Simulation of Thermal Oxidation: A Three-Dimensional Finite Element Approach

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Abstract

In this paper a new numerical model for the three-dimensional simulation of thermal oxidation of silicon is presented. The model takes into account that the diffusion of oxidants, the chemical reaction, and the volume increase occur simultaneously in a so-called reactive layer. This reactive layer has a spatial finite width, in contrast to the sharp interface between silicon and silicon dioxide in the convential formulation. The oxidation process is numerically described with a coupled system of equations for reaction, diffusion, and displacement. In order to solve the numerical formulation of the oxidation process the finite element scheme is applied.

1. Introduction

If a surface of a silicon body has contact with an oxidizing atmosphere, the chemical reaction of the oxidant (oxygen or steam) with silicon forms silicon dioxide. The parts of silicon which should not be oxidized are masked by a layer of silicon nitride.
If a silicon dioxide domain is already existing, the oxidants diffuse through the oxide domain and react at the interface of oxide and silicon to form new oxide so that the oxide domain is penetrated. This reaction consumes silicon and the newly formed silicon dioxide has more than twice the volume of the original silicon.
Thermal oxidation is a complex process where the three subprocesses oxidant diffusion, chemical reaction, and volume increase occur simultaneously. The volume increase is the main source of mechanical stress and strain, and these cause displacement [1].
From the mathematical point of view the problem can be described by a coupled system of partial differential equations, one for the diffusion of the oxidant through the oxide, the second for the conversion of silicon into silicon dioxide at the interface, and a third for the mechanical problem of the $\mathrm{Si-SiO_2-\ Si_3Ni_4-}$body.
Novel in our model is that all subprocesses are coupled simultaneously and the oxidation process is simulated in three dimensions. Earlier oxidation models decouple them into a sequence of quasi-stationary steps.
We will restrict the following explanation to the most simple physical model of linear oxidant diffusion and linear elastic displacement of the $\mathrm{Si-SiO_2-Si_3Ni_4-}$body.

2. Model

Analogously to [2] we use a normalized silicon concentration

$$\eta(\vec{x},t) = \frac{C_{Si}(\vec{x},t)}{C_{0Si}} \tag{1}$$

where $C_{Si}(\vec{x},t)$ is the silicon concentration at time t and point $\vec{x}$ (x, y, z) and C_{0Si} is the concentration in pure silicon. So η is 1 in pure silicon and 0 in pure silicon dioxide. The oxidant diffusion is described by

$$D\Delta C(\vec{x},t) = k(\eta)C(\vec{x},t). \tag{2}$$

Here D is the diffusion coefficient and $k(\eta)$ is the strength of a spatial sink and not just a reaction coefficient at a sharp interface like in the standard model [3].$k(\eta)C(\vec{x},t)$ defines how many particles of oxygen per unit volume react in a unit time interval to silicon dioxide.
The change of η is described by

$$\frac{\partial\eta(\vec{x},t)}{\partial t} = -\frac{1}{\lambda}k(\eta)C(\vec{x},t)/N_1 \tag{3}$$

where λ is the volume expansion factor (= 2.25) for the reaction from Si to $\mathrm{SiO_2}$ and N_1 is the number of oxidant molecules incorporated into one unit volume of $\mathrm{SiO_2}$.
We define in (4) that $k(\eta)$ is linearly proportional to η

$$k = \eta(\vec{x},t)k_{max}. \tag{4}$$

The chemical reaction of silicon and oxygen causes a volume increase. The normalized additional volume, where we assume that the oxidant concentration C is constant, is

$$V_{rel}^{add} = \frac{\lambda-1}{\lambda}\Delta t\ k(\eta)C(\vec{x},t)/N_1. \tag{5}$$

We assume that the $\mathrm{Si-SiO_2-}$body deforms elastically. In the theory of linear elasticity with small displacements $\vec{\theta}(x,y,z) = \{u(x,y,z)\,v(x,y,z)\,w(x,y,z)\}$ and strains ε_{ij} (i,j stands for x, y or z), the strain tensor $\tilde{\varepsilon}$ is

$$\tilde{\varepsilon} = L_D\vec{\theta} \tag{6}$$

where $\vec{\theta}$ is the displacement vector and L_D is a differential operator, so that e.g. $\varepsilon_{xx} = \frac{\partial u}{\partial x}$ and $\varepsilon_{xy} = \frac{1}{2}(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x})$.
Assuming a linear material, the stress tensor $\tilde{\sigma}$ is given by

$$\tilde{\sigma} = \mathbf{D}\tilde{\varepsilon} \tag{7}$$

where $\mathbf{D}$ is a (6x6) material matrix of elastic coefficients which are linear functions of Young's Modulus E and Poisson's ratio μ of the materials.

