Advantage of High-pressure Oxidation for Ge/GeO₂ Stack Formation

Choong Hyun Lee¹, Tomonori Nishimura¹,², Toshiyuki Tabata¹, Shengkai Wang¹, Kosuke Nagashio¹,², Koji Kita¹,², and Akira Toriumi¹,²

¹Department of Materials Engineering, The University of Tokyo
²JST-CREST
7-3-1 Hongo, Tokyo 113-8656, Japan
Phone: +81-3-5841-1907 E-mail: lee@adam.t.u-tokyo.ac.jp

1. Introduction
Since Germanium (Ge) has more symmetric and higher carrier mobilities than Si, Ge MOS has been considered as one of the promising candidates for beyond Si. Recently, high electron mobility in Ge n-MOSFETs, which exceeds the Si universality, has been reported [1,2], and the key technology for high performance Ge MOS is how to effectively passivate the Ge/GeO₂ interface. On the basis of thermodynamics, we reported the validity of high-pressure oxidation (HPO) which could suppress the GeO desorption from Ge/GeO₂ interface [3]. Furthermore, the effectiveness of low temperature oxygen annealing (LOA) in Ge/GeO₂ stack was thermodynamically proposed in terms of self-passivation at the interface as well [4]. In this paper, we systematically investigate the post oxidation annealing (POA) under various annealing conditions and suggest the importance of POA for the interface stabilization.

2. Experimental Details
To fabricate Ge/GeO₂ MOSCAPs, HPO and atmospheric-pressure oxidation (APO) were carried out at 550°C for 15 min with 70atm-O₂ and 1atm-O₂, respectively, after chemically cleaning the Ge surface. Subsequently, POA was carried out at 400°C with various ambient (N₂, FGA, O₂) as a function of annealing time. Au and Al were deposited by the vacuum evaporation for the gate electrode and ohmic contact of MOSCAPs, respectively, and their capacitance-voltage (C-V) curves were measured.

The film density, refractive index, and thickness of GeO₂ were measured by grazing incident X-ray reflectivity (GIXR) and spectroscopic ellipsometry (SE).

3. Results and Discussion
Fig. 1(a) shows the impact of LOA on Ge/GeO₂ stack, where the hysteresis significantly decreases as the annealing time increases. Here, the hysteresis was estimated at flatband voltage (VFB) of C-V curves. However, it is clearly observed that both N₂ annealing and FGA are much less effective than LOA. This is well consistent with previous report that conventional hydrogen passivation technique is not effective for Ge dangling bonds termination [5]. The bi-directional C-V characteristics of Al/GeO₂/Ge MOSCAP are shown in Fig. 1(b), where LOA was carried out at 400°C for 60 min after APO. A very small hysteresis and frequency dispersion indicate that the superior Ge/GeO₂ interface can be achieved by APO+LOA, which is close to Ge/GeO₂ interface prepared by HPO [3].

Fig. 2(a) and (b) shows C-V curves measured at 100 K and the energy distribution of the interface states density (D₀), respectively. It is shown that the value of D₀ in Ge/GeO₂ MOSCAPS with APO+LOA is as low as 8×10¹⁰ eV⁻¹cm⁻² near the midgap and 3×10¹ⁱ eV⁻¹cm⁻² near the conduction band edge. Thus, it is concluded that LOA is very important for passivating the dangling bonds at Ge/GeO₂ interface.

