ゲルマニウムの高圧熱酸化機構に関する研究

Thermal oxidation kinetics of Ge under high O_2 pressure

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1. Introduction

The control of the thermal oxidation is one of the most important processes in semiconductor device fabrication. Si oxidation is well described by the Deal-Grove model [1]. However, Ge oxidation kinetics has been proved to be different from Si experimentally [2, 3]. We have proposed a possible kinetic model based on oxygen vacancy (V_O) to describe relatively thick Ge oxidation at atmospheric pressure [3]. It is however, not clear in terms of anomalous oxidation rate under high p-O_2 [4].

In this paper, $^{18}O_2$ tracer is used to study Ge oxidation under high p-O_2 for the first time. Both oxygen vacancy and atomic O interstitial (O_i) diffusion are considered in Ge oxidation under high p-O_2.

2. Experiment

P-type Ge(100) wafers were thermally oxidized in wide ranges of temperatures (T) and p-O_2. The GeO_2 thickness was determined by the grazing incidence X-ray reflectivity (GIXR) measurement.

In isotope tracer experiments, Ge wafer was first oxidized in $^{16}O_2$ at 520ºC to form 89-nm-thick GeO_2. Then, it was re-oxidized in $^{18}O_2$ at 520ºC for 50 min, and the total oxide thickness was 93 nm. p-O_2 was fixed at 40 atm in both oxidations steps (HPO+HPO). Finally, 30-nm-thick $Ge^{16}O_2$ was deposited on the top by radio-frequency (rf) sputtering to minimize the surface effect in SIMS measurement. The depth profiles were analyzed by the SIMS.

3. Results and discussions

Fig. 1 shows an inverse p-O_2 dependence of the Ge oxidation rate over atmospheric pressure at all temperatures (oxidation time was fixed at 30 min.), which has never been observed in Si. **Fig. 2** shows the SIMS profiles of sample by HPO+HPO. An accumulation of ^{18}O at the interface indicates that some diffusion species may directly transport to the interface. Molecular O_2 interstitial and atomic O interstitial (O_i) are both considered. Since O_2 diffusion in GeO_2 is suggested much limited [5], O_i is more possible diffusion species in Ge oxidation process in HPO case.

We propose a possible model for the Ge oxidation by considering both V_O generation at the interface and O_i diffusion from oxide surface (**Fig. 3**). In APO, V_O diffusion is dominant with GeO desorption at the oxide surface. However, V_O formation is considerably suppressed in HPO, which has been clarified by thermodynamic calculation [6]. Thus O_i diffusion becomes important in HPO, resulting in an ^{18}O interfacial peak in **Fig. 2**. Considering that O_i contribution to the total Ge oxidation is limited, it is reasonable that the oxidation rate is lowered in HPO. This model can well explain why HPO is a good method to achieve high performance of GeO_2/Ge gate stacks [4]. High p-O_2 can improve the oxide quality by suppressing the formation of V_O, meanwhile O_i diffusion can terminate the interfacial dangling bonds to achieve a high quality Ge/GeO_2 interface.

4. Conclusions

The p-O_2 dependence of the Ge oxidation rate is well explained by considering both V_O and O_i diffusion. In HPO, V_O formation is suppressed, and O_i diffusion passivates dangling bonds at the interface.

Reference

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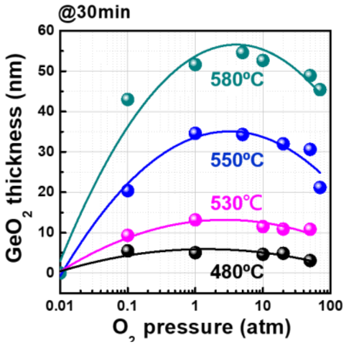

Fig. 1 GeO_2 thickness vs p-O_2 in a wide range of temperatures.

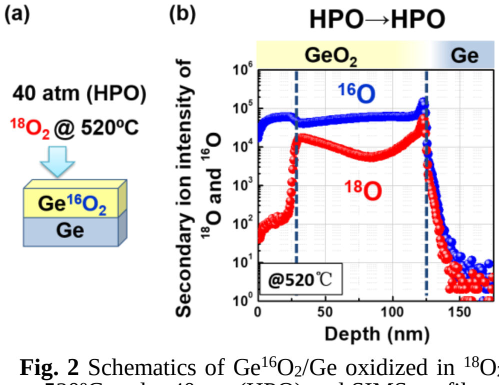

Fig. 2 Schematics of $Ge^{16}O_2$/Ge oxidized in $^{18}O_2$ at 520ºC under 40atm (HPO) and SIMS profile of GeO_2/Ge.

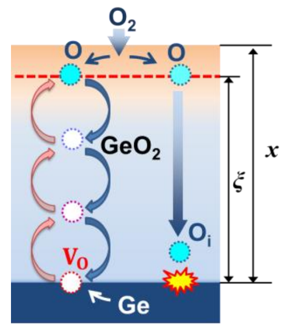

Fig. 3 Schematic of Ge oxidation model in HPO.