A Novel Diffusion Coupled Oxidation Model

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Abstract

A new approach to the three-dimensional local oxidation of silicon is presented, that is based on a parameter dependent smooth transition zone between silicon and silicon dioxide. The resulting two phase problem is solved by calculating a free diffusive oxygen concentration, which reacts with unsaturated silicon to silicon dioxide. This chemical reaction causes a volume dilatation which leads to mechanical stress concerning the surrounding boundary conditions. By a suitable set of parameters this kind of approach is equivalent to the standard sharp interface model based on the fundamental work of Deal and Grove. The main advantage is, that the mesh remains topologically invariant during the progress of oxidation and therefore no remeshing is necessary.

1. Introduction

The accurate simulation of an oxidation process is still an unsatisfactorily solved problem in process simulation. Although this process step is very important and a wide range of scientists are working towards a solution the physical mechanisms are not yet fully understood because of their complexity. Resulting from this lack of knowledge numerical modeling of silicon oxidation is still in experimental state. Furthermore, the different requirements such as diffusion processes, chemical reactions, mechanical deformations leading from elastic over viscoelastic to fully viscous material behavior are increasing the degree of complexity of a simulation tool drastically and the effort to develope a complex oxidation model is extremely high.
Using AMIGOS (Analytical Model Interface & General Object-Oriented Solver), a simulation tool which is especially designed for simple but efficient model development, an oxidation model has been developed which approximates the physical mechanisms in an acceptable manner in all three dimensions.
The idea is, instead of using the one-dimensional oxidation model from Deal and Grove [1], which is comparatively easy to simulate concerning the basic equations

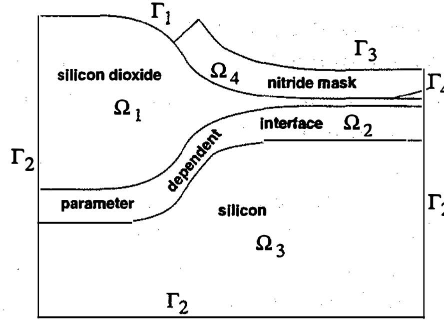

Figure 1: Domain and boundary settings

but leads to severe difficulties in reference to meshing especially in two or even three dimensions, we simulate the growth rate of silicon by coupling the oxygen diffusion and the resulting silicon dioxide generation with the mechanical volume dilatation respective to the different mechanical material behaviors. This extension leads to a much more complex numerical model description but restricts the growth of a single grid element to the physical ratio of volume dilatation from $Si : SiO_2$ to $1 : 2.2$. This effect keeps the grid quality within the bounds of acceptance, and neither remeshing after each time-step nor any grid merging algorithms are necessary.

2. The Model and its Simulation Results

For the definition of the model consider figure [1] as computation domain Ω which consists of a pure silicon dioxide range Ω_1, an interface range Ω_2 with a mixture of silicon and silicon dioxide, a pure silicon range Ω_3 and a nitride mask Ω_4 which is defined on a mesh of its own and is connected to Ω_1 via boundary Γ_4 to transmit mechanical displacements. For the nitride mask an elastic model is used to calculate its stress-strain contribution. To describe the different phases of oxygen within the domain $\Omega_1 \cup \Omega_2 \cup \Omega_3$ a generation/recombination ratio of oxygen

$$R_O = k_r \ (1 - \eta(x,t)) \ C_O \qquad (1)$$

is defined, where $\eta = f\left(\frac{C_{SiO_2}(x,t)}{C_{Si_0}}\right)$ is a function of a normalized silicon dioxide concentration related to the C_{Si_0} concentration of silicon in pure crystal. η varies between one (pure silicon dioxide) and zero (pure silicon). The generation of silicon dioxide itself is handled by the formulation

$$\frac{\partial C_{SiO_2}}{\partial t} = R_O. \qquad (2)$$

The free oxidant diffusion in $\Omega_1 \cup \Omega_2 \cup \Omega_3$ is described by

$$\frac{\partial C_O}{\partial t} = div\left[D\left(\eta(x,t)\right) \cdot grad\left(C_O\right)\right] - 2 \cdot R_O \qquad (3)$$

with the boundary condition

$$\frac{\partial C_O}{\partial n} = k \cdot (C_O - C^*) \quad \text{on} \quad \Gamma_1 \qquad \text{and} \qquad \frac{\partial C_O}{\partial n} = 0 \quad \text{on} \quad \Gamma_2, \Gamma_4. \qquad (4)$$

Thus, the mobility of oxygen is strongly influenced by the amount of the generated silicon dioxide since compounded oxygen atoms are immovable. On the other hand, the amount of generated silicon dioxide depends on the local concentration of already generated oxide as well as of free oxygen which is assumed to react with silicon immediately. This effect causes that in the beginning of oxidation of a pure silicon block the oxidation is enhanced, since nearly all oxide atoms are reacting with silicon. Later on, oxide has to diffuse through the silicon dioxide range and the growth of the oxide layer is reduced. Finally, the mechanical dilatation of the oxide is described by a Maxwell body which can handle both, elastic as well as viscous material behavior. The used strain relation is based on Hook's Law, which can be expressed so that the dilatational component of stress, which involves a volumetric expansion, and the deviatoric part, which only accounts for shape modification, are completely decoupled:

