Extended Abstracts of the 2010 International Conference on Solid State Devices and Materials, Tokyo, 2010, pp25-26

Advantage of High-pressure Oxidation for Ge/GeO_2 Stack Formation

Choong Hyun Lee[1], Tomonori Nishimura[1,2], Toshiyuki Tabata[1], Shengkai Wang[1], Kosuke Nagashio[1,2], Koji Kita[1,2], and Akira Toriumi[1,2]

[1]Department of Materials Engineering, The University of Tokyo
[2]JST-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 CMOS 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 CMOS is how to effectively passivate the Ge/GeO_2 interface. On the basis of thermodynamics, we reported the validity of high-pressure oxidation (HPO) which could suppress the GeO desorption from Ge/GeO_2 interface [3]. Furthermore, the effectiveness of low temperature oxygen annealing (LOA) in Ge/GeO_2 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/GeO_2 MOSCAPs, HPO and atmospheric-pressure oxidation (APO) were carried out at 550°C for 15 min with 70atm-O_2 and 1atm-O_2, respectively, after chemically cleaning the Ge surface. Subsequently, POA was carried out at 400°C with various ambient (N_2, FGA, O_2) 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 GeO_2 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/GeO_2 stack, where the hysteresis significantly decreases as the annealing time increases. Here, the hysteresis was estimated at flatband voltage (V_{FB}) of *C-V* curves. However, it is clearly observed that both N_2 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/GeO_2/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/GeO_2 interface can be achieved by APO+LOA, which is close to Ge/GeO_2 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 (D_{it}), respectively. It is shown that the value of D_{it} in Ge/GeO_2 MOSCAPs with APO+LOA is as low as 8x10^{10} eV^{-1}cm^{-2} near the midgap and 3x10^{11} eV^{-1}cm^{-2} near the conduction band edge. Thus, it is concluded that LOA is very important for passivating the dangling bonds at Ge/GeO_2 interface.

In order to properly evaluate the role of HPO in Ge, Ge/GeO_2 gate stack was prepared by APO+LOA and HPO+LOA, respectively, where all of the steps of experiment were exactly same except for O_2 pressure during the oxidation. **Fig. 3(a)** shows the refractive index of the GeO_2 films determined at λ of 632.8 nm as a function of the oxidation condition. The bulk properties of GeO_2 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 GeO_2 films, as shown in **Fig. 3(b)**. The GeO_2 film density estimated by GIXR as a function of O_2 pressure is shown in **Fig. 4(a)**. It clearly shows that GeO_2 film density increases with the increase of O_2 pressure. For comparison, the density of amorphous GeO_2 film [6] is also shown in **Fig. 4(a)**, which is in good agreement with APO-grown GeO_2 film. **Fig. 4(b)** shows the etching rate of GeO_2 film by C_2H_5OH+H_2O solution. Obviously, HPO-grown GeO_2 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 GeO_2 bulk than APO. In terms of the thermal process stability, we also compared the thickness reduction rate of GeO_2 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 ($dT_{ox}/dt = -\alpha/T_{ox}$, 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/GeO_2 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 GeO_2 preparation, the desorbed H_2O was measured by the thermal desorption spectrometry (TDS) as shown in **Fig. 6(b)**. It is revealed that APO-grown GeO_2 film has about 40% more H_2O molecules than HPO-grown one, which indicates HPO-grown GeO_2 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/GeO_2 interface can be effectively passivated by LOA, while robust GeO_2 bulk properties are determined by HPO.

Thus, it is concluded that the intrinsic difference between HPO- and APO-grown GeO_2 is primarily that of bulk properties of GeO_2. The combination of HPO with LOA, which can improve both GeO_2 bulk and Ge/GeO_2 interface, will be most suitable for Ge/GeO_2 stack formation.

