УДК 531

ВЛИЯНИЕ ЗАВИСИМОЙ ОТ СТРЕССА ПОВЕРХНОСТНОЙ ГЕНЕРАЦИИ МЕЖДОУЗЛИЙ НА РОСТ ДЕФЕКТОВ УПАКОВКИ И ДИФФУЗИЮ ЛЕГИРУЮЩИХ ПРИМЕСЕЙ В КРЕМНИИ

Лойко Константин Валерьевич
Ph.D.
Freescale Semiconductor, Остин, Техас, США

Разработана модель зависимой от стресса поверхностной генерации и рекомбинации точечных дефектов в кремнии. С ее помощью смоделированы такие явления, как рост дефектов упаковки и диффузия легирующих примесей в кремнии

Ключевые слова: КРЕМНИЙ, МЕЖДОУЗЛИЯ, ТОЧЕЧНЫЕ ДЕФЕКТЫ, ДЕФЕКТЫ УПАКОВКИ, ДИФФУЗИЯ ЛЕГИРУЮЩИХ ПРИМЕСЕЙ

UDC 531

INFLUENCE OF STRESS-DEPENDENT SURFACE GENERATION OF INTERSTITIALS ON STACKING FAULT GROWTH AND DOPANT DIFFUSION IN SILICON

Loiko Konstantin Valeryevich
Ph.D.
Freescale Semiconductor, Austin, Texas, U.S.A.

A model is developed for stress-dependent surface generation and recombination of point defects in silicon. Using the model, such phenomena as stacking fault growth and stress-mediated dopant diffusion in silicon are simulated

Keywords: SILICON, INTERSTITIALS, POINT DEFECTS, STACKING FAULTS, DOPANT DIFFUSION

Introduction

Silicon self-interstitials play an important role in the growth of stacking faults and contribute to dislocation nucleation. The effects of stress on dopant diffusion in silicon are also attributed to the behavior of intrinsic point defects in stress fields [1-5].

Equilibrium concentrations of silicon self-interstitials and vacancies are known to depend on stress as follows [6,7]:

$$C_i^* = C_{i0}^* \exp(-\frac{P\Delta V_i}{kT}), \tag{1}$$

$$C_v^* = C_{v0}^* \exp(\frac{P\Delta V_v}{kT}), \tag{2}$$

where C_i^* and C_v^* are the equilibrium concentrations of interstitials and vacancies, respectively, in the presence of the stress field, C_{i0}^* and C_{v0}^* are the stress-free equilibrium concentrations, P is pressure, ΔV_i and ΔV_v are the activation volumes, k is Boltzmann's constant, T is absolute temperature. The terms $P\Delta V_i$ and $P\Delta V_v$ describe a reversible work process of the point defect formation under stress. They show a change in the Gibbs free energy of the formation of an interstitial or vacancy due the presence of the stress field [7]. Therefore, the activation volumes in Equations 1 and 2, being the coefficients of pressure in the reversible work process, are indeed thermodynamic formation volumes. These activation volumes have been calculated based on the assumption of sphericity of the interstitial and vacancy with radii of 1.11 Å and 2.47 Å, respectively [1-3], or using *ab initio* calculations [4,5,8]. Nevertheless, there is no agreement in literature on the values for these parameters.

From Equations 1 and 2, the equilibrium concentration of self-interstitials decreases and the equilibrium concentration of vacancies increases under compressive stress. Tensile stress has an opposite effect on the equilibrium point defect concentrations. Since boron and phosphorus are known to diffuse mainly in pairs with interstitials [9], retardation of the diffusion of these dopants is expected under compressive stress. There is some experimental evidence of such retarded diffusion [3,10]. At the same time, boron diffusion enhancement under compressive stress has been reported as well [11,12]. This discrepancy could possibly be explained by differences in point defect interaction with the free surface [4]. Most models of stress-dependent point defect and dopant diffusion consider only bulk interactions. However, stress-dependent surface generation and recombination of point defects may cause significant changes in their distributions. These processes are not well understood due to a lack of experimental results.

In this paper, a model is developed for the stress-induced redistribution of intrinsic point defects in silicon. It incorporates equilibrium conditions different for defects at the surface and in the bulk of silicon, taking into account stress-dependent surface generation and recombination of point defects. Using the model, such phenomena as stacking fault growth and stress-mediated dopant diffusion are simulated.

