Thermal oxidation kinetics of Ge under high pressure O₂

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Abstract

O₂ pressure $(p-O_2)$ dependence of thermal oxidation of Ge is investigated by isotope tracer experiments for the first time. Thermal oxidation of Ge is described by both O-vacancy and O interstitial diffusion under high p-O₂. This can explain anomalous p-O₂ dependence of the Ge oxidation rate in high p-O₂, and better performance of GeO₂/Ge gate stacks formed by high p-O₂.

1. Introduction

The control of the thermal oxidation is one of the most important processes in semiconductor device fabrication. For Si, thermal oxidation can be well described by the Deal-Grove model [1]. However, Ge oxidation kinetics has been proved to be a non Deal-Grove type experimentally [2, 3]. A kinetic model based on oxygen vacancy (V₀) diffusion can well describe relatively thick Ge oxidation at atmospheric pressure [3], but it cannot explain anomalous oxidation rate under high p-O₂[4]. Therefore, a further investigation about Ge oxidation kinetics under high p-O₂ is needed.

In this paper, we focus on the Ge oxidation under high p-O₂ by using ¹⁸O₂ tracer for the first time. Both oxygen vacancy (V_o) and atomic O interstitial (O_i) diffusion are considered in Ge oxidation process under high p-O₂.

2. Experiments

P-type Ge(100) wafers were thermally oxidized in wide ranges of temperatures (T) and p-O₂ after chemical cleaning. The GeO₂ thickness was determined by the grazing incidence X-ray reflectivity (GIXR) measurement.

In isotope tracer experiments, two kinds of samples were prepared. For the sample A, Ge wafer was first oxidized in ${}^{16}O_2$ at 520°C to form 85-nm-thick GeO₂. Then, it was reoxidized in ${}^{18}O_2$ at 520°C for 50 min, and the total oxide thickness was 101 nm. *p*-O₂ was fixed at 1 atm in both oxidations steps (APO+APO). Finally, 30-nm-thick Ge¹⁶O₂ was deposited on the top of the stack by radio-frequency (rf) sputtering to minimize the surface effect in SIMS measurement. The same two-oxidation steps at 520°C was performed to prepare the sample B by increasing *p*-O₂ to 40 atm (at 300K) (HPO+HPO). 89-nm-thick GeO₂ was initially formed, and then 93-nm-thick GeO₂ was stotally formed after second oxidation. 30-nm-thick Ge¹⁶O₂ was also deposited on the top of the stack. The depth profile of ¹⁸O and ¹⁶O in both stacks were analyzed by the SIMS.

In double oxide layer stacks annealing experiments, both SiO₂/Ge and GeO₂/SiO₂/Ge stacks were prepared as shown in **Fig. 4(a)**. All oxide layers were deposited by sputtering followed by post-deposition annealing (PDA) in N₂ at 550°C. Then these stacks were annealed in 1-atm O₂ ambient at 550°C, and GeO₂ layer generated at Ge/SiO₂ interface was estimated by the grazing incidence X-ray reflectivity (GIXR) measurement after removing only the top GeO₂ layer.

3. Results and Discussions

Fig. 1 shows GeO_2 thickness versus $p-O_2$ relationship in wide ranges of oxidation temperatures, where the oxidation

time was fixed at 30 min. A reverse p-O₂ dependence of the oxidation rate was observed over atmospheric pressure at all temperatures. p-O₂ corresponding to the fastest oxidation rate at higher temperature shifts to higher p-O₂ (from 0.1 atm at 480°C to 5 atm at 580°C). This anomalous oxidation rate under high p-O₂ has never been observed in Si.



Fig. 1 GeO₂ thickness vs p-O₂ in a wide range of temperatures, where oxidation time is fixed at 30 min. A reverse p-O₂ dependence of the oxidation rate can be observed over atmospheric pressure at all temperatures

The isotope tracer experiments were carried out. In the sample A (shown in **Fig. 2**), the distribution of ¹⁸O is gradually decreasing from the surface without any accumulation at GeO₂/Ge interface. It can be well explained by the V_O diffusion model at 1 atm *p*-O₂. However, in the sample B, the accumulation of ¹⁸O at the interface is clearly observed in **Fig. 3**, which shows a long tail towards the oxide. It indicates that some diffusion species may directly transport to the interface. There are two possible diffusion species: molecular O₂ interstitial and atomic O interstitial (O_i).



