MODELING SiO_2 STRESS RELAXATION AND STRESS DEPENDENT OXIDATION

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Abstract

In this work, a model has been developed to account for the mechanical behavior of the oxide and its effect on oxidation kinetics. Conservation of mass, momentum balance, and the transport equation with the appropriate boundary conditions have been formulated. The material law for the oxide has been defined by the Navier-Stokes equation describing a compressible viscous (Voigt visco-elastic) material. The oxidation is modeled by a steady-state diffusion of oxidants. Reaction of oxidant species at the interface is applied through the interface boundary condition. Due to the volume difference the new oxide created at the interface is assumed to be highly compressed. The stressed oxide subsequently relaxes, further contributing to the growth of the oxide. The model is also matched to two-step oxidation experiments [1]. The stress dependent diffusivity and solubility parameters are optimized using both these experiments as well as standard oxidation kinetics experiments [2].

INTRODUCTION

Thermal oxidation of silicon is an essential step in VLSI technology. Modeling the process is necessary for predicting the oxide shape and thickness. Due to the volume expansion during oxidation, large stresses exist in the oxide. Study of oxide refractive index shows that the stress increases for oxide grown at lower temperatures [3]. This is in agreement with Landsberger's [1] observation that inert annealing of 800°C oxides causes the film to swell. Analysis of such experiments can give information about the mechanical characteristics of SiO_2 film.

The reduced oxide thickness grown on silicon corners indicates that stress can reduce the growth coefficients [4]. Experiments indicate that the diffusivity and also the solubility of oxidizing species are likely to be influenced by this stress [5]. Oxide layers with various stress levels can be generated by varying the growth temperatures. Thus, the dependence of growth rate parameters on stress in the oxide can be studied by comparing the additional thickness of the oxide grown underneath differently stressed layers.

MODELING

To be able to predict oxide thickness as a function of time, one must first establish the mechanical models for oxidation. Depending on temperature, one can expect the oxide to behave as a solid or fluid. Many models have been proposed to describe the behavior of oxide [6, 7, 8]. In this work, a compressible viscous model, related to that used by Rafferty [6] is proposed to account for the behavior of oxide.

To construct the above model, we first express the principle of conservation of mass in the oxide as:

$$\frac{\partial \rho}{\partial t} + \nabla(\rho V) = 0, \tag{1}$$

where ρ is the mass density of the material and V is the velocity. Next, the momentum balance is described by Navier-Stokes equations as:

$$\rho(\frac{\partial V}{\partial t} + (V \, . \, \nabla)V) = \frac{\partial \sigma}{\partial x}, \tag{2}$$

where σ denotes the stress. A steady flow is assumed for above equation. Finally, for a compressible viscous material, we have:

$$\sigma = -P + (\lambda + 2\mu)\,\frac{\partial V}{\partial x}, \tag{3}$$

where P is the pressure, λ is the Lame constant and μ is the viscosity. Furthermore, the pressure P is related to mass density by:

$$P = P_0 + P_1 \frac{\rho - \rho_1}{\rho_1}, \tag{4}$$

where P_0 is the atmospheric pressure, P_1 is the bulk modulus of Si, and ρ_1 is the equilibrium oxide density (~ 2.22 gr/cm^3). In this model, the viscosity (μ) is allowed to depend on stress such that [6]:

$$\mu = \mu_0 \, \frac{\sigma/\sigma_c}{\sinh(\sigma/\sigma_c)}. \tag{5}$$

Next, we have to account for the oxidant diffusion through the oxide and reaction at the interface. As mentioned previously, stress generated during oxidation can affect the diffusivity (D) and solubility (C^*) of the oxidant species. The diffusivity and solubility can be written in the form [5]:

$$D = D_0 \exp \frac{(-P \Delta V_d)}{kT}, \tag{6}$$

$$C^* = C_0^* \exp \frac{(-P \Delta V_c)}{kT} \tag{7}$$

For the 1D systems considered in this work, there is no normal stress so the interface reaction rate k_s is fixed.

