

Layer-by-Layer GeO₂ Formation in the Self-Limited Oxidation Regime of Ge

Choong Hyun Lee, Tomonori Nishimura, Toshiyuki Tabata, Kosuke Nagashio, and Akira Toriumi

Department of Materials Engineering, The University of Tokyo
JST-CREST

7-3-1 Hongo, Tokyo 113-8656, Japan

Phone: +81-3-5841-1907 E-mail: lee@adam.t.u-tokyo.ac.jp

Abstract

The Ge oxidation process is discussed from the viewpoints of the O₂ pressure dependence of oxidation and Ge/GeO₂ interfacial roughness formation in wide ranges of temperature and P_{O_2} . The atomic-scale roughness is formed by conventional oxidation, while the low-temperature and high-pressure oxidation (HPO) enable to achieve atomically flat interface.

1. Introduction

The progress of GeO₂-based MOS technology has reawakened the interest in all Ge CMOS beyond Si, and the key technology is how to form the superior Ge/GeO₂ interface. Recently we reported that the oxidation rate of Ge is reduced as the oxygen pressure (P_{O_2}) increases below 520°C, which has never been observed in Si [1]. Although we have suggested intuitively that the oxidant diffusion in GeO₂ film was suppressed by GeO₂ densification, a detailed mechanism of oxidation kinetics has not been clarified yet.

In this paper, we report the Ge oxidation properties from the viewpoints of the interfacial roughness at the Ge/GeO₂ interface as well as P_{O_2} dependence of the oxidation rate. The atomically flat Ge/GeO₂ interface can be achieved by controlling the oxidation kinetics. Finally, the possible oxidation kinetics in Ge is discussed.

2. Experimental Details

p-type Ge(100) and (111) wafers with resistivity of 0.5 Ω cm were used in this study. High-pressure oxidation (HPO) was carried out in a specialized furnace in wide ranges of temperatures and P_{O_2} . Note that P_{O_2} in this work is defined at room temperature before increasing the furnace temperature, and that actual P_{O_2} in the furnace during the oxidation should be higher than the P_{O_2} . The thickness of GeO₂ film was accurately determined by combined measurements of grazing incidence X-ray reflectivity with spectroscopic ellipsometry. The Ge/GeO₂ interface roughness was measured by AFM after etching of GeO₂ film by dilute HF.

3. Results and Discussion

To clearly see the anomalous behavior of thermal oxidation in Ge, the oxidation rate versus P_{O_2} relationship is shown in Fig. 1. The most striking feature of the oxidation process in Ge is that the oxidation rate is reduced as P_{O_2} increases below 520°C. Although the P_{O_2} dependent diffusivity of oxygen in GeO₂ due to GeO₂ densification was suggested for the reduction of oxidation rate [1], it is needed to employ an increase of activation energy (several eV). To better understand the thermal oxidation of Ge, the reaction kinetics of oxidation process at the Ge/GeO₂ interface should be considered. Since it is considered that the atomistic morphology alteration at the Ge/GeO₂ interface during thermal oxidation provides information on oxidation kinetics, we prepared the atomically flat Ge(111) surface by H₂

annealing [2]. The large step and terrace structure was clearly observed on Ge(111) surface, as shown in Fig. 2(a). The RMS roughness on the Ge terrace measured in 0.3x0.3 μm² area was very small (0.06 nm~the resolution limit). The step and terrace structure was maintained at the level of initial surface after oxidation in 70 atm P_{O_2} at 500°C, as shown in Fig. 2(b) in spite of 5 nm-thick GeO₂ formation. Note that the step and terrace was confirmed on both GeO₂ and Ge surface after oxidation. The RMS roughness on Ge terrace as a function of oxidation temperature is summarized in Fig. 2(c), where the thickness of GeO₂ is about 5 nm. In case of HPO (70 atm P_{O_2}), the atomically flat Ge surface can be preserved until 500°C, while conventional thermal oxidation shows an increase of the roughness on Ge terrace as oxidation temperature increases, resulting in disappearance of step and terrace structure after oxidation above 450°C. It indicates that Ge/GeO₂ interface roughness is induced by oxidation process, and a layer-by-layer oxidation on Ge occurs by HPO as high as 500°C.