4. Conclusion

The post oxidation annealing for Ge/GeO_2 stack has been systematically investigated, and it has been revealed that LOA is quite important for passivating Ge/GeO_2 interface, resulting in very low D_{it}. However, GeO_2 bulk properties are totally different between APO- and HPO-grown GeO_2 films in spite of dramatic improvement of *C-V* curves by LOA. This indicates that GeO_2 bulk properties are determined by HPO. It is also found that HPO has advantage

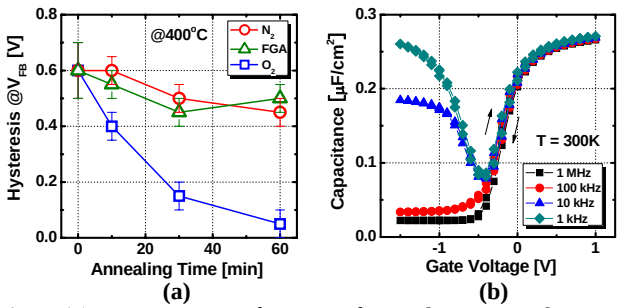
over APO in terms of the thermal process stability and the robustness to the air exposure. The combination of HPO with LOA, which can control both GeO_2 bulk and Ge/GeO_2 interface, will be most suitable for Ge/GeO_2 stack formation.

Acknowledgements

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

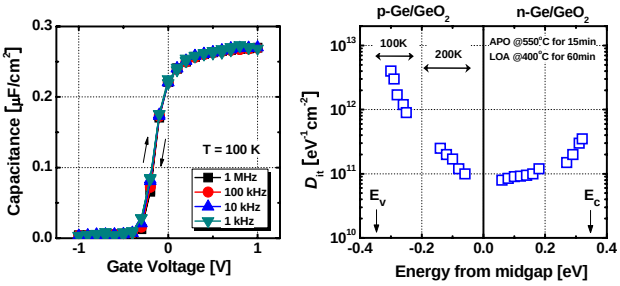
References

[1] C. H. Lee *et al.*, *IEDM Tech. Dig.*, (2009) 457.
[2] K. Morii *et al.*, *IEDM Tech. Dig.*, (2009) 681.
[3] C. H. Lee *et al.*, *APEX*, **2**, (2009) 071404.
[4] K. Kita *et al.*, *IEDM Tech. Dig.*, (2009) 693.
[5] V. V. Afanas'ev *et al.*, *APL*, **87**, (2005) 032107.
[6] N. M. Ravindra *et al.*, *Phy. Rev. B*, **36**, (1987) 6132.
[7] K. Kita *et al.*, *ECS Trans.*, (2008) 187.



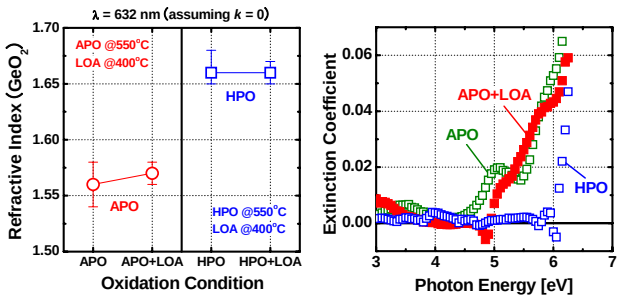
(a) (b)

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/GeO_2/Ge MOSCAP measured at 300 K, where GeO_2 was grown by APO and LOA.



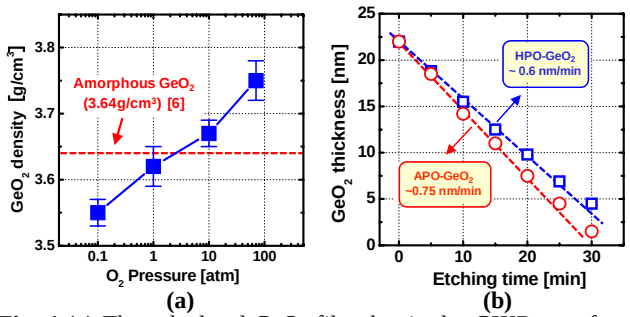
(a) (b)

Fig. 2 (a) Bi-directional *C-V* curves measured at 100K. No hysteresis and frequency dispersion are observed. **(b)** Energy distribution of D_{it} estimated by low temperature conductance method. D_{it} is as low as $8x10^{10}$ $eV^{-1}cm^{-2}$ near the midgap.