Incorporating the above assumptions one can represent the transport equation for oxidizing species as:

$$\frac{\partial}{\partial x} D C^* \frac{\partial C/C^*}{\partial x} = 0, \quad (8)$$

where C is the concentration and D is the diffusion constant of the oxidizing species. The above equation is assumed to be in steady state and subject to boundary conditions:

$$D C^* \frac{\partial C/C^*}{\partial x} = k_s C(x=0), \qquad D C^* \frac{\partial C/C^*}{\partial x} = h(C(x=x_o) - C^*), \quad (9)$$

where $x = 0$ denotes the Si/SiO_2 interface and $x = x_o$ the SiO_2/gas interface, and h is gas-phase transport coefficient. The solution of Eq. 8 provides the boundary conditions for the velocity. In addition, a region of high stress is created with density

$$\rho = m_{ox} C_{si} \quad (10)$$

where m_{ox} is the molecular mass of the oxide and C_{si} is the atom concentration of silicon. This high density region is relaxed by solving the coupled partial differential equation of mass and momentum balance. This relaxation also contributes to the growth of the oxide.

It can be noted that the equations for mass (Eq. 1) and momentum balance (Eq. 2) are two coupled PDEs. These PDEs cannot easily be solved by analytical techniques. Therefore numerical techniques are essential. A one dimensional finite element discretization of the above model has been implemented. Figure 1 shows the numerical computation flow chart for a typical time step.

RESULTS AND DISCUSSION

Figure 2 shows the result of the above model for a 500 min oxidation at 800°C. The high stress generated at the interface ρ=m$_{ox}$C$_{si}$ ($\sim$ 4.99 gr/cm^3) relaxes almost immediately to a value of about 2.31 gr/cm^3 at 800°C. This rapid relaxation is due to the nonlinear behavior of viscosity. For stress in the oxide greater than the critical stress σ_c, the viscosity reduces, causing the oxide to flow much more readily.

Using viscosity in unstressed SiO_2 (μ_0) from data on bulk silica [9], the model is matched to oxide relaxation data [1] to extract the parameter σ_c. The relaxation experiments were as follows. Dry oxide films grown on lightly doped p-type Si $\langle 111 \rangle$ wafers at 800°C were annealed in inert ambients. The annealing process caused the

