

Discovery of Activation Energy Enhancement during Initial Silicon-Oxide Growth and Its Physical Modeling for Accurate Process Simulation

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The dependance of surface reaction activation energy on silicon-dioxide film thickness has been studied for the first time, in the range of 10 - 200 Å. The discovery that activation energy increases around 30 Å of thickness is unveiled and discussed physically. In addition, a new oxidation model is proposed, including an initial-oxide growth region.

1. Introduction

For VLSI applications, there is a continuing effort to further reduce device dimensions. The thermal oxidation of silicon in the thin region (<100 Å) is of vital importance to VLSI device designers because thin layers of SiO₂ are exclusively used as the gate dielectrics for high performance MOS devices. In some of the first studies on the growth kinetics of SiO₂ in dry oxygen, it was observed that the oxidation rate in the early stages of SiO₂ growth is faster than described by the Deal-Grove equation¹⁾. The growth kinetics of these thin oxide films has been investigated and many models have been proposed. However, it can be seen that these models have a limited range of success and cannot be applied under all experimental conditions. Accordingly, we devised a new fundamental method, where we consider that the activation energy for surface

reactions, as a parameter, depends on the SiO₂ thickness. Using this method, we tried to estimate an elementary process of oxidation enhancement in the thin region and derived a new equation. In this paper, a new model is proposed to account for the growth of both thin and thick SiO₂ layers.

2. Proposed oxidation equation

Because the oxidation process is, in principle, surface reaction rate-limited in the thin region, any process that would result in enhancing the transport of oxidant through the oxide should have no effect on growth rate. Consequently, we describe the growth kinetics of these thin oxide films with an Arrhenius-type equation:

$$u(T,p;x) = u_0(p;x) \exp\left(\frac{-E_a(x)}{kT}\right), \quad (1)$$

where E_a is activation energy for surface reactions, u_0 is the constant that is independent of the temperature, T is the temperature, p

is the oxidant partial pressure, x is the oxidation thickness and k is the Boltzmann factor. Deal and Grove¹⁾ assumed that an activation energy for a surface reaction does not depend on the SiO_2 thickness. However, we suppose that oxidation enhancement is caused by the reduction of surface reaction activation energy. In Eq. (1), the activation energy, $E_a(x)$, and the constant, $u_0(p,x)$, are considered to be parameters that depend on the SiO_2 thickness. In addition, we can estimate the elementary process of oxidation enhancement by studying the dependence of activation energy on the SiO_2 thickness. Using Eq. (1), $E_a(x)$ and $u_0(p,x)$ are calculated from Massoud's²⁾ and the authors'³⁾ experimental results, and are illustrated respectively in Fig. 1 and Fig. 2. The universal parameter, $E_a(x)$, depends only on the SiO_2 thickness, and not on other oxidation conditions. To separate the two variables in $u_0(p,x)$, we assume that $u_0(p,x)$ is defined as $u_0 p^{0.8} f(x)$. This means that the oxidation rate in the thin region has a pressure dependence of $\sim p^{0.8}$ ²⁾, which is in agreement with the findings of a high pressure oxidation study in dry oxygen⁵⁾ where the linear rate constant, B/A , was found to have a $p^{0.7} \sim p^{0.8}$ pressure dependence. The $f(x)$ value calculated under the above assumption is illustrated in Fig. 3. It is also a universal parameter which depends only on the SiO_2 thickness and not on other oxidation conditions. Therefore, it is considered that the above assumption about pressure dependence is valid. Above all, two new equations can be

proposed. One, Eq. (2), can account for the oxidation enhancement in the thin region:

$$u(T,p;x) = \{u_{00}(1 \text{ atm})p^{0.8}\} f(x) \exp\left(\frac{-E_a(x)}{kT}\right), \quad (2)$$