(a) (b)

Fig. 3 (a) Refractive index of the HPO- and APO-grown GeO_2 films with and without LOA. **(b)** Sub-bandgap photo absorption of GeO_2 films. In case of APO, a significant sub-bandgap is observed even after LOA.



(a) (b)

Fig. 4 (a) The calculated GeO_2 film density by GIXR as a function of O_2 pressure. **(b)** Wet-etching rate of GeO_2 film by $C_2H_5OH+H_2O$ solution. Obviously, HPO-grown GeO_2 shows slower etching rate.

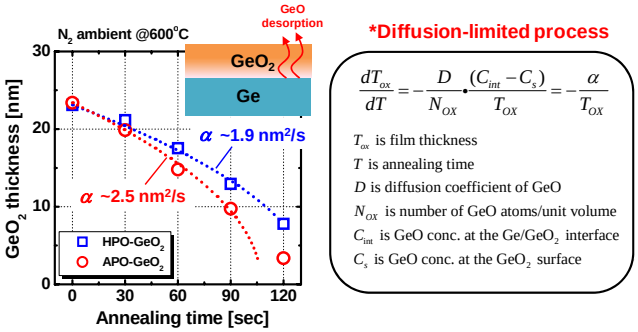
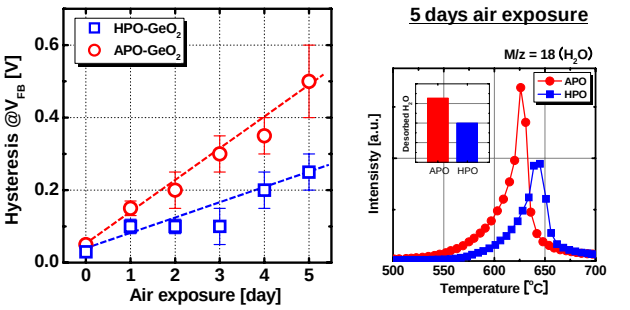


Fig. 5 The thickness reduction of GeO_2 on Ge as a function of N_2 annealing time at 600°C, where GeO_2 was grown by HPO and APO, respectively. The dotted lines are calculated ones by assuming that the GeO desorption rate obeys by the equation for the diffusion-limited process [7], where α = 1.9 and 2.5 for HPO and APO, respectively.



(a) (b)

Fig. 6 (a) Hysteresis as a function of air exposure, where Ge/GeO_2 stack was exposed to air before gate electrode formation. **(b)** TDS result of Ge/GeO_2 stack after air exposure in 5 days. APO-grown GeO_2 film has about 40% more H_2O molecules than HPO-grown one.

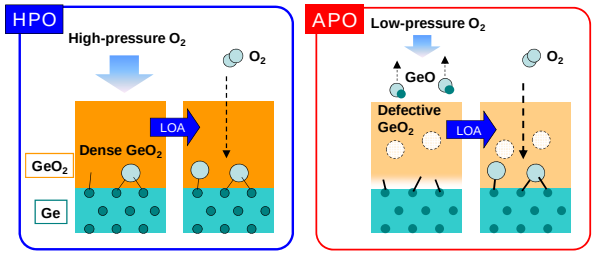


Fig. 7 Schematics of HPO and APO with LOA. Dangling bonds at Ge/GeO_2 interface can be effectively passivated by LOA, while robust GeO_2 bulk properties are determined by HPO. Thus, the combination of HPO with LOA will be most suitable for Ge/GeO_2 stack formation.