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The most important part is that the volume expansion causes displacement. The normalized additional volume from (5) can be written as

$$V_{rel}^{add} = \varepsilon_x + \varepsilon_y + \varepsilon_z \tag{8}$$

For an isotropic material the strain components are equal so that

$$\varepsilon_x = \varepsilon_y = \varepsilon_z = \frac{1}{3} V_{rel}^{add} \tag{9}$$

With (6) and (9) the relationship between the volume expansion and the displacement is fully determined.

3. Discretization

3.1. Weak Formulation

Before we start with the discretization we consider the weak formulation on (2) and (3). After using the Galerkin method with linear test functions $N_k(\vec{x})$ on the diffusion equation (2) and applying Green's theorem we obtain

$$k_{max} \int_V \eta\, C\, N_k\, dV = -D \int_V \nabla C\, \nabla N_k\, dV \tag{10}$$

The application of the Galerkin method with the same linear test functions $N_k(\vec{x})$ to the distribution function from (3) leads to

$$\int_V \frac{\partial \eta}{\partial t} N_k\, dV = k_{max} \int_V \eta\, C\, N_k\, dV\,. \tag{11}$$

3.2. Oxidant Diffusion

In order to solve (2) and (3) on a three-dimensional domain with the volume V_{global}, we split the domain up into tetrahedral elements with the volume V and perform a finite element discretization. The spatial discretization for $C(\vec{x})$ and $\eta(\vec{x})$ on a single tetrahedral element is

$$C(\vec{x}, t = t_n) = \sum_{i=1}^{4} c_i^{(t_n)} N_i(\vec{x}) \tag{12}$$

$$\eta(\vec{x}, t = t_n) = \sum_{i=1}^{4} \eta_i^{(t_n)} N_i(\vec{x}) \tag{13}$$

where $c_i^{(t_n)}$ is the oxidant concentration and $\eta_i^{(t_n)}$ is the normalized silicon concentration at node i and discrete time t_n. $N_i(\vec{x})$ is the linear form function on node i.
If we replace $C(\vec{x}, t)$ and $\eta(\vec{x}, t)$ in (10) with (12) and (13) we obtain

$$\begin{aligned} -D \int_V \Big(\sum_{i=1}^{4} c_i^{(t_n)} \nabla N_i\, \nabla N_k \Big) dV = \\ k_{max} \int_V \Big(\big(\sum_{i=1}^{4} \eta_i^{(t_n)}\, c_i^{(t_n)}\, N_i \big)\, N_k \Big) dV \end{aligned} \tag{14}$$

With the following substitution

$$M_{ki} = \int_V N_k(\vec{x})\, N_i(\vec{x}) dV \tag{15}$$

$$K_{ki} = \int_V \nabla N_k(\vec{x})\, \nabla N_i(\vec{x}) dV \tag{16}$$

(14) is simplified to

$$\sum_{i=1}^{4} \big(D\, K_{ki}\, c_i^{(t_n)} + k_{max}\, M_{ki}\, c_i^{(t_n)}\, \eta_i^{(t_n)} \big) = 0 \tag{17}$$

which is a non-linear equation system (k is the equation index) with the constants D, K_{ki}, k_{max} and M_{ki} and with the unknown variables $c_i^{(t_n)}$ and $\eta_i^{(t_n)}$ for one element.