Calculation of Activation Volumes for Interstitials and Vacancies

In the derivation of the activation volumes for intrinsic point defects, silicon is considered as an elastic continuum. A Si-interstitial is modeled as a non-compressible ball. The radius of the ball equals to the radius of a silicon atom, R_a = 1.32 Å [13]. The ball is inserted into a spherical hole having the radius R_i of an interstitial site. The radius of an interstitial site is the maximum radius of a ball that can be inserted into the interstitial site without deforming it. Two interstitial sites in silicon are considered. First, the octahedral site, such as the one which center has coordinates $^5/_8$, $^5/_8$, $^5/_8$ in a unit cell of the silicon lattice. The coordinates of the six nearest lattice sites are ½, ½, 1; ½, 1, ½; 1, ½, ½; $^1/_4$, $^3/_4$, $^3/_4$; $^3/_4$, $^1/_4$, $^3/_4$; $^3/_4$, $^3/_4$, $^1/_4$. The distance between the center of the octahedral site and these lattice sites is $\sqrt{11}\,a_0/8$. Therefore, $R_i = \sqrt{11}\,a_0/8 - R_a \approx$ 0.93 Å, where a_0 = 5.4307 Å is the silicon lattice constant. The second interstitial site is the tetrahedral one, for example the site with coordinates $^1/_2$, $^1/_2$, $^1/_2$. The four nearest lattice sites are $^1/_4$, $^1/_4$, $^1/_4$; $^1/_4$, $^3/_4$, $^3/_4$; $^3/_4$, $^1/_4$, $^3/_4$; $^3/_4$, $^3/_4$, $^1/_4$. Therefore, $R_i = \sqrt{3}\,a_0/4 - R_a \approx 1.03$ Å. The preferential interstitial site (the bigger one) has $R_i \approx 1.03$ Å. The difference of volumes of the Si atom and interstitial site $\Delta V = 4/3\pi(R_a^3 - R_i^3) \approx 5$ Å^3 might be regarded as the activation volume of self-interstitials. However, this approach does not take into account such factors as "compressibility" of the silicon atom, chemical-valency effects, and local relaxations [7]. Thus, the derived value is overestimated. A more reasonable activation volume of Si-interstitials seems to be $\Delta V_i = \frac{1}{2}\Delta V \approx 2.5$ Å.^{3}

A vacancy is considered to be formed by removing a spherical ball from the elastic continuum of silicon resulting in the formation of a hole. The radius of the ball is R_a. The size of the hole becomes smaller than the size of the ball because of surface tension. The activation volume of a vacancy is the difference in volumes of the ball V_a and the hole V_h. The surface energy of the hole before contraction $E_0 = 4\pi R_a^2\gamma$, where $\gamma \approx 1.5$ J/m^2 is the silicon surface energy [13]. After the contraction by ΔR, the energy of the hole $E = 4\pi(R_a - \Delta R)^2\gamma$. Thus, the total force of surface tension $F \approx (E_0 - E)/\Delta R \approx 8\pi R_a\gamma$. This gives the contracting pressure $P = F/(4\pi R_a^2) = 2\gamma/R_a$. This pressure causes the reduction in the radius of the hole by $u = 0.5PR_a(1+n)/Y$, where $n \approx 0.28$ is Poisson's ratio and $Y \approx 170$ GPa is Young's modulus of silicon [14]. Then, $u = \gamma(1+n)/Y \approx$ 0.113 Å. Finally, the activation volume of a vacancy is found as $\Delta V_v = 4/3\pi\{R_a^3 - (R_a-u)^3\} \approx 2.3$ Å.^{3}

The obtained values for the activation volumes of point defects are close to those suggested in some reports [2,3,8].

Diffusion Equations for Point Defects

The following diffusion equations are considered for interstitials and vacancies in the bulk of silicon:

$$\frac{\partial C}{\partial t} = -\nabla J - R_b, \tag{3}$$

$$J = -DC^*\nabla\left(\frac{C}{C^*}\right), \tag{4}$$

$$R_b = K_b(C_iC_v - C_i^*C_v^*), \tag{5}$$

where C, C^*, D, and J are the concentration, equilibrium concentration, diffusivity, and flux of interstitials or vacancies, R_b and K_b are the bulk recombination rate and its rate factor, i and v denote parameters for interstitials and vacancies, respectively.

