A Comprehensive Kinetic Model for Wet Oxidation of Silicon Germanium Alloys

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ABSTRACT

We propose a complete model for the oxidation of silicon-germanium. Our model is capable of predicting, as a function of time, the oxide thickness, the profile of the silicon in the underlying alloy, and the profile of germanium in the oxide. The parameters of the model vary with temperature, alloy composition and oxidizing ambient. The model shows excellent agreement with published results, with the model parameters following trends consistent with the physical phenomena hypothesized.

Keywords: SiGe, oxidation, modeling.

1 INTRODUCTION

There has been renewed interest [1, 2] in studying the kinetics of silicon germanium (SiGe) oxidation as SiGe finds increasing use in CMOS technology and integration issues become more important. SiGe oxidation produces a low quality oxide due to several factors: Ge is piled up between the oxide and the substrate [3], there is a high trap density ($\sim 10^{12}/cm^2eV$) at the oxidizing interface, and the fixed charge density is high ($\sim 10^{11}$-10^{12} cm^{-2}) [4]. To avoid these problems, the current practice in industry is to deposit a sacrificial layer of Si over the SiGe alloy and oxidize it instead [5]. There is a need for a physically-based model that accurately predicts the kinetics of SiGe oxidation and an understanding of how the SiGe oxide and interface quality may be improved. In this paper we focus on the kinetic model. However, this already gives some indication of how the issue of oxide quality may be approached.

Despite the numerous attempts made to model the oxidation process of SiGe [6-9], none of the existing models capture the full range of phenomena that occurs during the oxidation of SiGe. We have developed a model [10] that would explain all the different aspects of the SiGe oxidation process. The model parameters depend on both temperature and the germanium fraction. Unfortunately, there are insufficient published data to quantitatively establish the relationship between the model parameters and the Ge fraction. In this paper, we focus in demonstrating the ability of the model to account for all the observed phenomena and we show that the dependence of the parameters on the Ge fraction fits with the underlying physical processes hypothesized. We leave to future studies the theoretical and experimental determination of the quantitative dependence of the model parameters on the Ge fraction. The model presented here predicts all the measurable quantities describing the oxidation process: the oxide thickness, the Si profile in the underlying SiGe layer, and the profile of GeO_2 fraction in the oxide. Section 2 summarizes the physical assumptions, development, and governing equations of the model. Section 3 discusses the model parameters, how these parameters relate to physical quantities, and expected trends in these parameters with respect to temperature and Ge fraction. Finally, we present simulation results compared to experimental measurements.

2 THE MODEL

For the purpose of mathematical modeling we take the initial condition to be a Si_yGe_{1-y} layer covered by a layer of oxide of very small thickness L_{ox}. The oxidation process can be modeled in terms of the fluxes of the oxidant towards the oxidizing interface and the fluxes of the reactions occurring at the oxidizing interface. As shown in figure 1, the fluxes involved in the mathematical model are:

1. F_1: flux of oxidant moving through the oxidizing gas towards the top surface;
2. F_2: flux of oxidant molecules diffusing through the oxide layer towards the oxidizing interface;
3. F_3: flux of oxidant molecules reacting with Si to form SiO_2;
4. F_4: flux of oxidant molecules reacting with Ge to form GeO_2; and
5. F_5: flux of Si atoms replacing Ge in the oxide.

Note that the first three fluxes are the conventional fluxes described by Deal and Grove [11] in their model for the oxidation of pure Si.

We can carry out a very similar analysis to that of the Deal-Grove model [11]. We will have to note that in this case:

$$F_3 = k_{Si} y_i C_i \tag{1}$$

and,

$$F_4 = k_{Ge}(1 - y_i) C_i \tag{2}$$

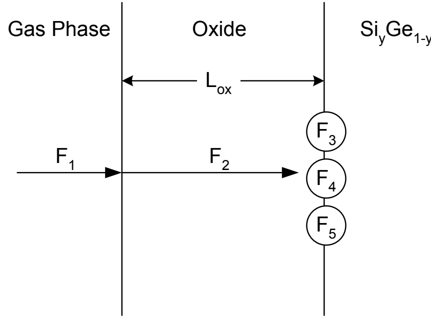

Figure 1: A schematic diagram showing all fluxes used in the model.