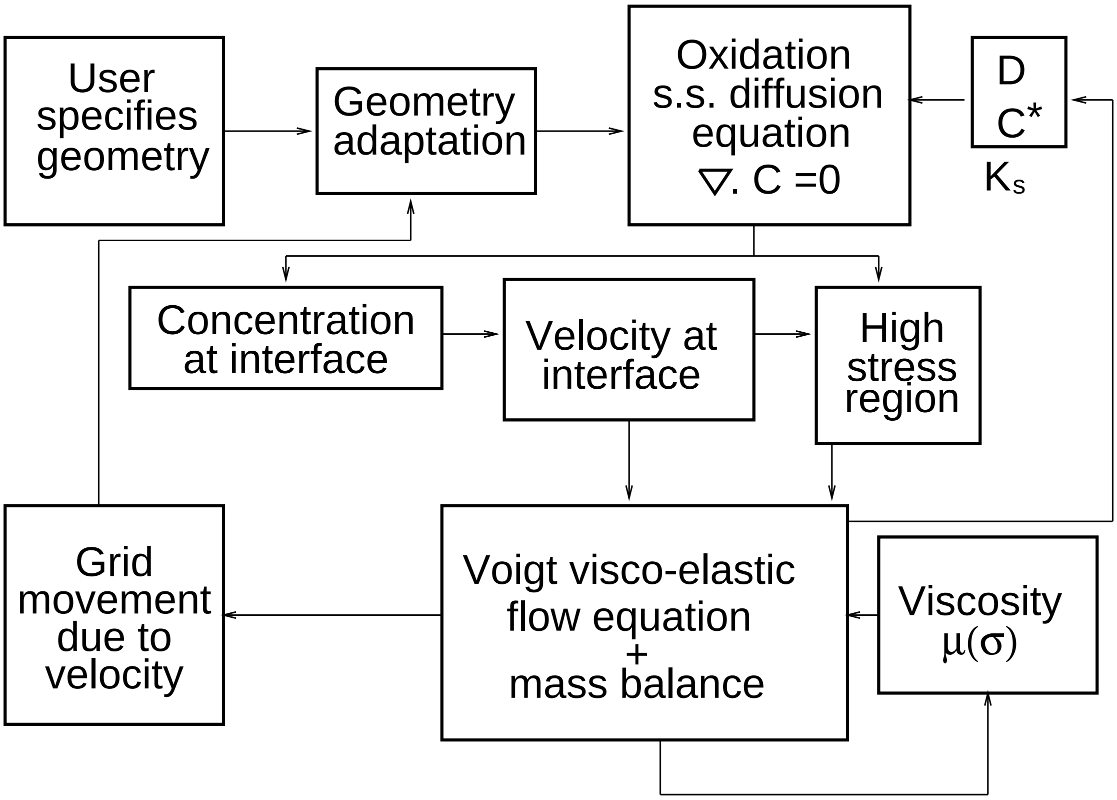

Figure 1: An overview of the 1D finite element solver

oxide to swell by $\sim$ 3% of its original thickness. Figure 4 shows the fit of the model to this data and Table I shows the extracted σ_c for various temperatures.

Once the mechanical parameters are established, the model is further matched to two-step oxidation experiments [1] and standard one-step oxidation kinetics [2], optimizing the stress dependent diffusivity and solubility parameters. The solubility of O_2 at 1 atm in unstressed oxide is taken from permeation experiments for vitreous silica (C_0^*=1.1x10^{16} exp$(0.17/kT)$ [10]) and V_C is assumed equal to V_D.

In two-step oxidation experiments [1], the amount of oxide grown in the second step depends greatly on the growth temperature used in the first step. This is accounted for by the dependence of the diffusivity and solubility on the stress distribution in the oxide. Figure 3 shows the simulated density distributions in oxides grown to a thickness of 1070Å at 1100 or 800°C and then oxidized at 800°C for 65 hours. As seen experimentally, the films which are grown with an initial higher temperature oxidation experience an enhanced oxidation rate for the second step. The reasons for this behavior are illustrated in Figure 3, where the lower density of oxide grown at

Extracted Viscosity Parameters					
Temp	800°C	900°C	1000°C	1050°C	1100°C
σx10^9 dynes/cm^2	0.584	0.586	0.800	0.955	1.358

Table I: Extracted value of σ_c for various temperatures.

higher temperature leads to higher oxidant solubility and diffusivity.

The model accounts for both two-step and one-step oxidation kinetics data over a temperature range of 800-1180°C as illustrated in Figure 5. Figures 6 and 7 show the extracted values of interface reaction rate (k_s) and unstressed diffusivity (D_0) for dry oxidation of $\langle 111 \rangle$ Si. Also plotted is the value of k_s and D from Massoud *et al.* [11]. It can be noted that the optimized values of the interface reaction rate and diffusivity are larger than values reported by Massoud and other workers [12]. This difference is attributed to the fact that effective values extracted for these parameters are generally reduced due to the stress dependencies, while values for these parameters extracted from our model reflect the diffusivity and reaction rate for an unstressed oxide. At higher temperature, bulk density approaches the equilibrium density and effective parameters should approach the values in unstressed oxide. Figure 7 depicts this trend; at higher temperatures the diffusivity from above model seems to overlap with reported effective diffusivities. Also the activation energy for D_0 (1.0 eV) is similar to that reported for high temperature oxidation [12, 13].