Equation 4 is different from the standard expression for the diffusion flux $J = -D\nabla C$ [15] and accounts for non-uniformity in the equilibrium concentrations of point defects due to their interaction with external fields. Substituting Equations 1 and 2, which describe the exponential dependency of the equilibrium point defect concentrations on pressure, into Equation 4, and ignoring the drift of charged point defects in the electric field, it is possible to express the total point defect flux as a sum of the diffusion flux and the drift flux in the pressure field:

$$J_i = -D_i \nabla C_i - \frac{D_i C_i \Delta V_i}{kT} \nabla P \,, \tag{6}$$

$$J_v = -D_v \nabla C_v + \frac{D_v C_v \Delta V_v}{kT} \nabla P \,. \tag{7}$$

Surface Generation and Recombination of Point Defects

At a stress-free surface, self-interstitial and vacancy fluxes due to surface generation and recombination are given by [15]

$$J_{is} = -K_{is}(C_i - C_{i0}^*) + G_{is} \,, \tag{8}$$

$$J_{vs} = -K_{vs}(C_v - C_{v0}^*) \,, \tag{9}$$

where C_{i0}^* and C_{v0}^* are the stress-free equilibrium concentrations of interstitials and vacancies, K_{is} and K_{vs} are their surface generation-recombination rate factors, and G_{is} is the interstitial injection rate due to oxidation. Terms $K_{is}C_i$ and $K_{vs}C_v$ describe surface recombination, while $K_{is}C_{i0}^*$ and $K_{vs}C_{v0}^*$ describe surface generation of point defects.

In the presence of the stress field, these equations have to be modified to account for the free energy change associated with the surface generation-recombination process:

$$J_{is} = -K_{is}[C_i \exp(-\frac{P(\Delta V_s - \Delta V_i)}{kT}) - C_{i0}^* \exp(\frac{P(\Delta V_s - \Delta V_i)}{kT})] + G_{is} \,, \tag{10}$$

$$J_{vs} = -K_{vs}[C_v \exp(\frac{P(\Delta V_s - \Delta V_v)}{kT}) - C_{v0}^* \exp(-\frac{P(\Delta V_s - \Delta V_v)}{kT})] \,, \tag{11}$$

where ΔV_s is the silicon volume change occurring when a silicon atom is added to or removed from the silicon surface. $\Delta V_s \approx 20$ Å^3, which is the volume of silicon per atom.

The process of surface generation-recombination of point defects is illustrated in Figure 1 showing the generation of a Si-interstitial. When an interstitial is formed by removing an atom from the silicon surface and inserting it into the crystal, there is a thermodynamic volume expansion ΔV_i, associated with the fact that the size of the Si atom is larger than the size of the interstitial site. On the other hand, there is a decrease in the volume of the whole Si crystal because one atom has left its surface. This volume change is equal to the volume of silicon per atom $\Delta V_s \approx 20$ Å^3 > ΔV_i. The difference of these two volumes ($\Delta V_s - \Delta V_i$) is found in the exponents in Equation 10, which shows how interstitial surface generation and recombination change under pressure.

As follows from Equations 10 and 11, the surface generation of interstitials, leading to the thermodynamic volume decrease, increases with pressure while their recombination decreases. The effect of pressure on vacancies is opposite. Since ($\Delta V_s - \Delta V$) is positive for both interstitials and vacancies, interstitial generation increases under compression and vacancy generation increases under tension.

Under the equilibrium conditions, the surface flux of point defects is zero. Therefore, Equations 10 and 11 effectively describe the deviation of equilibrium defect concentrations at the surface from their values in the bulk.