where

$$u_{00}(1 \text{ atm}) = 1.29 \times 10^9 (\text{\AA}/\text{min}) \quad (2')$$

The other, Eq. (3), is an extended Deal-Grove equation which accounts for the growth of both the thin and thick SiO_2 layers:

$$\frac{dx}{dt} = \frac{1}{\frac{2x}{D} + \frac{1}{u(T,p;x)}}, \quad (3)$$

where

$$D = D_0 \exp(-E_b/kT), \quad (3')$$

$$u(T,p;x) = \{u_{00}(1 \text{ atm})p^{0.8}\} f(x) \exp\left(\frac{-E_a(x)}{kT}\right), \quad (3'')$$

t is the oxidation time, D is the diffusion constant of the oxidant and E_b is an activation energy for the diffusion.

3. Kinetics of oxidation enhancement

We consider the kinetics of the reduction of activation energy illustrated in Fig. 1 to be the analogous to the kinetics proposed by Cabrera and Mott^{3),4)}. This kinetics model is illustrated in Fig. 4. The electrons can pass through the oxide layer from silicon to the oxygen because of the tunnel effect. Some of the adsorbed oxygen is converted into ions, setting up an electric field across the oxide layer. This field reduces activation energy.

It has been found that the model of Cabrera and Mott cannot explain oxidation enhancement in the thin region⁶⁾. This is because the following factors. A growth rate of about 1 Å/min at 850°C requires 3×10^{12} cm⁻²/sec⁻¹ of oxidant flux. The same amount of electron flux from the silicon surface to the oxide is required to ionize the oxidant species negatively. The flux of the electrons due to the thermionic-emission is much lower than the oxidant flux required by the growth of thin SiO₂ layers. The tunneling effect cannot provide oxygen molecules with sufficient electrons at the oxide surface when the SiO₂ is thicker than 30 Å. However, as illustrated in Fig. 1, activation energy is reduced only when the SiO₂ is thinner than 30 Å. Consequently, we confirm that the model of Cabrera and Mott is valid to explain the reduction of activation energy, and also that the electrons are provided by the tunnel effect, not by the thermionic-emission.

In Fig. 1, a more interesting phenomenon, which has not been reported before, can be seen. Activation energy has a peak around 30 Å of silicon dioxide. This phenomenon cannot be explained by the models proposed before now. Nevertheless, although we cannot explain it explicitly, it is believed that the oxygen ions at the silicon surface contribute to activation energy enhancement around 30 Å of SiO₂.

4. Conclusion

It was found that $E_a(x)$ is a universal parameter, which depends only on the SiO₂ thickness and not on

other oxidation conditions, and that oxidation rate in the thin region has a pressure dependence of $\sim p^{0.8}$. Thus, a new equation which accounts for the growth of both thin and thick SiO₂ layers was derived. In addition, it was discovered that activation energy peaks around 30 Å of silicon dioxide. Moreover, this new model will be able to be applied to the growth kinetics of natural oxides.

Reference

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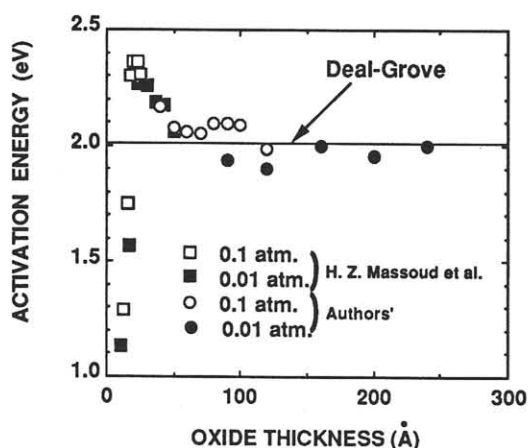


Fig. 1. $E_a(x)$ calculated from Massoud's²⁾ and authors'³⁾ experimental results using Eq. (1). $E_a(x)$ is a universal parameter, which depends only on SiO₂ thickness and not on other oxidation conditions.