where y_i is the fraction of Si in the SiGe at the oxidizing interface, C_i is the concentration of oxidant molecules in the oxide at the oxidizing interface, k_{Si} and k_{Ge} are the Si & Ge oxidation rate constants respectively. Following this reasoning leads to (see [10] for details):

$$\frac{dL_{ox}}{dt} = \frac{F}{N_1} = \frac{(k_1 + k_2 y_i)C^* / N_1}{1 + (k_1 + k_2 y_i)/h + (k_1 + k_2 y_i)L_{ox} / D_{ox}} \quad (3)$$

where N_1 is the number of oxidant molecules incorporated into a unit volume of the oxide layer, C^* is the equilibrium concentration of the oxidant in the oxide, D_{ox} is the effective diffusion coefficient of the oxidant in the oxide, and L_{ox} is the oxide thickness.

To predict the profile of the Si in the SiGe layer we solve the diffusion equation:

$$\frac{\partial y}{\partial t} = D_{SiGe} \frac{\partial^2 y}{\partial z^2} \quad (4)$$

where y is the fraction of Si in the SiGe, z is depth into the substrate measured from the original position of the SiGe-oxide interface, and D_{SiGe} is the effective coefficient of Si-Ge interdiffusion.

To solve Eq. (9) for y, a boundary condition is needed at the oxidizing interface. As an approximation, we assume that the total number of atoms at the oxidizing interface is constant. When Si atoms are oxidized, the total number of atoms at the interface is decreased by the flux of silicon reacting with the oxidant. The oxidizing interface moves downwards and the oxidized silicon atoms are replaced with both Si and Ge atoms to keep the total number of atoms at the interface constant. Similar scenario happens for Ge atoms. The replacement reaction is another reaction occurring at the interface affecting the numbers of silicon and germanium atoms at the interface. The boundary condition on y has to account for the effect of each of the three fluxes F_3, F_4, and F_5:

$$D_{SiGe} \frac{d(yC_{Si})}{dz}\Big|_{\text{interface}} = F_3 + F_5 - F_4 \quad (5)$$

F_3 and F_4 are given by equations (1) and (2) respectively. The flux of Si replacing Ge in the oxide may be written as:

$$F_5 = k_3 \theta N y_i \quad (6)$$

where k_3 is the reaction rate constant of the replacement reaction and N is the molecular concentration of the oxide.

Using (1), (2), (5), and (6) we get:

$$\frac{dy}{dz}\Big|_{\text{interface}} = \frac{1}{D_{SiGe}}\left[\frac{((2k_1 + k_2)y_i - k_1)C^* / C_{Si}}{1 + (k_1 + k_2 y_i)/h + (k_1 + k_2 y_i)L_{ox} / D_{ox}} + \frac{k_3 \theta N y_i}{C_{Si}}\right] \quad (7)$$

Note that as the oxide grows, the oxidizing interface moves. The movement of the oxidizing interface into the SiGe substrate is due to the oxidation of SiGe layers. This movement is described by

$$z_{boundary} = \frac{N_{SiO_2}}{C_{Si}} L_{ox} \quad (8)$$

where $z_{boundary}$ is the distance by which the oxidizing interface boundary moved from its initial location given zero initial L_{ox}.

To complete our model of the oxidation process we need to solve for the profile of GeO_2 in the oxide. θ is the variable representing the fraction of GeO_2 in the oxide. The rate of change of the oxide thickness due to GeO_2 is given by the difference of the fraction of the rate of growth of the oxide layer due to the oxidation of Ge and the loss of GeO_2 in the replacement reaction. This can be expressed mathematically by:

$$\frac{d(\theta L_{ox})}{dt} = \frac{F_4 - F_5}{N_1} \quad (9)$$

Substituting from (2), (4), and (11) we get:

$$\frac{d(\theta L_{ox})}{dt} = \frac{k_1(1 - y_i)C^* / N_1}{1 + (k_1 + k_2 y_i)/h + (k_1 + k_2 y_i)L_{ox} / D_{ox}} - \frac{k_3 \theta N y_i}{N_1} \quad (10)$$

The complete model then consists of the system of equations (3), (5), and (10) subject to the boundary condition (7) and (8). The quantities C^*, D_{ox}, N_1, and N that appear in the equations are computed as weighted averages of the respective quantities in Si and Ge. The quantities k_1, k_2, k_3, and D_{SiGe} are effective rate constants. These parameters are all discussed in the next section. The independent variables are z (depth into the substrate measured from the initial SiGe-oxide interface) and t (time). The solution variables are L_{ox} (oxide thickness), $z_{boundary}$ (the position of the moving interface), θ (the fraction of Ge in the oxide), and y (the fraction of Si in the SiGe film). The first three are functions of time only, while

the last one is a function of time and depth into the substrate.