We also investigated how oxidation process changes the Ge/GeO₂ interface roughness. Fig. 3(a) shows the RMS roughness as a function of P_{O_2} , where the thickness of GeO₂ is about 5 nm. It is interesting to see that HPO at 500°C improves the interface roughness, while HPO at 550°C roughs the surface compared to the initial one. We characterized the roughness of AFM images by constructing a histogram and calculating the standard deviation of the distribution. Histograms of the corresponding height distribution over 10x10 μm² area of the Ge surfaces are presented in Fig. 3(b). It clearly shows that Ge surface oxidized by HPO at 500°C exhibits a much smoother surface than initial one. Fig. 4 shows the oxidation rate as a function of temperature. It seems that the dominant oxidation mechanism is different from the low (below 450°C) to high temperatures (above 500°C). Note that there is no significant change of oxidation rate from 400 to 450°C regardless of P_{O_2} . However, we observed the dramatic changes in oxidation rate at 500°C, where the reverse P_{O_2} dependence of oxidation rate occurs.

The results in Figs. 2, 3 and 4 are quite exciting and informative for understanding the Ge oxidation kinetics. A schematic of Ge thermal oxidation is shown in Fig. 5. We assumed that the initial oxidation occurs with the formation of small GeO₂ islands on uppermost layer same as Si oxidation, as shown in Fig. 5(a) [3,4]. Although the strain is accumulated on the top surface after increase of small GeO₂ islands, it is reported by the first-principles calculation that Ge atom is not emitted from substrate to GeO₂ unlike Si oxidation [5]. In addition, HPO can suppress the V_o formation during oxidation [6], resulting that there is no freedom of oxidation and the oxidation proceeds with extremely low oxidation rate without stress relaxation because of no GeO desorption and no viscous flow. Therefore, we can observe the layer-by-layer oxidation, as shown in Fig. 2. It

indicates that low-temperature HPO is limited by surface reaction and atomically flat surface can be achieved, as shown in Fig. 5(b). In fact, high-temperature and/or low P_{O_2} oxidation cause viscous flow of GeO_2 and V_o formation at the Ge/ GeO_2 interface, respectively. This process will break the Ge-Ge back-bond and enhance the oxidation with defective GeO_2 growth, resulting in an increase of interface roughness as shown in Fig. 5(c). Here we should mention that oxidation-induced stress at the Ge/ GeO_2 interface has not been so far detected by the depth resolution of Raman spectroscopy (He-Cd) in Ge (now still under investigation). Finally, it should be emphasized that the intrinsic difference of oxidation kinetics in Ge and Si is attributed to the high flexibility of Ge-O-Ge bond as understood in V_o formation and no Ge atom emission.

4. Conclusion

We investigated the oxidation kinetics of Ge based on interfacial roughness formation and P_{O_2} dependence of oxidation during thermal oxidation. It was found that surface roughness was formed by conventional oxidation, while HPO provided atomically flat Ge surface. The layer-by-layer oxidation was confirmed at low temperature HPO and the mechanism of reverse P_{O_2} dependence of oxidation rate was discussed. This understanding will be the key to high mobility Ge MOSFETs with sub-nm EOT.

References

[1] C. H. Lee *et al.*, *APEX*, **5**, 114001, 2012. [2] T. Nishimura *et al.*, *APEX*, **5**, 121301, 2012. [3] H. Watanabe *et al.*, *PRL*, **80**, 345, 1998. [4] K. Shiraishi *et al.*, *JJAP*, **39**, 1263, 2000. [5] S. Saito *et al.*, *APL*, **95**, 011908, 2009. [6] S. K. Wang *et al.*, *JAP*, **08**, 054104, 2010.

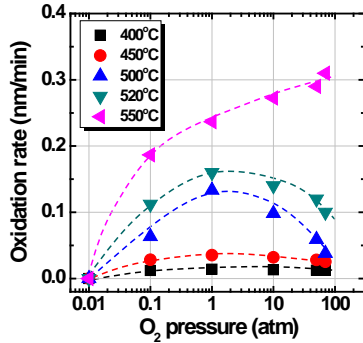


Fig. 1 Relationship of oxidation rate vs P_{O_2} in Ge, where oxidation rate was estimated in parabolic regime. The oxidation rate is reduced as P_{O_2} increases below 520°C within our experimental range.

