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A new kinetic model for thermal oxidation of Ge

Xu Wang, Tomonori Nishimura, Takeaki Yajima and Akira Toriumi

Department of Materials Engineering, The University of Tokyo
7-3-1 Hongo, Tokyo 113-8656, Japan
Phone & Fax: +81-3-5841-1907, e-mail: xuwang@adam.t.u-tokyo.ac.jp

Abstract

Oxidant diffusion behavior in GeO_2 during Ge oxidation was investigated by re-oxidation experiments of SiO_2/GeO_2 stacked oxide-layer. A new kinetic model which is different from the Deal-Grove mechanism is proposed for thermal oxidation of Ge.

1. Introduction

The oxidation is one of the most important processes in the semiconductor device fabrication. Si is well described by the Deal-Grove model [1]. Ge oxidation has so far been assumed to follow the Deal-Grove model [2], as the structure of GeO_2 is similar with that of SiO_2. However, different aspects between Si and Ge oxidations have been revealed thermodynamically and experimentally in recent years [3-7], and the oxidation kinetics is not clear. Thus, a kinetic model for Ge oxidation with direct experimental results is needed now.

In this paper, re-oxidation results of double-oxide-layer stacks are first reported to determine the diffusion behavior of oxidant species in GeO_2. And, the possible kinetics of Ge oxidation is next discussed.

2. Experiment Details

In the double layer stack experiment, three kinds of SiO_2/GeO_2 gate stacks were prepared, and the structure of each stack is shown in **Fig. 1**. All stacks were thermally treated in O_2 ambient at different temperaments, and the thickness of each oxide layer was estimated by the grazing incidence X-ray reflectivity (GIXR) measurement.

3. Results and Discussions

Fig. 1 (a) shows the increase of GeO_2 thickness with the oxidation time at 550ºC for various cap-SiO_2 thicknesses. The GeO_2 thickness increase depends on the SiO_2 thickness which limits the O_2 diffusion in SiO_2. This is consistent with the Deal-Grove model that O_2 molecule diffusion in SiO_2 is through the interstitial channels. Fig. 1 (b) shows no oxidation of Ge in GeO_2/SiO_2/Ge stacks, which implies that GeO_2/Ge interface reaction is needed for Ge oxidation. This interfacial reaction has been studied from the GeO desorption viewpoint in vacuum condition [8], which suggests that Ge can be oxidized by GeO_2 in a thermal treatment even without oxygen being present, and large amounts of oxygen vacancies (Vo's) are generated. It is thus probable to assume that oxygen vacancies may be involved in the thermal oxidation of Ge. In GeO_2/SiO_2/Si stacks re-oxidation experiment as shown in Fig 1 (c), no oxidation of Si occurred, implying few O_2 diffusion in GeO_2. These results further suggest that just oxygen interstitial diffusion is not the case for Ge oxidation, and V_O is needed for oxygen diffusion in Ge oxidation.

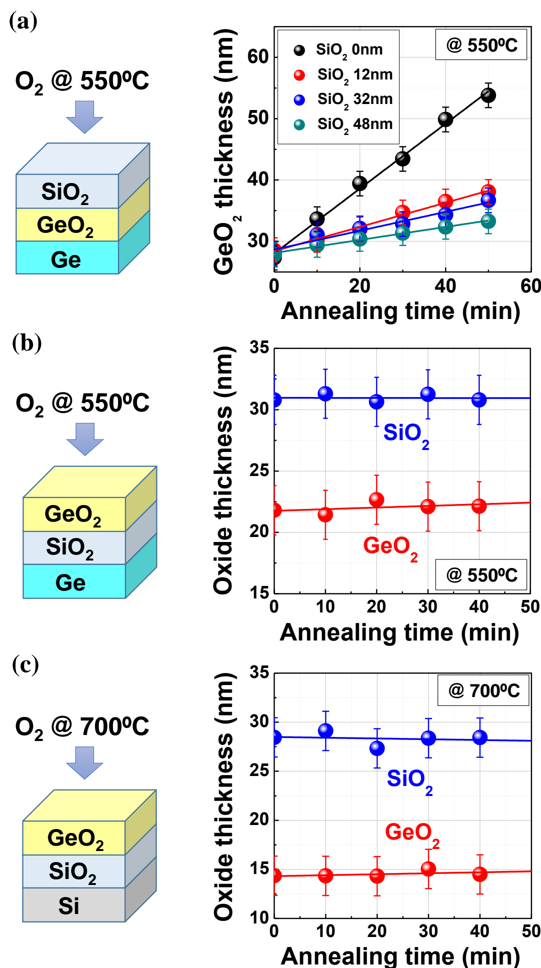
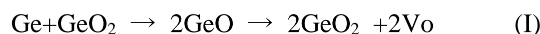