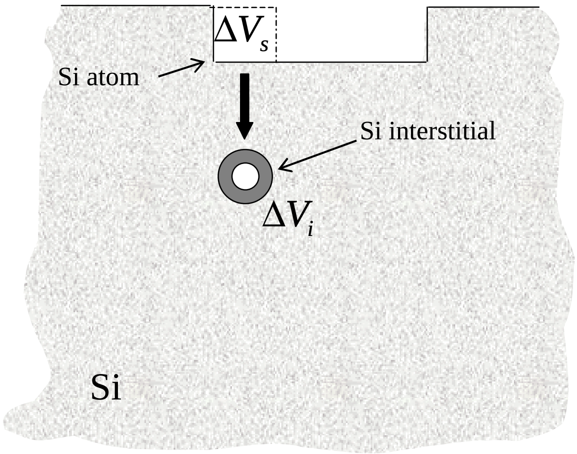

Figure 1: Self-interstitial formation in silicon by surface generation. $\Delta V_s > \Delta V_i$.

Simulation of Stacking Fault Growth

Stacking faults in silicon are oxidation-induced defects. Therefore, their preferential growth in the field areas, where interstitial injection due to oxidation has the highest rate, seems logical and is supported by experimental results. At the same time, the appearance of stacking faults at the edges of active areas has been reported by Jarreau [16]. An enhancement in stacking fault growth at active edges can be explained by either an increased density/size of their nucleation centers due to some damage (for example, plasma-induced damage) or by enhanced interstitial generation in this area. The later is consistent with the proposed model for stress-dependent surface generation and recombination of point defects.

Figure 2 shows simulated pressure, equilibrium concentration and concentration of interstitials, as well as stacking fault radius after steam field oxidation performed at 1100 °C. The results were obtained using a 2D process simulator TSUPREM-4 [17]. Stress-dependent surface generation and recombination of point defects was taken into account. As can be seen, pressure is at maximum under the nitride edge (Figure 2a). This decreases equilibrium concentration of interstitials in this area (Figure 2b), but increases their concentration due to enhanced surface generation (Figure 2c). Consequently, stacking fault size is also increased under the nitride edge (Figure 2d). The stacking fault radius at the position of the pressure peak is about the same as that under the field oxide. A uniform density of stacking fault nucleation centers and their constant size was used in this simulation. To obtain even larger stacking faults at the active edge, higher density or larger size of their nucleation centers should be assumed.