3 MODEL PARAMETERS

To be able to use the model in predicting the values of the solution variables, we need to understand the physical behavior of each of the parameters of the model. In this section, we investigate the dependence of the model parameters on the kinetic factors, and we estimate the behavior of the parameters that have no published data.

The simplest of these parameters are N and N_1, which are well known for both Si & Ge. N_{SiO_2} = 2.2x10^{22} cm^{-3}, N_{GeO_2} = 2.44x10^{22} cm^{-3}, N_{1SiO_2} = 4.4x10^{22} cm^{-3}, and N_{1GeO_2} = 4.87x10^{22} cm^{-3}. The values of the solid solubility and diffusivity for SiO_2 are given by: $C^*_{Si}=3\times10^{19}$cm^{-3}[11], $D_0=10^{-6}$cm^2/s and E=0.79eV [12]. For GeO_2, no values are reported for either the solid solubility or diffusivity of the oxidant in the oxide. A number of studies have indicated that we expect D_{oxGe} to be approximately the same and C^*_{Ge} to be significantly higher than that of Si [13, 14].

Si-Ge interdiffusion in the SiGe layer is modeled using an effective diffusivity, D_{SiGe}. To date there is little agreement on modeling the interdiffusion behavior as a function of composition and strain. For the purposes of this study we have chosen to model the diffusion behavior using a single effective coefficient of interdiffusion, which we expect to depend on the highest concentration of Ge in the SiGe layer, i.e. the initial Ge fraction.

Finally, we have three reaction rate constants; the rate constant of the oxidation reaction of Ge, k_1, the rate constant of the oxidation reaction of Si, k_1+k_2, and the rate constant of the replacement reaction, k_3. The reaction rate constants are expected to exhibit an Arrhenius dependence on temperature. However, the specific dependence of these reaction constants on composition has not been studied. The oxidation reaction rates for both Ge and Si are expected to depend on the Ge composition. Ge is known to have a catalytic effect on the Si oxidation reaction itself. This is evident from studies on the oxidation of Ge-implanted Si (e.g. [15]). Hence, the oxidation reaction rates are expected to increase significantly with the increase in Ge content. Finally, there have been no previous studies on the replacement by Si of Ge in GeO_2, but this parameter should not depend significantly on Ge fraction.

In summary, the three reaction rates and the Si-Ge interdiffusivity should be considered as free parameters in the model with some minimal idea available from the literature regarding reasonable values. For C^* and D_{ox}, the values for a pure SiO_2 are well-known. For GeO_2, D_{oxGe} is expected to be similar to the Si case and C^*_{Ge} is expected to be significantly higher. N and N_1 should be treated as well-known constants.

4 SIMULATION RESULTS AND DISCUSSION

We now examine the predictive strength of this model by considering in detail published data on wet oxidation. We consider three studies that provide data on oxidation using steam or wet oxygen [3, 13, 16]. These studies provide consistent results on the enhancement of SiGe oxidation rate compared with pure Si.

The experimental results used for our simulations are summarized as follows. Liu et al. [13] did steam oxidation for SiGe samples having 28% and 36% Ge at 700°C. The oxide obtained was a mixed oxide (SiO_2 + GeO_2). In both experiments, the percent of GeO_2 in the oxide was very similar to the percent of Ge in the original epi-layer and the oxide composition uniform throughout. No Ge-rich layer was obtained for Liu et al.'s experiments. Zhang et al. [16] used wet oxygen to oxidize a SiGe sample with 50% Ge at 1000°C. For the initial period of oxidation, Zhang et al. obtained a mixed oxide (SiO_2 + GeO_2.). After the first 10 minutes of oxidation, the oxide obtained was pure SiO_2. A Ge-rich layer did form but they did not report any details about the layer's thickness or Ge concentration. LeGoues et al. oxidized SiGe with 14% Ge in wet oxygen at 800°C, and obtained a pure SiO_2 with a Ge-rich layer between the oxide and substrate.