Fig. 1 Schematics of the three kinds of gate stack structures and the thickness change of oxide layers in each gate stacks during the re-oxidation process.

Based on the results so far obtained, Ge oxidation model can be discussed by considering two kinds of diffusion steps for oxygen diffusion in Ge oxidation, which is schematically illustrated in **Fig. 2 (a)** and **(b)**. In the O rich region near the oxide surface, interstitial O_2 diffusion is dominant. At a point ξ (the hypothetical boundary between O-sufficient and O-deficient region), the O_2 decomposes into two O atoms. These fluxes can be expressed as,

$$F_1 = h(C^* - C_{Os}) = D_1 \frac{C_{Os} - C_{O\xi}}{x - \xi} = k_\xi C_{O\xi} \quad (1)$$

From ξ, O atoms diffuse towards the deeper inside by exchanging with neighboring oxygen vacancies, or via vacancy diffusion from the interface, which come from the interfacial reaction,



$$\text{Ge} + \text{GeO}_2 \rightarrow 2\text{GeO} \rightarrow 2\text{GeO}_2 + 2\text{Vo} \quad \text{(I)}$$

The diffusion and reaction fluxes can be written as,

$$F_2 = D_2 \frac{\sqrt{k_\xi C_{O\xi}} - C_{Oi}}{\xi} = k_i C_{Oi} \quad (2)$$

Since it is reported that the diffusivity of Ge is much lower than that of oxygen in GeO_2 [9], Ge diffusion may be ignored in the first order approximation. Under a steady state condition, all fluxes should be maintained as follows,

$$2F_1 = F_2 = F \quad (3)$$

From Eq. (1) to (3), the reaction point ξ can be written as,

$$\xi = \frac{D_2 C_{Oi}\left(\sqrt{\frac{k_i}{2C_{Oi}}} - 1\right)\left(1 + \frac{k_\xi}{h} + \frac{k_\xi}{D_1}x\right)}{2k_\xi C^* + \frac{k_\xi D_2 C_{Oi}}{D_1}\left(\sqrt{\frac{k_i}{2C_{Oi}}} - 1\right)} \quad (4)$$

Note that it is proportional to the oxide thickness. Furthermore, it is determined by the diffusion and reaction of oxygen and V_O. If N is the number of oxidant incorporated into a unit volume of the oxide layer, the oxidation rate can be described by the differential equation $dx/dt=F/N$. By combining the above equations, two extreme cases corresponding to GeO_2 thickness can be solved like the Deal-Grove model. For $t \gg \tau$, it follows the parabolic law.

$$x^2 \cong Bt = \frac{2}{N}\left[2D_1 C^* + D_2 C_{Oi}\left(\sqrt{\frac{k_i}{2C_{Oi}}} - 1\right)\right]t \quad (5)$$

In this case, the oxidation is dominantly limited by the diffusion processes of both oxygen and V_O. On the other hand, when $t \ll \tau$, a linear law can be obtained by,

$$x \cong \frac{B}{A}(t+\tau) = \frac{2C^* + C_{Oi}\left(\sqrt{\frac{k_i}{2C_{Oi}}} - 1\right)\frac{D_2}{D_1}}{N\left(\frac{1}{h} + \frac{1}{k_\xi}\right)}(t+\tau) \quad (6)$$

In this thin oxide limiting case, ξ is approaching to 0. The ratio D_2/D_1 is also approaching to 0 and thus the two diffusion steps may be ignored in this approximation. Therefore, for short time it is dominantly a reaction controlled process.