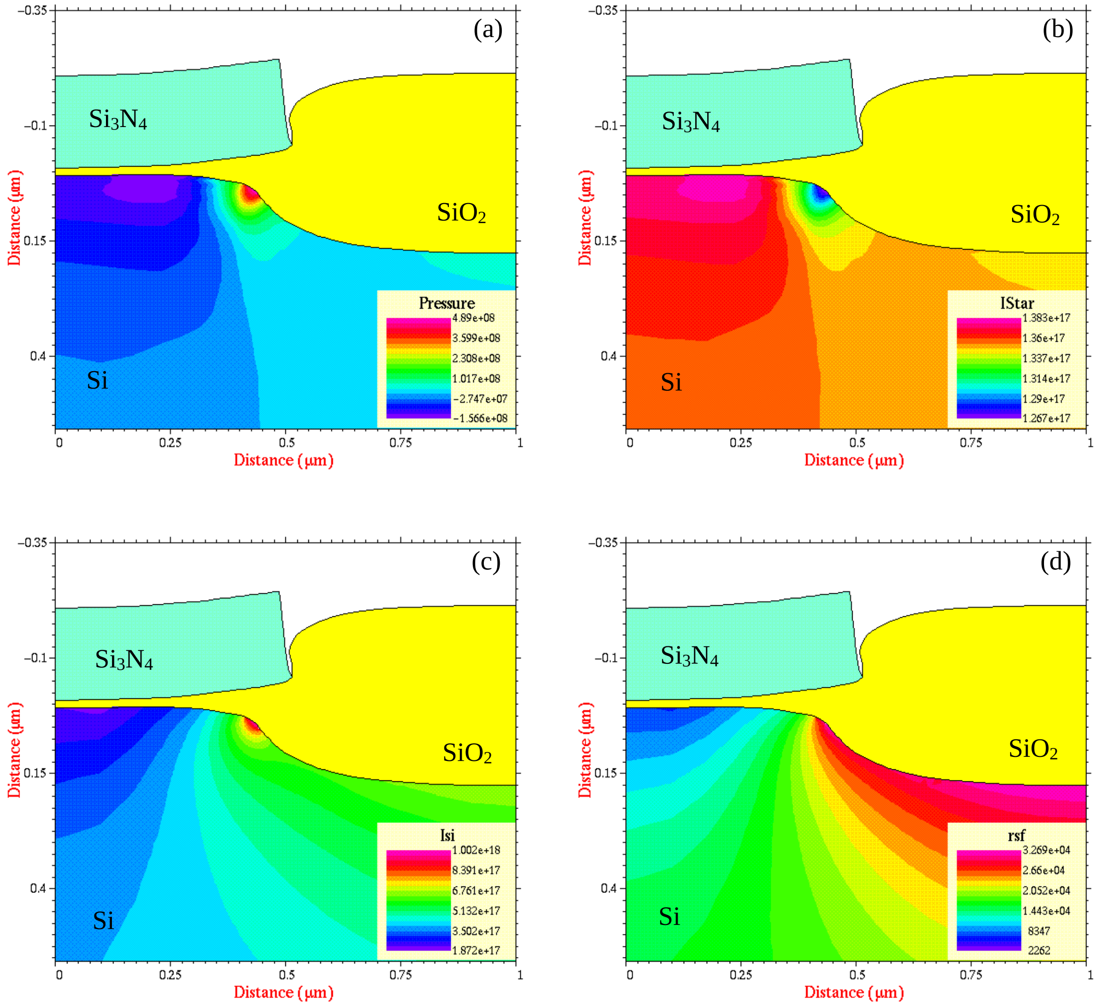

Figure 2: Contour plots of simulated (a) pressure (Pa), (b) equilibrium concentration and (c) concentration of interstitials (cm^{-3}), (d) stacking fault radius (Å) after steam field oxidation performed at 1100 °C. Stress-dependent surface generation and recombination of point defects was taken into account.

Simulation of Stress-Mediated Dopant Diffusion

The effect of stress on dopant diffusion in silicon is usually attributed to the behavior of intrinsic point defects and dopant-defect pairs in stress fields [1-5]. Since boron and phosphorus are known to diffuse mainly in pairs with interstitials [9], retardation of the diffusion of these dopants is expected under compressive stress reducing the equilibrium concentration of interstitials. However, the existing models for stress-mediated dopant diffusion fail to explain conflicting experimental results. Both retardation [10] and enhancement of boron diffusion under compressive stress have been reported [11,12].

This discrepancy could possibly be explained by considering point defect interaction with the silicon surface. In different experiments, surface generation and recombination of point defects could play more or less pronounced role in the defect and therefore dopant distribution depending upon the proximity of the surface to the studied region.

Using the developed model for the stress-induced point defect redistribution and their surface generation and recombination, the impact of stress on boron diffusion was simulated. In TSUPREM-4, the five-stream diffusion model was used for boron [18]. This model assumes that dopant diffusion occurs through the formation of dopant/defect pairs that diffuse as a unit. The concentration of such pairs depends upon dopant concentration and point defect supersaturation. Therefore, a change in point defect concentrations due to their redistribution in the stress fields is expected to directly affect boron diffusion.

In the simulation, an experimental setup used by Osada *et al.* [10] was replicated. Boron with a dose of 7.5×10^{13} cm^{-3} was implanted at 70 keV into a p-type (100) Si substrate through a 50 nm thick screen oxide. After 30 min annealing at 900 °C in N_2 and removing SiO_2, a 500 nm thick Si_3N_4 film was deposited and patterned. Then an anneal in N_2 at 1014 °C for 120 min was performed.

Simulation results on the pressure distribution and equilibrium concentration of self-interstitials, as well as concentrations of interstitials, boron-interstitial pairs, and boron are shown in Figures 3 - 6. Two groups of the results are presented. In one simulation, stress-dependent surface generation and recombination of point defects was taken into account. In the other simulation, it was neglected.