CONCLUSIONS

A compressible viscous model has been developed to account for the oxidation of silicon. In this model, a highly compressed oxide is created at the Si/SiO_2 interface and is relaxed by solving the equations for mass and momentum balance in the bulk of the oxide. A 1D oxidation code has been developed to solve these equations and mechanical parameters were optimized to relaxation data. The model was further extended to include the stress dependence oxidation rate parameters. These parameters were fitted to oxidation kinetics reported in the literature. A stress-dependent diffusivity (D) and interface reaction rate (k_s) have been extracted for $\langle 111 \rangle$ Si. The model accounts for the relaxation as well as history effects of oxidation.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge Dr. Norbert Strecker for his assistance with modeling the mechanical system and his helpful discussion in developing the numerical code. This work was supported by SRC grants SJ-530 and BJ-530.

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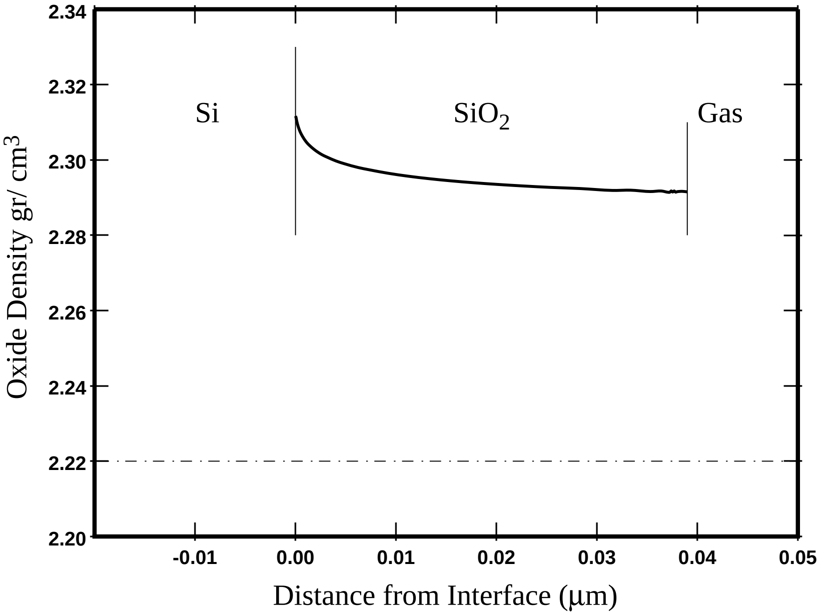

Figure 2: Simulated density distribution for oxide grown at 800°C. The equilibrium oxide density is also displayed as reference.

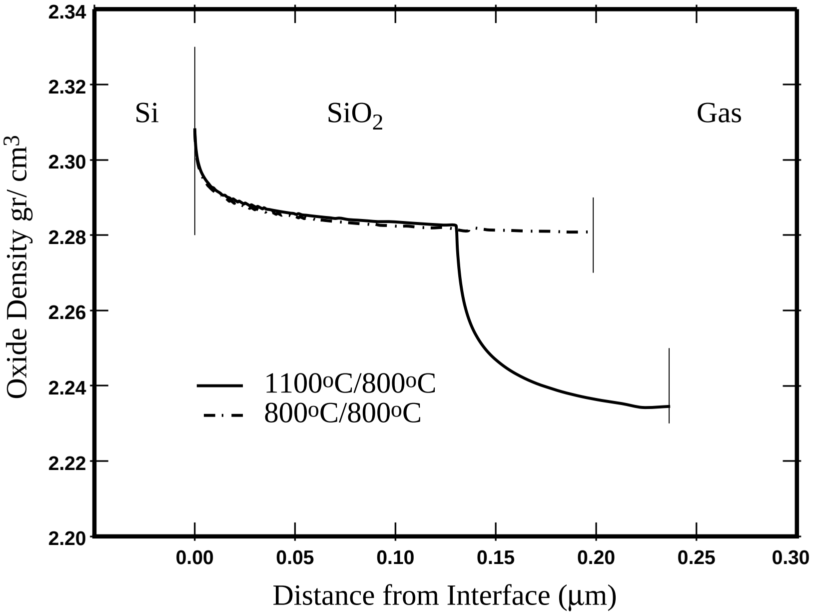

Figure 3: Simulated density distribution for oxides grown at 1100 and 800°C and reoxidized at 800°C.