3.3. Change of η

The spatial discretization for $C(\vec{x})$ and $\eta(\vec{x})$ on (3) is the same like in the last subsection and is already described by (12) and (13). The time discretization of $\frac{\partial \eta(\vec{x},t)}{\partial t}$ is performed with the simple Backward-Euler method as

$$\frac{\partial \eta(\vec{x}, t = t_n)}{\partial t} \cong \frac{\eta(\vec{x}, t_n) - \eta(\vec{x}, t_{n-1})}{\Delta t} \tag{18}$$

where t_n and t_{n-1} are two successive discrete times.
If we replace $C(\vec{x}, t)$, $\eta(\vec{x}, t)$ and $\frac{\partial \eta(\vec{x},t)}{\partial t}$ in (11) with the discrete expressions (12), (13) and (18), we obtain

$$\begin{aligned} \frac{1}{\Delta t} \int_V \Big(\sum_{i=1}^{4} \big(\eta_i^{(t_n)} - \eta_i^{(t_{n-1})} \big) N_i\, N_k \Big) dV = \\ k_{max} \int_V \Big(\big(\sum_{i=1}^{4} \big(\eta_i^{(t_n)}\, c_i^{(t_n)} \big) N_i\, N_k \Big) dV \end{aligned} \tag{19}$$

With the substitution (16) the last equation is simplified to a non-linear equations system (k is the equation index)

$$\sum_{i=1}^{4} \Big(M_{ki} \big(\eta_i^{(t_n)} - \eta_i^{(t_{n-1})} - k_{max}\, c_i^{(t_n)}\, \eta_i^{(t_n)} \big) \frac{1}{\Delta t} \Big) = 0 \tag{20}$$

with the unknown variables $c_i^{(t_n)}$ and $\eta_i^{(t_n)}$ and with the constants M_{ki}, k_{max} and $\frac{1}{\Delta t}$ for one finite element. The values for $\eta_i^{(t_{n-1})}$ are already determined at the previous time step.

3.4. Mechanics

The finite element discretization for a mechnical system has been already often described, e.g. by [4]. Because of this fact we will restrict this subsection only to some steps which are important for the oxidation simulation.
After discretization of the continuum, the relationship between strain and displacement (6) can be written as

$$\tilde{\varepsilon}^e = \mathbf{B}\, \vec{d}^e = [\mathbf{B_i}, \mathbf{B_j}, \mathbf{B_m}, \mathbf{B_p}]\, \vec{d}^e \tag{21}$$

in which $\tilde{\varepsilon}^e$ is the strain tensor, $\vec{d}^e$ is the displacement vector (12x1) and $\mathbf{B_i}$ is the (3x3) submatrix for the node i.
The entire inner virtual work on a finite element is

$$W_{inner} = \int_V \{\tilde{\varepsilon}^e\}^T\, \sigma^e dV \tag{22}$$

in which the transposed strain tensor is

$$\{\tilde{\varepsilon}^e\}^T = \vec{d^e}^T \, \mathbf{B^T} \tag{23}$$

and the stress tensor (7) can be written as

$$\sigma^e = \mathbf{D}\,\tilde{\varepsilon}^e = \mathbf{D}\,\mathbf{B}\,\vec{d^e}\,. \tag{24}$$

That leads to the following equation for W_{inner}

$$W_{inner} = \vec{d^e}^T \int\limits_V \mathbf{B^T D B}\,\vec{d^e}\,dV\,. \tag{25}$$

The outer virtual work on a finite element, caused by the node forces is

$$W_{outer} = \vec{d^e}^T \vec{f^e}. \tag{26}$$

On an element the inner work must be equal to the outer work, that leads to

$$\vec{d^e}^T \int\limits_V \mathbf{B^T D B}\,\vec{d^e}\,dV = \vec{d^e}^T \vec{f^e} \tag{27}$$

With the substitution

$$\mathbf{K^e} = \int\limits_V \mathbf{B^T D B} dV \tag{28}$$

where $\mathbf{K^e}$ is the so-called stiffnes matrix, we obtain a linear equation system for the mechanical problem

$$\mathbf{K^e}\,\vec{d^e} = \vec{f^e}. \tag{29}$$

The most important part is, how the volume increase (5), caused by the chemical reaction of silicon to silicon dioxide, loads the displacement problem.
Due to (9) we obtain the components ε_x^e, ε_y^e and ε_y^e for the strain tensor $\tilde{\varepsilon}^e$ and with

$$\vec{f_i^e} = -\mathbf{B_i^T D}\tilde{\varepsilon}^e\,V \tag{30}$$

the relationship between the volume expansion and the node forces is given, and with (29) and (30) the displacements on the nodes is fully determined.

By coupling (17), (20), and (29) a local equation system for one finite element is given, which is a complete numerical formulation of the oxidation process at any time.