$$\begin{bmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \\ \sigma_{xy} \\ \sigma_{yz} \\ \sigma_{zx} \end{bmatrix} = \left(\chi(\eta) \begin{bmatrix} 1 & 1 & 1 & 0 & 0 & 0 \\ 1 & 1 & 1 & 0 & 0 & 0 \\ 1 & 1 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} + G(\eta) \begin{bmatrix} \frac{4}{3} & -\frac{2}{3} & -\frac{2}{3} & 0 & 0 & 0 \\ -\frac{2}{3} & \frac{4}{3} & -\frac{2}{3} & 0 & 0 & 0 \\ -\frac{2}{3} & -\frac{2}{3} & \frac{4}{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \right) \begin{bmatrix} \varepsilon_{xx} \\ \varepsilon_{yy} \\ \varepsilon_{zz} \\ \varepsilon_{xy} \\ \varepsilon_{yz} \\ \varepsilon_{zx} \end{bmatrix} \quad (5)$$

For the volumetric expansion we solve the equilibrium condition

$$\left(\int_V \mathcal{L}^T \cdot \mathcal{D}(\eta(x,t)) \cdot \mathcal{L} \cdot dV \right) \cdot \{u\} = \int_V \mathcal{L}^T \cdot \mathcal{D}(\eta(x,t)) \cdot \{\epsilon_o\} \cdot dV \quad (6)$$

where u, ϵ_o, $\mathcal{L}$ and $\mathcal{D}$ represents the displacement vector, the strain caused by silicon dioxide generation, the mechanical operator defined as $\{\epsilon\} = \mathcal{L} \cdot \{u\}$ and the elasticity matrix, respectively. The right hand side of equation [6] can be interpreted as an energy term caused by the chemical reaction between silicon and silicon-dioxide. For the dilatation effect within the oxide we assume a hydrostatic pressure term

$$p = -\chi \cdot (\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz}) \quad \Longrightarrow \quad \Delta V \quad (7)$$

The stress histories have to be calculated in order to get a correct stress-strain distribution within the different materials. Assuming the model suggested in [2] stress within elastic material is calculated by

$$\sigma(n \cdot \Delta T) = \sum_{i=1}^{n} \sigma_i(\Delta T) \qquad \text{with} \qquad \sigma_i(\Delta T) = \chi \cdot \epsilon(\Delta T) \quad (8)$$

and within viscous material by

$$\sigma(n \cdot \Delta T) = \sum_{i=1}^{n} \sigma_i(\Delta T) \cdot e^{-\frac{(n-i)\cdot \Delta T}{\tau}} \qquad \text{with} \qquad \sigma_i(\Delta T) = G_{eff} \cdot \epsilon(\Delta T) \quad (9)$$

where ΔT is interpreted as the time-step length, τ as the relaxation ratio, χ as the compressibility and $G_{eff} = G \cdot \frac{\tau}{\Delta T} \cdot \left(1 - e^{\frac{\Delta T}{\tau}}\right)$ as the effective modulus of rigidity.

As an example two typical three-dimensional effects arising in the corners of the nitride mask have been calculated [Fig. 2]. Starting from a pure silicon block the results show, that the introduced model can even handle structures without pad oxide below the nitride mask, which leads to the effect, that the interface meets the nitride layer vertically, which can hardly be solved by algorithms based on a sharp interface formulation.

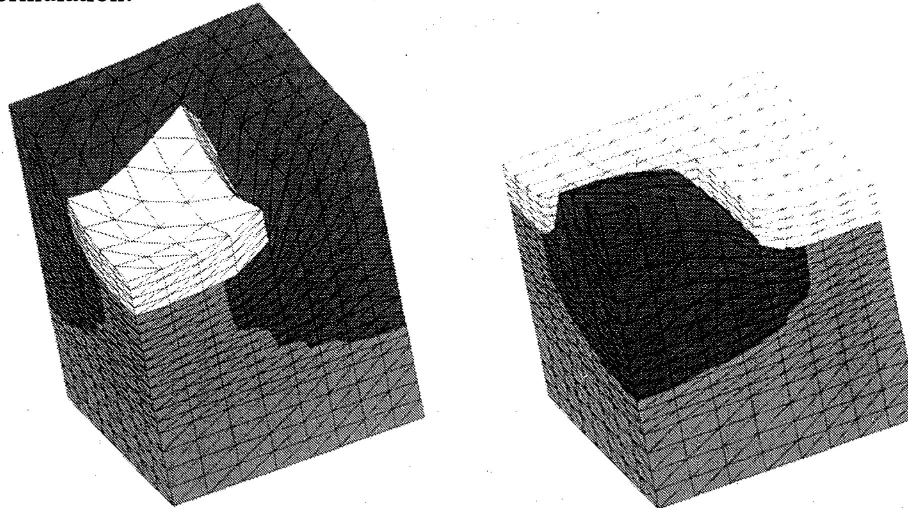

Figure 2: Oxidation of typical three-dimensional effects arising in the corners of the nitride mask

3. Conclusion

A new approach for the simulation of local oxidation of silicon in three dimensions has been presented, considering the interface between silicon and silicon dioxide as a smooth transition layer. According to theoretical investigations it can be shown that by a suitable set of parameters identical results to the standard Deal-Grove model can be obtained [3]. Furthermore, this extension offers the possibility to handle much more complex physical effects than it can be done with remeshing or grid-merging algorithms, since especially topology changing oxidation is hardly solvable with interface tracking algorithms.

References

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