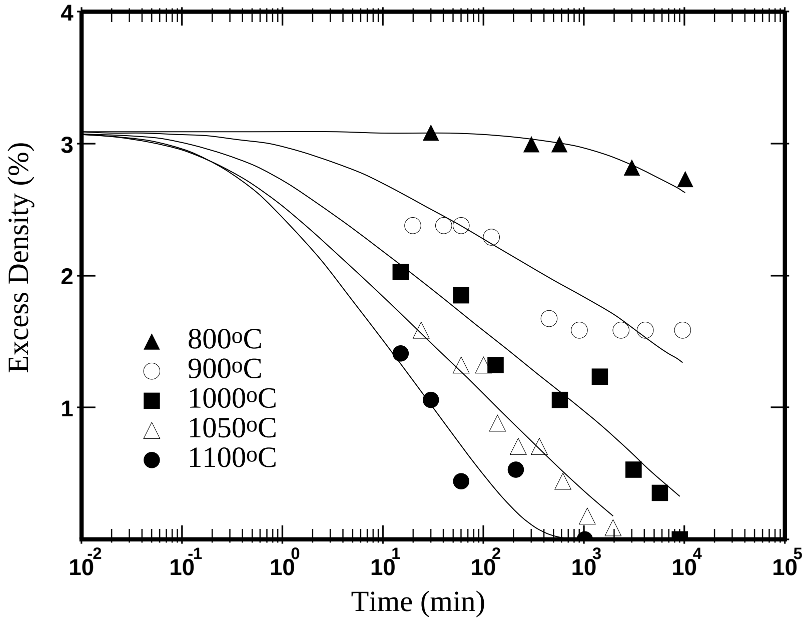

Figure 4: Comparison of model simulation to oxide relaxation data of Landsberger [1].

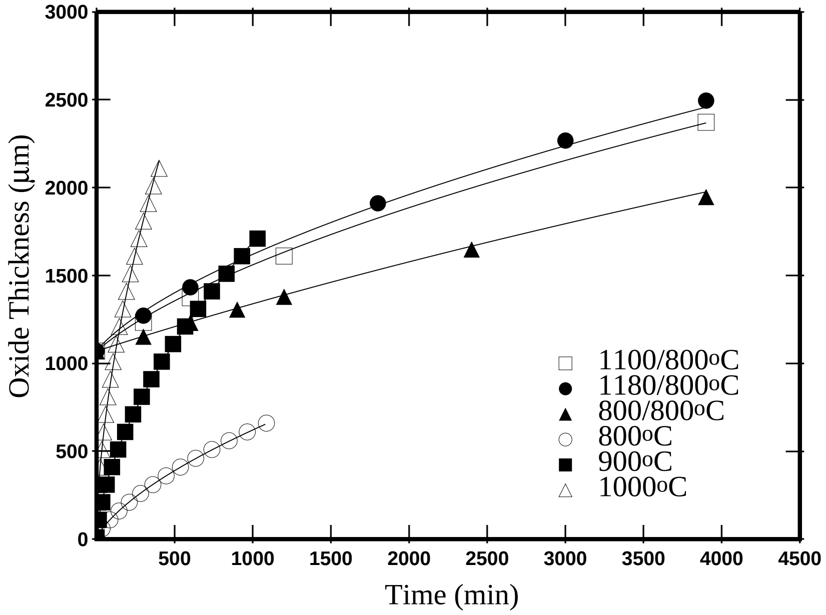

Figure 5: Comparison of model simulation to two-step oxidation of Landsberger [1] and one-step oxidation data extracted from Han's two-stream oxidation model [2]