Fig. 2 (a) Schematics of $Ge^{16}O_2/Ge$ oxidized in ${}^{18}O_2$ at 520°C under 1 atm (APO). (b) SIMS profile of GeO₂/Ge. No accumulation of ${}^{18}O$ is observed at GeO₂/Ge interface.



Fig. 3 (a) Schematics of $Ge^{16}O_2/Ge$ oxidized in ${}^{18}O_2$ at 520°C under 40atm (HPO). (b) SIMS profile of GeO_2/Ge . Accumulation of ${}^{18}O$ with a long tail is observed at interface.

We first consider the molecular O₂ diffusion like that in the Deal-Grove model. To prove whether it is right, double oxide layer stacks annealing experiments were carried out as shown in **Fig. 4**. As the relatively high diffusion energy of V_0 and O_i in $\tilde{Si}O_2$ (V_0 is 5.48eV and O_i is 2.79eV) [5], O_2 diffusion (diffusion energy is 1.40eV) is more favored in SiO_2 [5]. Thus, only O_2 can diffuse through the oxide layers in both stacks, and reacts with Ge wafer to form the GeO₂ interfacial layer at Ge/SiO2 interface. Therefore, the growing rate of GeO_2 interlayer reflects the diffusion of O_2 in the oxide layers in two stacks. In Fig. 4(b), the growing rate of GeO₂ interlayer in SiO₂/Ge is much faster than that in GeO₂/SiO₂/Ge stacks, indicating that molecular O₂ interstitial diffusion in GeO₂ layer should be quite limited. Therefore, atomic O interstitials are more possible diffusion species in Ge oxidation process in HPO case [5].



Fig. 4 (a) Schematics of SiO₂/Ge and GeO₂/SiO₂/Ge stacks structure. (b) Thickness change of the GeO₂ interfacial layer at Ge/SiO₂ interface in two stacks after annealing in O₂ at 550° C.

Based on the results, Ge oxidation model can be discussed by considering two major diffusion processes, which is schematically illustrated in **Fig. 5**. Since O₂ diffusion is limited, near the surface (point ξ) it decomposes into O atoms. From ξ , O atoms diffuse towards the deeper inside in two ways: exchanging with neighboring oxygen vacancies, which come from the interfacial reaction, and O interstitial diffusion.



Fig. 5 Schematics of Ge oxidation model in APO and HPO. Both O-vacancy and O interstitial diffusion are considered in Ge oxidation, which are determined by p-O₂.

In APO, large amounts of V₀ can be formed at the interface. V₀ diffusion is dominant in Ge oxidation process, and GeO desorption at the oxide surface occurs. However, V₀ formed at the Ge/GeO₂ interface is considerably suppressed in HPO, which has been already clarified by the thermodynamic calculation of GeO₂, GeO(g) and O₂(g) system [6]. Therefore, V₀ diffusion flux is highly reduced. However, since more oxygen are dissolved in the oxide, the O_i diffusion becomes enhanced in HPO, resulting in an ¹⁸O interfacial peak in **Fig. 3(b)**. Since the results in Fig. 3 suggests that O_i contribution to the total Ge oxidation is limited, it is reasonable that the oxidation rate is lowered in HPO. This is the possible reason of the reverse *p*-O₂ dependence of the oxidation rate observed over atmospheric pressure in **Fig. 1**.

This model is helpful to explain why HPO is an effective way to achieve high performance of GeO₂/Ge gate stacks. The V_O formation at the interface is the origin of deterioration in Ge/GeO₂ gate stack [7], and it is limited under high oxygen pressure. Meanwhile, O_i diffusion directly to the interface can terminate the dangling bonds at Ge/GeO₂ interface even if it is not a large amount, which is effective to achieve a high-quality Ge/GeO₂ interface in HPO.

4. Conclusion

The p-O₂ dependence of the Ge oxidation rate is well explained by considering both O-vacancy and O interstitial diffusion. In HPO, V_O formation is suppressed, and O_i diffusion passivates dangling bonds at the interface. It can provide us a strong guideline for achieving high-quality Ge gate stacks.

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