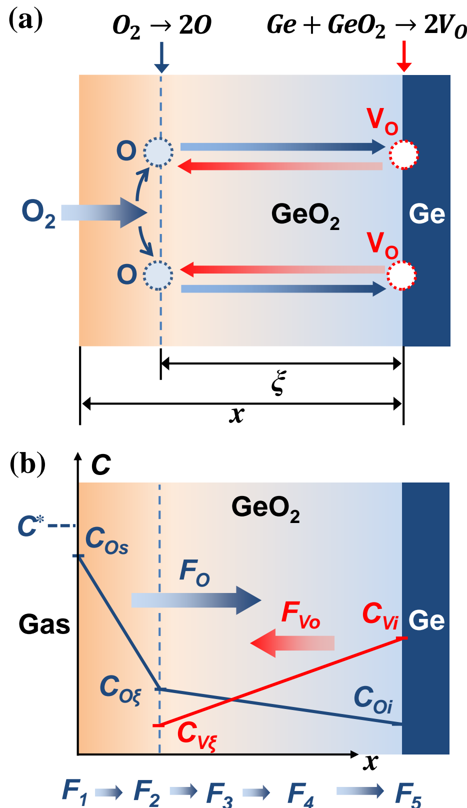


Fig. 2 (a) Schematics of Ge oxidation model. (b) Schematic concentration gradient of both oxygen and V_O in Ge oxidation process.

Fig. 3 shows the oxide thickness as a function of time and temperature for thermal oxidation of Ge in dry O_2. At all temperatures, the linear-parabolic relationship is in agreement with our model.

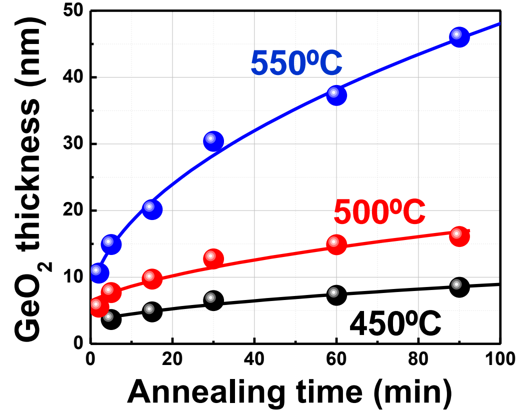


Fig. 3 GeO_2 thickness as a function of time and temperature for dry thermal oxidation of Ge. Solid lines indicate fitting by liner-parabolic law.

Although the exact position of ξ where the cracking from O_2 molecule to O atom occurs cannot be clarified so far, it should be near the surface if the relatively high migration barrier for O_2 interstitial state exists in GeO_2 [7]. Therefore, we can assume the limiting case that ξ approaches to x, and all fluxes should be changed as follows,

$$F = 2h(C^* - C_{Os}) = 2k_x C_{Ox} = D_2\frac{\sqrt{k_x C_{Ox}} - C_{Oi}}{x} = k_i C_{Oi} \quad (7)$$

To solve the above equations, a parabolic law can be obtained. This approximation is consistent with the thick oxide case, implying that O atoms diffusion by exchange with vacancies is dominant in thick oxide. It is worthwhile to mention that all diffusion species are assumed neutral in this study. Possible ionic species diffusion should be taken into consideration for further modification.

4. Conclusion

We have proposed a new kinetic model for thermal oxidation of Ge, by considering two kinds of oxidant diffusion processes. The oxygen vacancy facilitates the O diffusion in Ge oxidation, and Ge is oxidized by GeO_2 at GeO_2/Ge interface. This should be taken into consideration for modeling the Ge gate stack formation and achieving well controlled gate stacks on Ge.

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