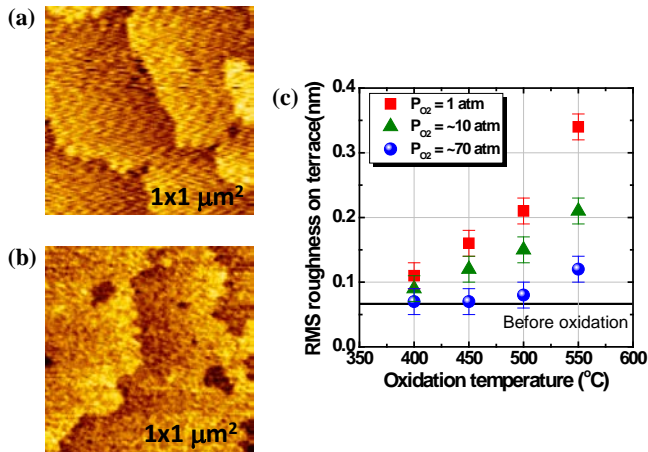


Fig. 2 (a) AFM image of atomically flat Ge(111) surface prepared by H_2 annealing at 650°C for 10 min. (b) AFM image of Ge/ GeO_2 stack after HPO at 500°C with atomically flat Ge(111) surface. The large step and terrace structure is clearly remained. (c) RMS roughness on Ge terrace as a function of P_{O_2} , where GeO_2 thickness is about 5 nm. The atomically flat Ge surface can be preserved until 500°C with HPO.

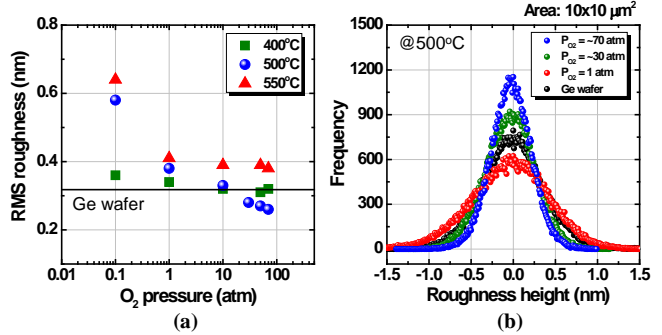


Fig. 3 (a) RMS roughness of Ge/ GeO_2 interface after thermal oxidation. Low-temperature oxidation is better in terms of surface roughness, indicating a different oxidation mechanism. (b) Histogram of surface roughness oxidized at 500°C. It is found that roughness is improved as P_{O_2} increases.

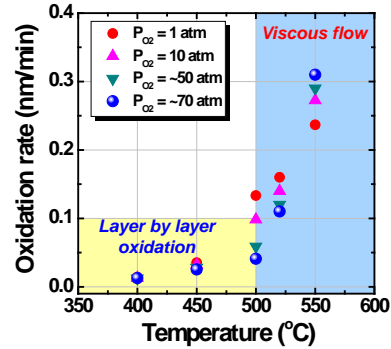


Fig. 4 Oxidation rate as a function of oxidation temperature. The dominant oxidation mechanism seems to be different from low-temperature to high-temperature in terms of oxidation rate. In HPO, layer-by-layer oxidation occurs with extremely low oxidation rate below 500°C. It is expected that GeO_2 grows with stress relaxation, because the viscous flow of GeO_2 occurs above 500°C.

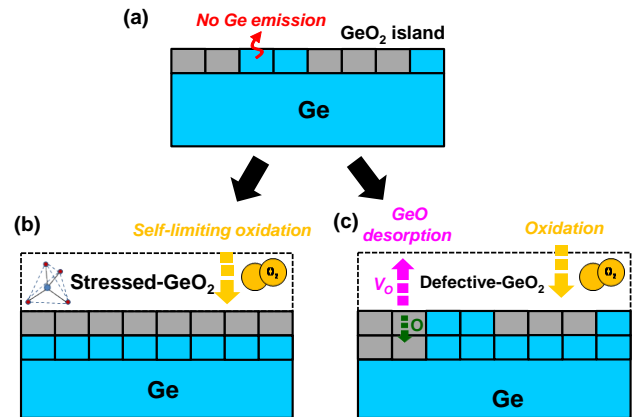


Fig. 5 Schematics of Ge thermal oxidation. (a) Initial oxidation with formation of small GeO_2 islands on uppermost layer. Although the stress is accumulated on neighboring Ge atom, Ge is not emitted to GeO_2 due to no energy advantage of emission. (b) Oxidation under low-temperature HPO. Since HPO can suppress V_o formation during oxidation, there is no freedom of oxidation and oxidation proceeds very slowly without breaking Ge-Ge back bonds. (c) Oxidation with high temperature and/or low P_{O_2} . The break of Ge-Ge back-bond is expected due to V_o formation, resulting in enhancement of oxidation and interface roughness.