1.2 nm-EOT Al₂O₃/Ge Gate Stack with GeO_X-free Interface

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1. Introduction

Ge is one of the promising semiconductor materials for the post Si-CMOS. In fact, very high electron mobility (peak μ_{eff} =1,920 cm²/Vs) was accomplished in n-MOSFET with Y_2O_3 gate stack [1]. It is almost 2.5x larger than the Si-universal mobility. The EOT scaling is, however, still challenging, because the above MOSFET actually has a relatively thick GeO₂ interface layer (IL) due to employing high pressure oxygen annealing (HPOA). On the other hand, relatively low processing temperatures have been used in device fabrication to suppress GeO desorption, but high temperature process (~600°C) will be desirable when device stability and reliability are considered. Above requirements suggest us to use Al₂O₃ for gate dielectric film on Ge, because among various high-k oxides, Al₂O₃ has high resistances against oxygen diffusion and thermal reaction [2]. Furthermore, when the scalability is concerned, the direct Al_2O_3 on Ge might be desired than GeO_X -IL insertion [3].

So, this paper discusses Al_2O_3 potentiality in Ge gate stack with GeO_x -free interface even after relatively high temperature process (600°C), and then demonstrate thin EOT Al_2O_3 /Ge MIS capacitor (MISCAP) characteristics with GeO_x -free interface.

2. Experimental

 Al_2O_3 film was deposited on p-type Ge (100) wafer by rf-sputtering in Ar. Al_2O_3 film thickness was determined by the X-ray reflectivity measurement. After the deposition, the post deposition annealing (PDA) was performed at 600°C for 30 sec in 1-atm O₂, and at 600°C and 550°C for 30 sec in 10-atm O₂ (at room temperature), as shown in **Fig. 1**. Then, Au and Al were evaporated as the gate electrode and the back ohmic contact, respectively.

3. Results and Discussion

The oxygen blocking capability of thin Al_2O_3 film is discussed. **Fig. 2 (a)** and **(b)** show the Ge3d core level spectra in XPS. Almost no GeO_x growth was detected at the interface of as–sputtered Al_2O_3 on Ge. This means that Ge was not oxidized in the sputtering process, while it was grown in O₂-PDA at 600°C through ultra-thin Al_2O_3 . We have noted, however, that the peak intensity of Ge⁴⁺ dramatically decreased with the increase of Al_2O_3 thickness. This indicates that only 2~3 nm- Al_2O_3 is thick enough to suppress the oxidation of Ge even at 600°C.

In Ge MIS gate stacks, GeO desorption should degrade the Ge interface quality and increase the D_{it} . [4]. **Fig. 3** shows the TDS (thermal desorption spectroscopy) results of GeO desorption for (i) Al₂O₃/Ge, (ii) Al₂O₃/GeO₂/Ge, and (iii) GeO₂/Ge stacks, respectively. From the comparison between (i) and (ii), it is revealed that there is no GeO desorption without GeO₂-IL at the interface.

Furthermore, from comparison between (ii) and (iii), we can understand that Al_2O_3 works as a diffusion barrier than thick GeO₂ layer, because almost no GeO desorption was observed even at 600°C in the case of (ii).

The oxygen blocking effect of thin Al_2O_3 film was also observed in HPOA. **Fig. 4** shows the Ge3d core level spectra of 3-nm-thick- Al_2O_3 /Ge with HPOA at 600°C and 550°C. As-deposited sample is also shown. It is noted that GeO_x-IL growth is entirely suppressed at 600°C even in HPO. We reported that a relatively thick GeO₂-IL growth was observed in the cases of rare-oxides though C-V characteristics were surprisingly good [5]. It is in striking contrast to the present results. This fact is a great advantage of Al_2O_3 gate stack for suppressing the interface degradation due to GeO desorption and for reducing the CET in terms of the scalability.