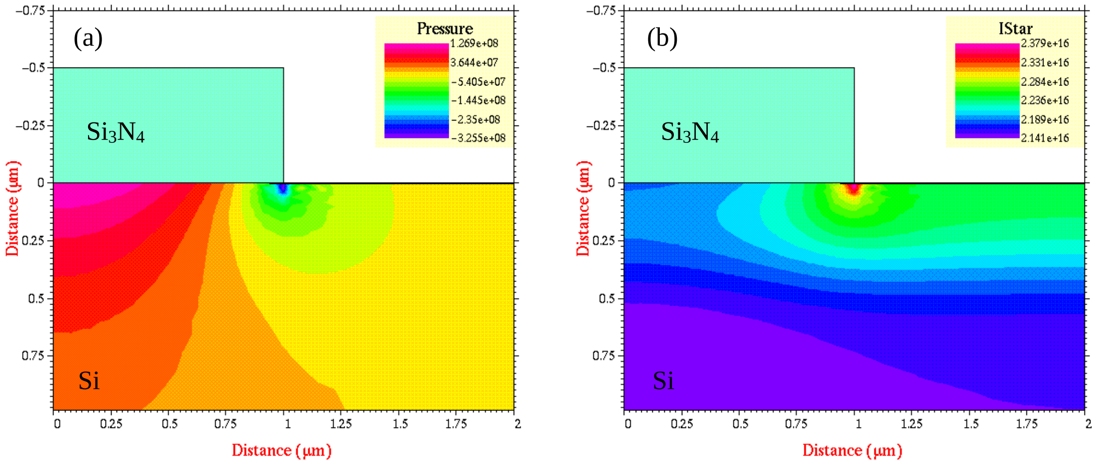

Figure 3: Simulated (a) pressure (Pa) and (b) equilibrium concentration of interstitials (cm^{-3}) after 1014 °C anneal in N_2 for 120 min.

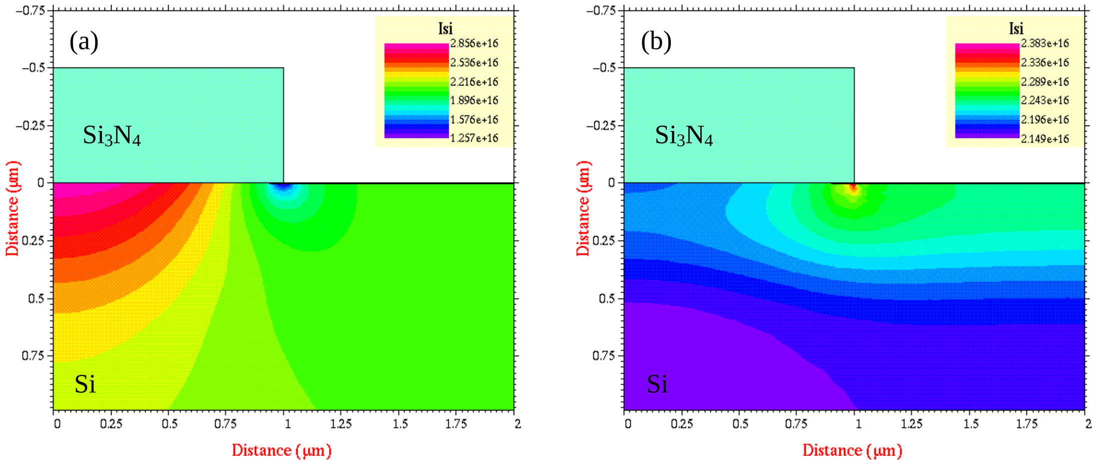

Figure 4: Simulated interstitial concentration (cm^{-3}) after 1014 °C anneal in N_2 for 120 min (a) with and (b) without taking into account stress-dependent surface generation and recombination of point defects.

As can be seen in Figure 3, the equilibrium concentration of self-interstitials decreases under the nitride, in the region of compression. It increases at the nitride edge under tensile stress. The concentration of interstitials increases under the nitride in Figure 4a due to their enhanced surface generation. In Figure 4b, the interstitial concentration almost exactly follows the contours of the equilibrium concentration.

In Figure 5a, the concentration of boron-interstitial pairs decreases under the nitride edge due to a lower interstitial supersaturation and slightly increases

