1}$$

where C_I^f is the interstitial concentration at sufficiently large time, and k_g is the inverse of the effective time constant to obtain supersaturation in the buried layer region. The value of C_I^f for dry oxidation at 900 °C has been found to be about 11 times as large as the equilibrium concentration C_I^*.[7]

When there are dislocation loops, the effective continuity equation for C_I can be formulated in two ways, depending on the nature of interaction:

(i) Diffusion-limited interaction. The capture of interstitials at the loop layer boundary is determined by actual concentration C_I and effective local equilibrium concentration at the loop layer boundary C_{Ib}, which is calculated in terms of defect formation energy variation due to self-force and pressure of the dislocation loops:

$$\frac{\partial C_I}{\partial t} \cong -k_d(C_I - C_{Ib}) + g(t), \tag{2}$$

where k_d is the diffusion-limited loop-interstitial reaction constant, and $g(t)$ is the effective rate of interstitial supersaturation without the loops, i.e., time derivative of Eq. (1). As a simplifying assumption in Eq. (2), we ignore the possibility that $g(t)$ in the presence of loops can vary due to the large diffusive flux towards the loop layer. Also it is reasonably assumed that the small change in C_{Ib} due to time variation of loop distribution is negligible. Solving Eq. (2) with proper initial conditions, we obtain the time-dependent function of interstitial supersaturation below the loop layer:

$$\frac{C_I}{C_I^*} = \left(\frac{C_I^f - C_I^*}{C_I^*}\right)\left(\frac{k_g}{k_d - k_g}\right)(e^{-k_g t} - e^{-k_d t}) + \frac{C_{Ib}}{C_I^*}. \tag{3}$$

The OED of boron below the loop layer is expressed approximately in terms of the fraction of interstitialcy mechanism in boron diffusion $f_I (\cong 0.8)$[7] and the time-average of Eq. (3), when the smaller vacancy component is ignored:

$$\frac{\langle D_B \rangle}{D_B^*} = f_I\left(\frac{C_I^f - C_I^*}{C_I^*}\right)\left[\left(\frac{k_g}{k_d - k_g}\right) \times \left(\frac{e^{-k_d t}}{k_d t} - \frac{e^{-k_g t}}{k_g t}\right) + \frac{1}{k_d t}\right] + f_I \frac{C_{Ib}}{C_I^*}. \tag{4}$$

Equation (4) shows that the time dependence of boron OED with the loops is governed by the difference of time constants k_g and k_d.

(ii) Reaction-limited interaction. In this case, the effect of dislocation loops on interstitial distribution is independent of the actual concentration C_I, and is determined by the loop self-force reflected on C_{Ib} at the core boundary and the pressure-dependent equilibrium concentration C_I^*, as defined in a model for stacking faults:[8]

$$\frac{\partial C_I}{\partial t} \cong -k_r(C_{Ib} - C_I^*) + g(t), \tag{5}$$

where k_r is the constant of loop-interstitial reaction through the reaction-limited process. Similarly to the case (i),

$$\frac{\langle D_B \rangle}{D_B^*} \cong f_I\left[\left(\frac{C_I^f - C_I^*}{C_I^*}\right)\left(1 - \frac{1}{k_g t} + \frac{e^{-k_g t}}{k_g t}\right) - \frac{k_r}{2}\left(\frac{C_{Ib} - C_I^*}{C_I^*}\right)t + \frac{C_{Ib}}{C_I^*}\right]. \tag{6}$$

It is noted that at large t, the linear dependence term dominates the reaction-limited process of reduced OED. The degree of linear decrease in diffusivity is governed by k_r and the small difference $C_{Ib} - C_I^*$.

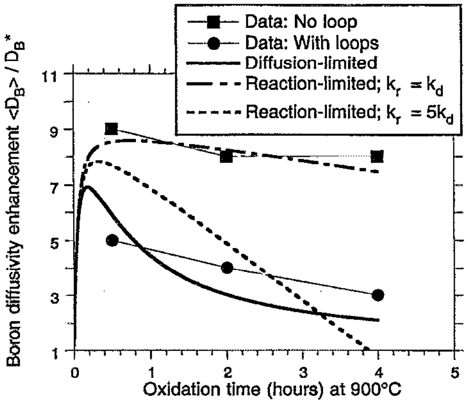

FIG. 2. The time dependence of B enhanced diffusion obtained from the SIMS data, compared with analytic solutions for the two limiting cases of loop interaction. For the reaction-limited interaction, two different solutions are shown for different values of k_r ($k_r=k_d$ and $k_r=5k_d$).