4. Simulation Procedure

In the first step of the simulation procedure, we perform a finite element discretization. With this aim in view we split up the $\mathrm{Si-SiO_2}$–body into tetrahedral elements. The size of the tetrahedrons and, as a result of that, the number of finite elements can be influenced by the meshing module.
In the next step we set the initial values for the oxidant concentration C and the normalized silicon concentration η on the grid nodes. For example η must be 1 in a pure silicon domain.

As shown in Fig. 1, we iterate over all finite elements and build the local equation system for one element for every actual discrete time. The local system describes the oxidation process numerically for one element.
In order to describe the global oxidation process we need a global coupled equation system. The components of the global equation system are assembled from the local equation system by using the superpostition principle. In our case "global" has a spatial meaning and stands for the whole discretized domain.

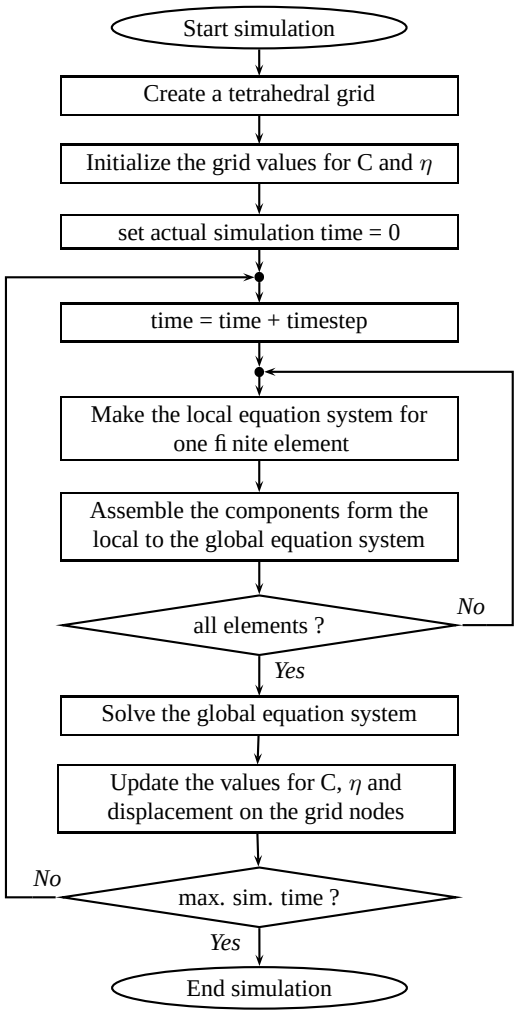

Figure 1. Simulation procedure

After the iteration over all elements is finished, the global assembled equation system is also completed. Now the global non-linear equation system can be solved and we obtain the results for the C, η and displacement values for the global discretized oxdidation process for the actual time step.
With these results we update the values for C, η and displacement on the grid nodes and so these values are always kept pace with the actual simulation time.
When the above described procedure is finished, we increase the actual simulation time and start with the assembling loop again. The same assembling and solving procedure is repeated for each time step until the desired end of the simulation.

5. A Demonstrative Example

As example a $Si-Si_3Ni_4-$body as shown in Fig. 2 is oxidized. In this example only the upper surface of the $Si-Si_3Ni_4-$body has contact with the oxidizing atmosphere. The upper layer is a silicon nitride mask that prevent the oxidant diffusion on the subjacent silicon layer.
For the simulation the following parameters were chosen:
$C^* = 3 \cdot 10^7\,[\frac{\text{part.}}{\mu m^3}]$, $D = 0.08\,[\frac{\mu m^2}{s}]$, $k_{max} = 40\,[\frac{1}{s}]$.

As shown in Figs. 2 – 4 the bottom surface is fixed, the lateral surfaces can only move vertically and on the upper surface a free mechanical boundary condition is applied.
In the Figs. 2 – 4 the angel of view is always the same and the proportions of the body geometry are also right, so that the displacement effects caused by the volume increase can be observed correctly.
The color in the silicon layer shows the value of the normalized silicon concentration. This means that blue is pure silicon dioxide and red is pure silicon and the other colors are the reaction layer.