We carried out simulations for these three experiments. Our simulation results for the oxide thickness are in excellent agreement with the measurements as shown in figures 2-3. Not shown are the simulations of Ge fraction in the oxide for the experiments of Liu et al. and LeGoues et al. These were approximately constant for the entire film for the experiments with 28% and 36% Ge and were approximately zero for the entire film in the 14% Ge case. We have also not shown the oxidation rate simulation for the 14% case but the fit there was of similar qualities to the ones shown in figures 2-3.

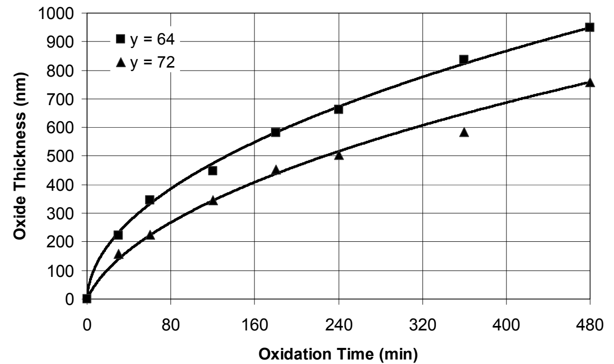

Figure 2: Simulation results compared to Liu's measurements [13].

Table 1 shows the values used for the rate constants involved in the model. As expected, the replacement reaction rate constant, k_3, is not to be affected by the Ge concentration in the alloy and is a function of temperature only. k_1 is a function of both temperature and Ge

concentration. k_1 increases dramatically as the Ge concentration in the substrate increases. Similarly, k_1+k_2 is a function of both temperature and Ge concentration as well. These variations in the model parameters with Ge concentration and with temperature are consistent with our expectations discussed in the previous section.

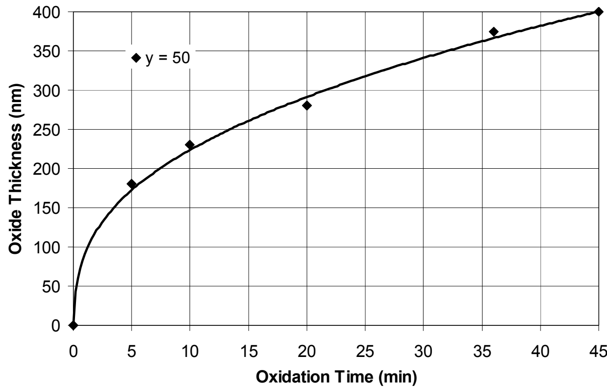

Figure 3**:** Simulation results compared to Zhang's measurements [16].

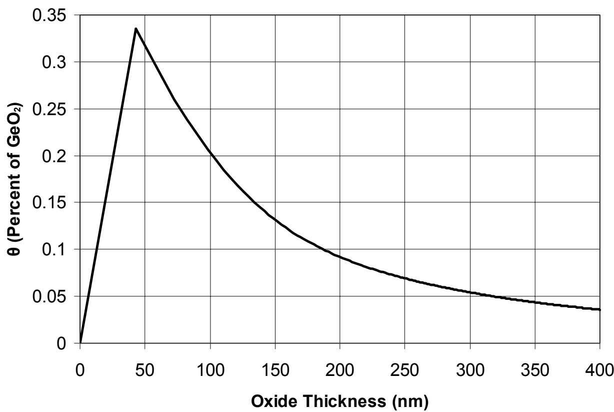

Figure 4: Percent of GeO_2 in the oxide versus the oxide thickness for the Zhang's [16] experiment.

Experiment	k_1 (nm/min)	k_1+k_2 (nm/min)	k_3 (nm/min)
T = 700°C 36% Ge [13]	3.1×10^4	3.1×10^4	2.5
T = 700°C 28% Ge [13]	4.4×10^3	4.54×10^3	2.5
T = 800°C 14% Ge [3]	42.49	9.77×10^3	87.1
T = 1000°C 50% Ge [16]	8.3×10^5	8.3×10^5	390

Table 1: Reaction rate constants used in simulations.

No Ge-rich layer was observed in Liu's experiments. In agreement with this results, the simulation results showed that the profile of Si remains constant after the oxidation. Zhang et al. and LeGoues et al. reported the formation of Ge-rich layers in their experiments. The simulation results were consistent with this observation.

Zhang did not report the percent of GeO_2 incorporated in the oxide but observed a mixed oxide layer for the first 10 minutes (the top 220 nm of oxide) followed by a pure SiO_2 layer. The simulation results agree with this (figure 4).

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