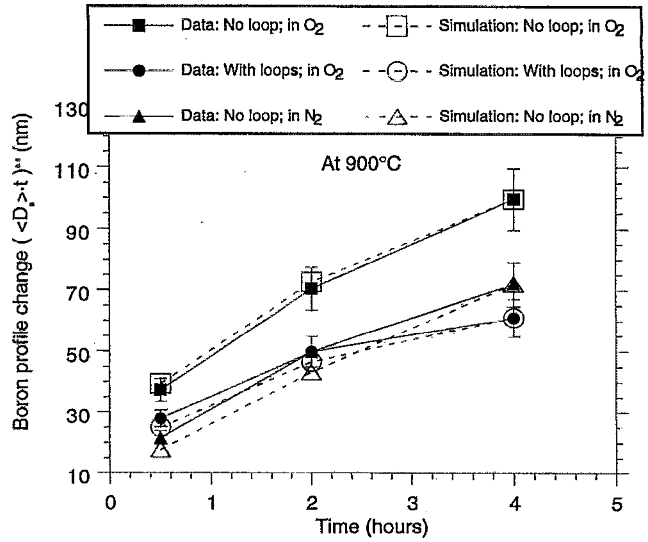

FIG. 3. SIMS (Ref. 5) and simulation of B junction depth movement in terms of $\sqrt{\langle D_B \rangle\, t}$ with 10% error bars applied to all the time conditions.

Equations (4) and (6) show that the two interaction mechanisms result in different time dependence of boron OED. Comparison of the effective diffusivities from the analytic solution and from the data will demonstrate which case represents the loop interaction better. Figure 2 shows the boron diffusivity enhancement extracted from the SIMS profiles in Meng *et al.*[5] The enhanced diffusivity $\langle D_B \rangle$ was quantified through profile matching with the diffusivity D_B^* under inert intrinsic condition.[7] The most important characteristic of the time dependence of $\langle D_B \rangle$ in the presence of dislocation loops is that the OED is limited substantially by about 50% already at 30 min and continues to diminish at larger times. Analytic solutions of Eqs. (4) and (6) are also shown in Fig. 2. First, we used one value (6×10^{-4} s^{-1}) for both k_d and k_r, in order to attest relative importance of the two different cases with the same reaction constant (solid and semi-dotted lines). The value of k_g used in the calculation is 0.01 s^{-1}. Figure 2 clearly shows that the diffusion-limited interaction of loops and interstitials fits the data much better than the reaction-limited case, in terms of the functionality of time dependence. The diffusion-limited case demonstrates correctly the rapid reduction in short times and a further gradual decrease in OED. On the other hand, the reaction-limited case rather emulates the normal OED without the dislocation loops, which means that through a process independent of concentration, the injected interstitials are not captured efficiently enough to reduce the OED of boron in the buried layer. Even with a larger value of k_r ($k_r=5k_d$; dotted line in Fig. 2), Eq. (6) always fails to correctly represent the slope of time dependence pattern of data in Fig. 2, since it does not account for the efficient interstitial suppression at short times. Consistent results were obtained with different values of k_r and k_d pairs.

The simple analysis qualitatively justifies the model incorporating the diffusion-limited interaction of the dislocation loops and interstitials.[2] Fully numerical simulations with complete defect diffusion equations and statistical loop growth equations were performed for the data in Figs. 1 and 2. Figure 3 represents the displacement of B profiles $\sqrt{\langle D_B \rangle\, t}$ from the simulation and the SIMS data for the three different groups of samples in the experiment.[5] The simulation agrees with the data for all three time conditions. The normal OED data in Fig. 3 are correctly fitted by simulations using D_B^* obtained by Packan,[7] which gives a consistent reference for dry oxidation. The simulation simultaneously fits the TEM data on dislocation loop size, density, and number of captured Si atoms.[2,3] The unusual enhancement in the nitrogen ambient is considered to be caused by oxygen precipitates at the epi substrate interface, which may have worked as interstitial injection source in the bulk. Even with the additional injection in the bulk, which is not screened by the loop layer near the surface, the data show that the loops reduce the enhancement from OED to the value found under an inert ambient.

In conclusion, the dislocation loops effectively capture most interstitials injected from the surface. The time dependence of boron diffusion enhancement in the buried layer is explained better with a diffusion-limited process.

The authors wish to thank Sematech, IBM, SRC, and NSF for support of this work. We would also like to thank David Sieloff for help in performing the SIMS analysis.

[1] H. Park and M. E. Law, the 183th Meeting of Electrochemical Society, Proceedings of the Third International Symposium on Process Physics and Modeling in Semiconductor Technology, Honolulu, Hawaii, May 19–21, 1993, p. 228.
[2] H. Park, K. S. Jones, and M. E. Law, J. Electrochem. Soc. **141**, 759 (1994).
[3] H. Park and M. E. Law, Extended Abstract of TECHCON'93, p. 56, September 28–30, Atlanta, Georgia, 1993.
[4] H. L. Meng, S. Prussin, M. E. Law, and K. S. Jones, J. Appl. Phys. **73**, 955 (1993).
[5] H. L. Meng, J. Chen, H. G. Robinson, M. E. Law, J. A. Slinkmann, and K. S. Jones, the 183th Meeting of Electrochemical Society, Proceedings of the Third International Symposium on Process Physics and Modeling in Semiconductor Technology, Honolulu, Hawaii, 1993, p. 236.
[6] R. Y. S. Huang and R. W. Dutton, J. Appl. Phys. **74**, 5821 (1993).
[7] P. A. Packan, Ph.D. thesis, Stanford University, 1991.
[8] D. A. Antoniadis, J. Electrochem. Soc. **129**, 1093 (1982).