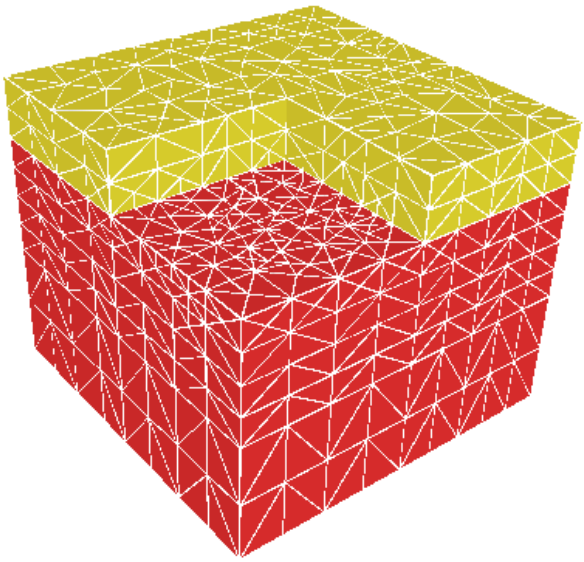

Figure 2. Initial $Si-Si_3Ni_4-$body before oxidation.

6. Conclusion

A three-dimensional oxidation model which is based on the finite element technique has been proposed. In this model it is assumed that the interface beween silicon and oxide is a reaction layer with finite width instead of a sharp interface. In this layer there is a mixture of the three components silicon, oxidants, and oxide.
The numerical formulation of the complete physical oxidation process, consisting of a coupled differential equation system, takes into account that the oxidant diffusion, the chemical reaction, and the volume increase occur simultaneously. So this model enables a realistic and accurate simulation of the whole oxidation process.
As demonstrated on a numerical example, this model is a powerful tool to simulate the whole oxidation process on three-dimensional semiconductor structures.

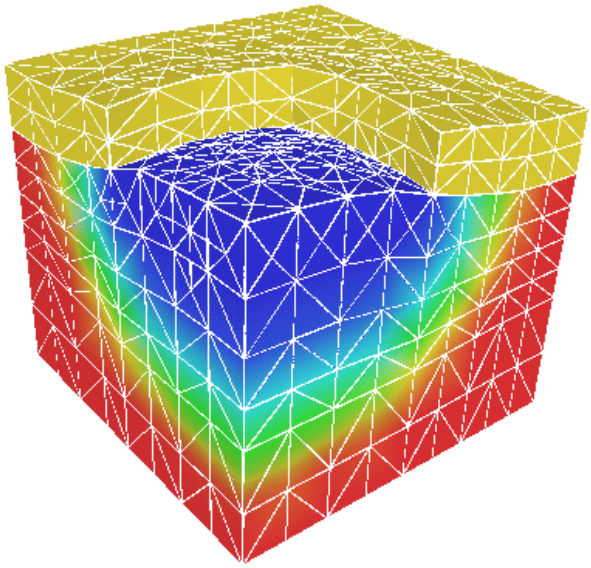

Figure 3. Deformation and silicon dioxide distribution (blue region) at some time t_1.

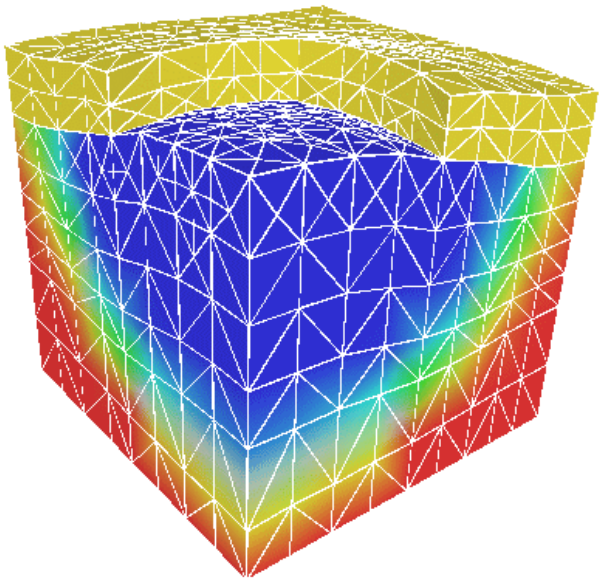

Figure 4. Deformation and silicon dioxide distribution (blue region) at time $2 * t_1$.

References

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