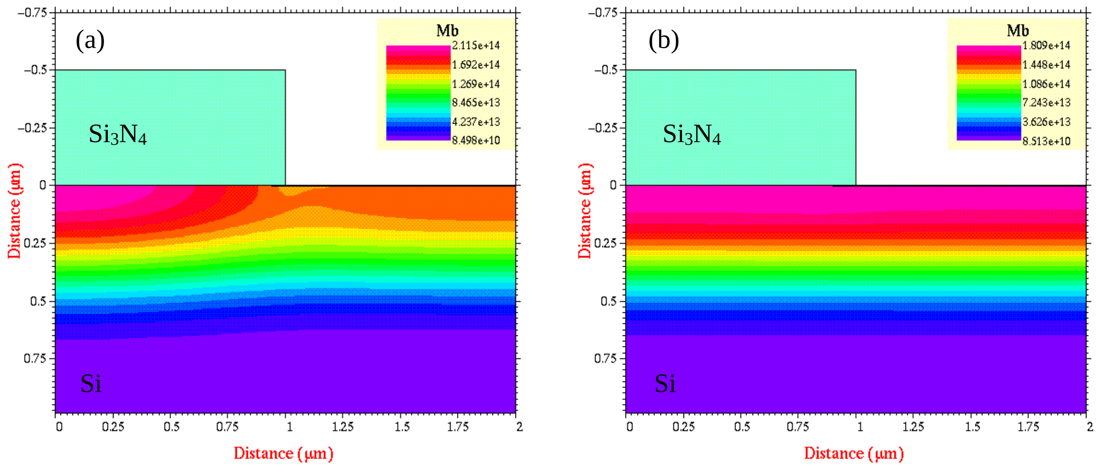

Figure 5: Simulated concentration of boron-interstitial pairs (cm^{-3}) after 1014 °C anneal in N_2 for 120 min (a) with and (b) without accounting for stress-dependent surface generation and recombination of point defects.

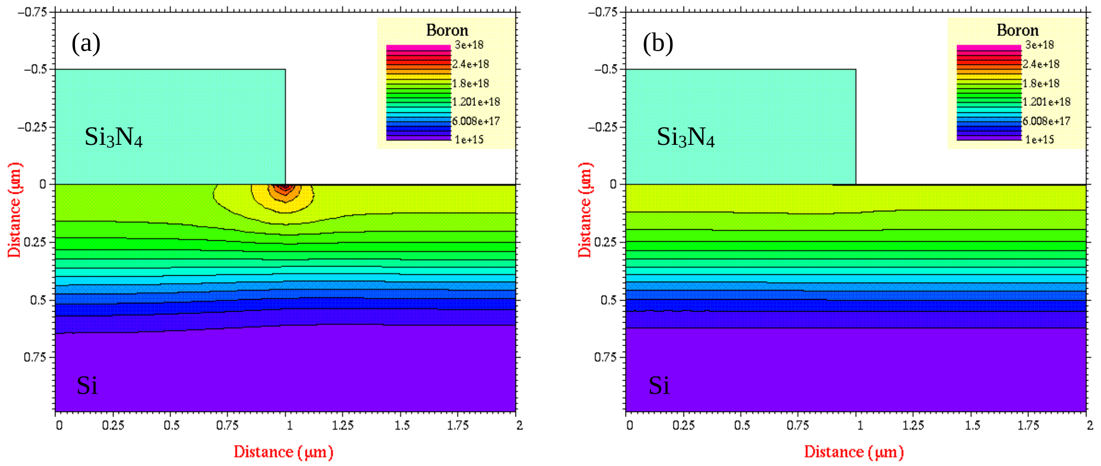

Figure 6: Contour plots of simulated boron concentration (cm^{-3}) after 1014 °C anneal in N_2 for 120 min (a) with and (b) without accounting for stress-dependent surface generation and recombination of point defects.

under the nitride. On the contrary, in Figure 5b the concentration of boron-interstitial pairs is almost independent of a lateral position. Same relative lateral uniformity of the boron concentration can be seen in Figure 6b.

Figure 6a shows that taking into account the stress-dependent surface generation and recombination of point defects results in an increase in boron concentration under the nitride edge at the peak of tensile stress. At the same time, the boron concentration is decreased in the bulk. This is opposite to what can be seen under the nitride, where stress is compressive. Near the surface, the boron concentration is lower than that in the open area, and the contours lie closer to the interface, which might be interpreted as a slower diffusion. However, deeper in the substrate, the boron concentration under the nitride is slightly higher than that in the open region. This shows an increase in boron diffusion and agrees with the results of Zhao *at al*. [11,12], whose measurements suggest enhanced boron diffusivity under compressive stress. Therefore, our results demonstrate the importance of surface proximity in analyzing the effect of stress on dopant diffusion.