In order to properly evaluate the role of HPO in Ge, Ge/GeO₂ gate stack was prepared by APO+LOA and HPO+LOA, respectively, where all of the steps of experiments were exactly same except for O₂ pressure during the oxidation. Fig. 3(a) shows the refractive index of the GeO₂ films determined at λ of 632.8 nm as a function of the oxidation condition. The bulk properties of GeO₂ are not changed by LOA in spite of dramatic improvement of C-V curves (see Fig. 1), which indicates that bulk properties are determined by HPO. The sub-bandgap photo-absorption also supports the difference of bulk properties between HPO- and APO-grown GeO₂ films, as shown in Fig. 3(b). The GeO₂ film density estimated by GIXR as a function of O₂ pressure is shown in Fig. 4(a). It clearly shows that GeO₂ film density increases with the increase of O₂ pressure. For comparison, the density of amorphous GeO₂ film [6] is also shown in Fig. 4(a), which is in good agreement with APO-grown GeO₂ film. Fig. 4(b) shows the etching rate of GeO₂ film by C₂H₅OH+H₂O solution. Obviously, HPO-grown GeO₂ film shows slower etching rate (~0.6 nm/min) than APO-grown one (~0.75 nm/min). From the results of bulk properties as shown in Fig. 3 and 4, it is concluded that HPO can provide higher quality GeO₂ than APO. In terms of the thermal process stability, we also compared the thickness reduction rate of GeO₂ on Ge prepared by HPO and APO, respectively, as shown in Fig. 5. The dotted lines are calculated ones by assuming that the GeO desorption rate obeys by the equation for the diffusion-limited process (dTox/dt = -αTox, where α = 1.9 and 2.5 for HPO and APO, respectively) [7]. Fig. 6(a) shows the hysteresis of C-V curves as a function of the air exposure time, where Ge/GeO₂ stack was exposed to the air before gate electrode formation. A clear difference of C-V degradation rate between HPO and APO against the air exposure is observed. In 5 days in the air after GeO₂ preparation, the desorbed H₂O was measured by the thermal desorption spectrometry (TDS) as shown in Fig. 6(b). It is revealed that APO-grown GeO₂ film has about 40% more H₂O molecules than HPO-grown one, which indicates HPO-grown GeO₂ has the stronger immunity to the air exposure as well as the thermal process stability. Fig. 7 shows schematics of HPO and APO with LOA. Dangling bonds at Ge/GeO₂ interface can be effectively passivated by LOA, while robust GeO₂ bulk properties are determined by HPO. Thus, it is concluded that the intrinsic difference between HPO- and APO-grown GeO₂ is primarily that of bulk properties of GeO₂. The combination of HPO with LOA, which can improve both GeO₂ bulk and Ge/GeO₂ interface, will be most suitable for Ge/GeO₂ stack formation.

4. Conclusion
The post oxidation annealing for Ge/GeO₂ stack has been systematically investigated, and it has been revealed that LOA is quite important for passivating Ge/GeO₂ interface, resulting in very low D₀. However, GeO₂ bulk properties are totally different between APO- and HPO-grown GeO₂ films in spite of dramatic improvement of C-V curves by LOA. This indicates that GeO₂ bulk properties are determined by HPO. It is also found that HPO has advantage.
over APO in terms of the thermal process stability and the robustness to the air exposure. The combination of HPO with LOA, which can control both GeO₂ bulk and Ge/GeO₂ interface, will be most suitable for Ge/GeO₂ stack formation.

Acknowledgements
This work was partly supported by a Grant-in-Aid from the MEXT of Japan and partly performed in collaboration with STARC.

References

Fig. 1 (a) Hysteresis as a function of annealing time, where post oxidation annealing was carried out 400°C under various ambient (b) Bi-directional C-V curves for Au/GeO₂/Ge MOSCAP measured at 300 K, where GeO₂ was grown by APO and LOA.

Fig. 2 (a) Bi-directional C-V curves measured at 100K. No hysteresis and frequency dispersion are observed. (b) Energy distribution of Dₓ estimated by low temperature conductance method. Dₓ is as low as 8x10¹⁰ eV⁻¹cm⁻² near the midgap.

Fig. 3 (a) Refractive index of the HPO- and APO-grown GeO₂ films with and without LOA. (b) Sub-bandgap photo absorption of GeO₂ films. In case of APO, a significant sub-bandgap is observed even after LOA.

Fig. 4 (a) The calculated GeO₂ film density by GIXR as a function of O₂ pressure. (b) Wet-etching rate of GeO₂ film by C₆H₅OH:H₂O solution. Obviously, HPO-grown GeO₂ shows slower etching rate.

Fig. 5 The thickness reduction of GeO₂ on Ge as a function of N₂ annealing time at 600°C, where GeO₂ was grown by HPO and APO, respectively. The dotted lines are calculated ones by assuming that the GeO desorption rate obeys by the equation for the diffusion-limited process [7], where α = 1.9 and 2.5 for HPO and APO, respectively.

Fig. 6 (a) Hysteresis as a function of air exposure, where Ge/GeO₂ stack was exposed to air before gate electrode formation. (b) TDS result of Ge/GeO₂ stack after air exposure in 5 days. APO-grown GeO₂ film has about 40% more H₂O molecules than HPO-grown one.

Fig. 7 Schematics of HPO and APO with LOA. Dangling bonds at Ge/GeO₂ interface can be effectively passivated by LOA, while robust GeO₂ bulk properties are determined by HPO. Thus, the combination of HPO with LOA will be most suitable for Ge/GeO₂ stack formation.