

A Composite Model for Oxidation and Point-defect Diffusion

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A new model describing the interaction between Si oxidation and point-defect diffusion is proposed. The kinetics of point-defects during oxidation has been investigated and integrated into simulators already, but these only models the effect of the oxidation on the point-defect diffusion in the Si area. Dunham [1], Taniguchi et al. [2] indicated that most of the interstitials generated at the Si/SiO₂ interface diffuse into the oxide and that interstitial flux into the Si substrate is dominated by the flux into the oxide. Also, experiments using oxygen-18 show the existence of oxide reacted at the surface [3] [4]. This indicates that generation of interstitials is bigger than assumed. Thus the effect of interstitial generation on the oxidation cannot be neglected.

To connect the oxidation equation with the point-defect diffusion equation consistently, we introduce the concentration (or we should say density) of "reactable Si," which means Si that can be oxidized or can migrate from the lattice site to form interstitials. Thus the equations for the point-defects, oxidants and reactable Si are expressed as:

$$\frac{\partial C_I}{\partial t} = -\nabla(-D_I \nabla C_I) - k_I C_O C_I - K(C_I C_V - C_I^* C_V^*) - K_I(C_I - C_I^*) + \Theta k_S C_S C_O \quad (1)$$

$$\frac{\partial C_V}{\partial t} = -\nabla(-D_V \nabla C_V) - K(C_I C_V - C_I^* C_V^*) \quad (2)$$

$$\frac{\partial C_O}{\partial t} = -\nabla(-D_O \nabla C_O) - \gamma \left\{ (1 - \Theta) k_S C_S + k_I C_I \right\} C_O \quad (3)$$

$$\frac{\partial C_S}{\partial t} = -k_S C_S C_O + K(C_I C_V - C_I^* C_V^*) \quad (4)$$

where K is the recombination rate constant between interstitials and vacancies, and K_I is the recombination rate constant of interstitials at traps. D is the diffusivity, and C is the concentration. The subscripts I, V, O, S indicate interstitials, vacancies, oxidants and reactable Si, respectively, and the superscript * indicates the equilibrium state. Initially $C_S = 5.0 \times 10^{22} (/cm^3)$ in the Si region and $C_S = 0 (/cm^3)$ in the oxide region. k_I, k_S are the reaction rate constant between oxidants and interstitials and between oxidants and reactable Si, respectively. Θ is the ratio of generated interstitials to reacted Si. γ is the reaction ratio of oxidants to Si. So $\gamma=1$ for dry O₂ and $\gamma=2$ for H₂O.

As for the oxidant continuity equation, eq. (3), this is different from the one generally used, because the oxidation reaction is represented by the annihilation term. Rank [5] uses a similar term to treat topological change easily. But here C_S (and the other concentrations) indicate discontinuity at the Si/SiO₂ interface and k_S has a value only at places where the Si has dangling bonds (e.g. the Si/SiO₂ interface or regions suffering from damage). The right hand side of equation of the reactable Si, eq. (4), is composed of two components: 1) consumption by reaction with oxidants, 2) recovery by bulk recombination of point-defects.

After solving the above eq. (1)-(4), consistently, the shape of the oxide and Si is given by the Si consumption volume rate and oxide generation volume rate expressed as

$$R_{Si} = \frac{\alpha}{N} \left(\frac{\partial C_S}{\partial t} \right) \quad (5)$$

$$R_{ox} = \frac{1}{N} \{ (1 - \Theta) k_S C_S + k_I C_I \} C_O \quad (6)$$

where α is the ratio of consumed volume of Si to generated volume of Si and N is the number of Si atoms (not oxidant molecules as is general) incorporated into a unit volume of oxide.

To determine the surface of the oxide, the deformation equation must be solved with an initial strain rate $R_{ox} - R_{Si}$. To determine the Si/SiO₂ interface, the deformation equation must be solved with an initial strain rate $-R_{Si}$. In this case the deformation involves shrinking of the Si. Concentrations must be recalculated because of the changes of the volume occur.

This model explains the existence of the oxide reacted at the oxide surface as Rochet et al. [3]. Costello et al. [4] indicate. In the oxide, only the diffusion term and interstitial oxidation term remain in the right hand side of the eq. (1) and eq. (3). So C_I and C_O can be estimated as:

$$C_I = \left\{ \Theta k_S C_S A \exp\left(-\frac{x_d}{L_O}\right) + C_I^* \right\} \exp\left(-\frac{x}{L_I}\right) \quad (7)$$

$$C_O = A \exp\left(\frac{x - x_d}{L_O}\right) \quad (8)$$

where x_d is the thickness of oxide and A is a constant. L_O , L_I are the diffusion length. Oxidants are thought to diffuse faster than interstitials in the oxide, so $L_O > L_I$. Thus the ratio of oxide generated at the surface to that at the interface is given by

$$R_{S/I} = \frac{k_I \left\{ C_I^* + \Theta k_S C_S A \exp\left(-\frac{x_d}{L_O}\right) \right\} A \exp\left(-\frac{x_d}{L_I}\right)}{(1 - \Theta) k_S C_S + k_I \left\{ C_I^* + \Theta k_S C_S A \exp\left(-\frac{x_d}{L_O}\right) \right\} A \exp\left(-\frac{x_d}{L_O}\right)} \quad (9)$$

If Θ is not negligible, the thinner x_d becomes, the bigger $R_{S/I}$ becomes. This result fits in generally with the experimental data by Rochet et al. [3]. Although there are some unmeasured parameters, this model has a lot of potential in explaining Si oxidation related phenomena.

- [1] S. T. Dunham, "Interstitial Kinetics Near Oxidizing Silicon Interfaces," *J. Electrochem. Soc.*, Vol. 136, pp. 250-254, 1989.
- [2] K. Taniguchi, Y. Shibata, and C. Hamaguchi, "Theoretical model for self-interstitial generation at the Si/SiO₂ interface during thermal oxidation of Silicon," *J. Appl. Phys.*, Vol. 65, pp. 2723-2727, 1989.
- [3] F. Rochet, B. Agius, and S. Rigo, "An ¹⁸O Study of the Oxidation Mechanism of Silicon in Dry Oxygen," *J. Electrochem. Soc.*, Vol. 131, pp. 914-923, 1984.
- [4] J. A. Costello and R. E. Tressler, "Isotope Labeling Studies of the Oxidation of Silicon at 1000 and 1300 C," *J. Electrochem. Soc.*, Vol. 131, pp. 1944-1947, 1984.
- [5] E. Rank and U. Weinert, "A Simulation System for Diffusive Oxidation of Silicon: A Two-Dimensional Finite Element Approach," *IEEE Trans. CAD*, Vol. 9, pp. 543-550, 1990.