It is necessary to point out that the stress-dependencies of dopant-defect pairing coefficients and equilibrium pair concentrations were not taken into account in this simulation. Since these effects may play a more or less significant role in stress-mediated dopant diffusion, a detailed study of them is required in the future.

Conclusions

In this paper, the model was developed for the stress-induced redistribution of point defects in silicon device structures. It incorporates equilibrium conditions different for defects at the surface and in the bulk of silicon and takes into account stress-dependent surface generation and recombination of point defects. In the model, equilibrium concentrations of intrinsic point defects depend exponentially on hydrostatic pressure in silicon. For bulk interactions, the calculations yielded the activation volumes of about 2.5 $Å^3$ and 2.3 $Å^3$ for interstitials and vacancies, respectively. The activation volumes for surface generation and recombination of point defects close to 18 $Å^3$ were used.

Computer simulations showed that the enhancement in surface generation of interstitials under compressive stress may explain the growth of larger stacking faults at the edges of active areas.

The importance of taking into account the proximity of the silicon surface in analyzing the effect of stress on dopant diffusion was demonstrated using simulations. It is shown that surface generation and recombination of point defects play a pronounced role in the point defect and therefore dopant distribution.

References

[1] H. Park, K. S. Jones, and M. E. Law, *J. Electrochem. Soc.*, Vol. 141, No. 3, p. 759 (1994).

[2] H. Park, K. S. Jones, J. A. Slinkman, and M. E. Law, *J. Appl. Phys.*, Vol. 78, No. 6, p. 3664 (1995).

[3] S. Chaundry and M. E. Law, *J. Appl. Phys.*, Vol. 82, No. 3, p. 1138 (1997).

[4] M. Laudon, N. N. Carlson, M. P. Masquelier, M. S. Daw, and W. Windl, *Appl. Phys. Lett*, Vol. 78, No. 2, p. 201 (2001).

[5] M. S. Daw, W. Windl, N. N. Carlson, M. Laudon, and M. P. Masquelier, *Physical Review B*, Vol. 64, p. 045205 (2001).

[6] J. Lothe and J. P. Hirth, *J. Appl. Phys.*, Vol. 38, No. 2, p. 845 (1967).

[7] J. P. Hirth and J. Lothe, *Theory of Dislocations*, Second Edition, p. 497, 506, John Wiley & Sons, New York (1982).

[8] W. Windl, M. S. Daw, N. N. Carlson, and M. Laudon, in *Advances in Materials Theory and Modeling - Bridging Over Multiple-Length and Time Scales,* V. Bulatiov, F. Cleri, L. Colombo, L. Lewis, Editors, Materials Research Society Proc. Vol. 677, p. AA9.4.1, Warrendale, PA (2001).

[9] P. M. Fahey, P. B. Griffin, and J. D. Plummer, *Reviews of Modern Physics,* Vol. 61, No. 2, p. 289 (1989).

[10] K. Osada, Y. Zaitsu, S. Matsumoto, M. Yashida, E. Arai, and T. Abe, *J. Electrochem. Soc.*, Vol. 142, No. 1, p. 202 (1995).

[11] Y. Zhao, M. Aziz, H. J. Gossmann, and S. Mitha, *Appl. Phys. Lett,* Vol. 74, p. 31 (1999).

[12] Y. Zhao, M. Aziz, H. J. Gossmann, S. Mitha, and D. Schiferl, *Appl. Phys. Lett,* Vol. 75, p. 941 (1999).

[13] H. R. Huff, *Encyclopedia of Applied Physics*, Vol. 17, p. 437 (1996).

[14] L. D. Landau and E. M. Lifshitz, *Theory of Elasticity*, p. 19, Butterworth-Heinemann, Oxford (1997).

[15] S. M. Hu, *J. Appl. Phys.*, Vol. 57, No. 4, p. 1069 (1985).

[16] K. M. Jarreau, *M.S. Thesis*, The University of Texas at Dallas (August 2002).

[17] *TSUPREM-4 User's Manual*, Version 2000.4, p. 2-40, Avant! Corporation, Fremont, CA (2000).

[18] S. T. Dunham, A. H. Gencer, and S. Chakravarthi, *IEICE Trans.*, Vol. E00-A, No. 1, p. 1 (1998).