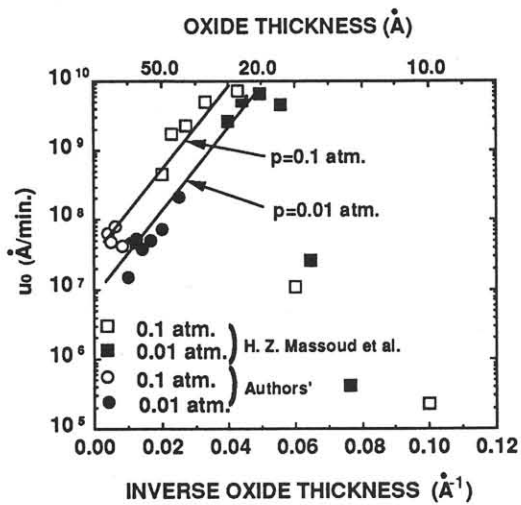


Fig. 2. $u_0(p, x)$ calculated from Massoud's²⁾ and authors'³⁾ experimental results using Eq. (1).

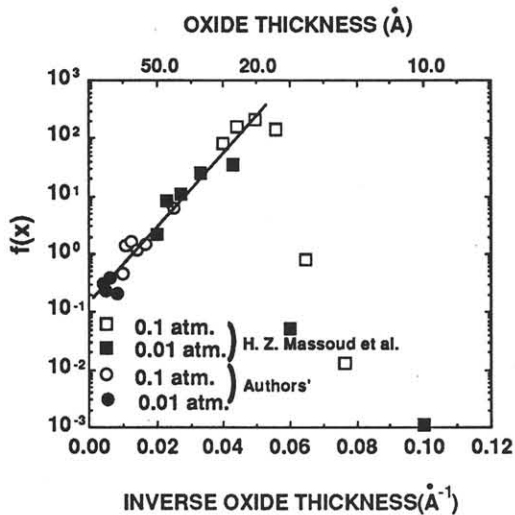


Fig. 3. $f(x)$ calculated from Massoud's²⁾ and authors'³⁾ experimental results using Eq. (2). $f(x)$ is a universal parameter, which depends only on SiO_2 thickness and not on other oxidation conditions.

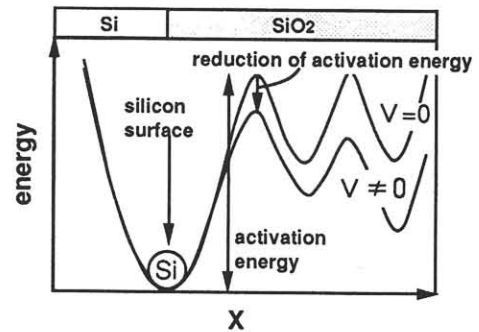
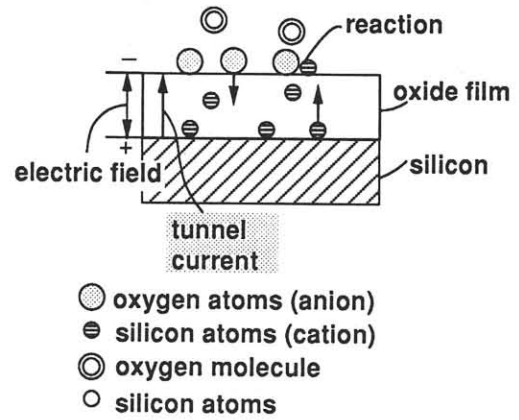


Fig. 4. Kinetics of the reduction of an activation energy illustrated in Fig. 1. This kinetics is analogous to the kinetics proposed by Cabrera and Mott^{3),4)}. The electrons pass through the oxide layer from silicon to the oxygen because of the tunnel effect. Some of the adsorbed oxygen is converted into ions, setting up an electric field across the oxide layer. This field reduces activation energy.