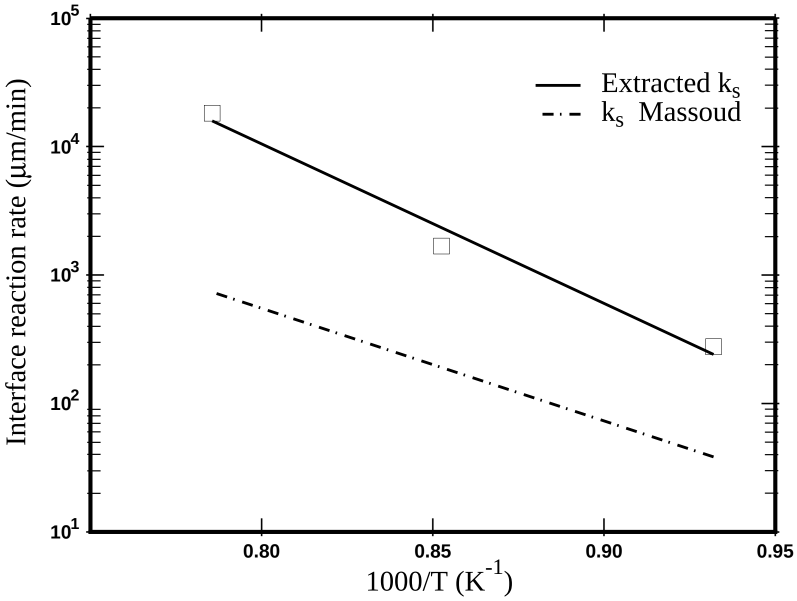

Figure 6: Reaction rate as function of temperature for oxidation of ⟨111⟩ silicon.

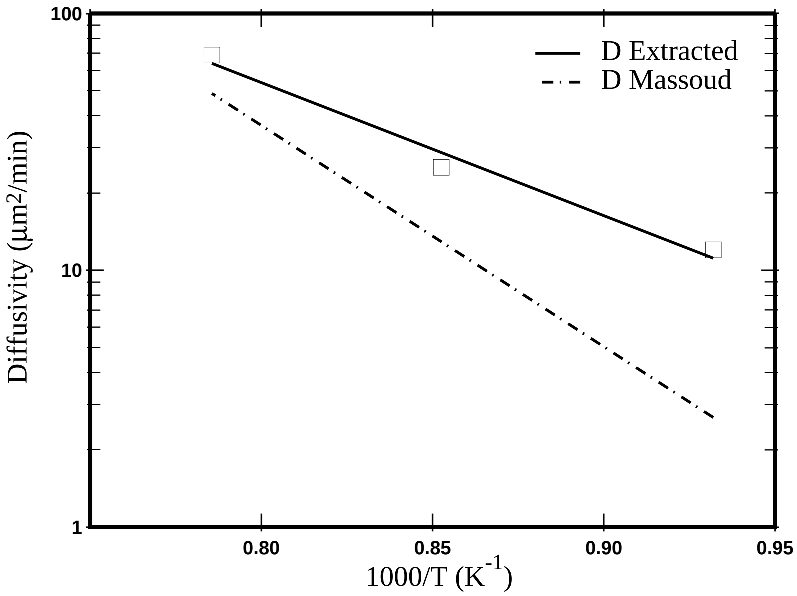

Figure 7: Diffusivity in unstressed SiO_2 as function of temperature for oxidation of ⟨111⟩ silicon.

KEY WORDS

Si, SiO_2, stress, viscosity, relaxation, diffusivity, reaction rate, solubility, oxide density, finite element.