Next, electrical properties are discussed. The question is whether GeO_x-free interface is really improved by HPOA or not. C-V characteristics of 3-nm-thick-Al₂O₃/Ge MISCAPs with N₂-PDA (1-atm), O₂-PDA (1-atm), and HPOA (10-atm) at 600°C, are shown in Fig. 5, respectively. The oxygen rich PDA clearly improves the interface in spite of GeO_X-IL formation. Fig. 6 (a) shows bi-directional C-V characteristics of 3-nm-thick-Al₂O₃/Ge MISCAP in HPOA at 600°C as a parameter of measurement frequency. A small frequency dispersion at depletion region indicates that the interface was considerably improved by HPOA. Although the interface has not been clarified yet, the results are significantly different from those in HfO₂ gate stacks [6]. We infer that the interface might be stabilized due to the different valency between Ge and Al, which was also discussed in Y₂O₃/Ge gate stack [7], as well as the possible interface Al-Ge bonds might be recovered to Al-O-Ge one.

The accumulation capacitance is 2.1 μ F/cm² (EOT~1.2 nm). Since the relative dielectric constant, *k*, of the present Al₂O₃ was ~7.5, and Al₂O₃ has a large band offset against Ge thanks to no d-electron, quite a low gate leakage is expected. **Fig. 6 (b)** shows I-V characteristic with a low leakage current density (4.0×10⁻⁶ A/cm²) at V_{GS}=V_{FB}-1 (V).

4. Conclusions

We have studied Al_2O_3 gate stack on Ge together with HPOA. Al_2O_3 shows the high resistance against O_2 diffusion, and no interfacial GeO_x layer was formed even in HPOA. However, it was found that HPOA improved the interface very much. Further optimization is obviously needed, but we think that Al_2O_3 gate stack will provide a potential for Ge device expansion.

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References

- [1] C. H. Lee et al., Tech. Dig. IEDM, p.416 (2010).
- [2] Y. Oishi and W. D. Kingery, J. Chem. Phys. 33, 480 (1960).
- [3] R. Zhang et al., APL 98, 112902 (2011).
- [4] C. H. Lee et al., APEX 2, 071404 (2009).
- [5] T. Tabata et al., ECS-Trans. 16 (5), 479 (2008).
- [6] K. Kita et al., Ext. Abst. SSDM, p.292 (2003).
- [7] T. Nishimura et al., APEX 4, 064201 (2011).



Fig. 1. Schematic views of sample preparation. Intentional IL was not formed before Al_2O_3 deposition. HPOA was performed in a closed furnace with 10-atm O_2 at room temperature in this experiment.



Fig. 2. The Ge3d core level spectrums of (a) as-sputtered and (b) 1-atm O_2 -PDA at 600°C samples of thin Al_2O_3 /Ge stacks. Only a very small amount of GeO_X layers are detected for samples with Al_2O_3 thicker than 2.5 nm.



Fig. 3. TDS spectrums of GeO (m/Z=90) desorption from Al_2O_3/Ge , $Al_2O_3/GeO_2/Ge$, and GeO_2/Ge stacks. The heating rate of the measurement was 20°C/min. Note that a significant difference of the desorption temperature between w/ and w/o Al_2O_3 cap on GeO_2/Ge . The Q-Mass current intensity difference comes from the sample size difference.



Fig. 4. The Ge3d core level spectrums of as-sputtered and HPOA samples of 3-nm-thick-Al₂O₃/Ge stacks. HPOA was applied at 600° C in 10-atm O₂ (at room temperature).



Fig. 5. The 1MHz C-V characteristics of 3-nm-thick- Al_2O_3/p -Ge MISCAPs with N₂-PDA (1-atm), O₂-PDA (1-atm), and HPOA (10-atm) at 600°C.



Fig. 6. (a) The frequency dispersion of C-V characteristics of 3-nm-thick- Al_2O_3/p -Ge MISCAP with 10-atm HPOA. EOT~1.2 nm was obtained from the accumulation capacitance. The k-value of Al_2O_3 was ~7.5. (b) I-V characteristics of 3-nm-thick- Al_2O_3/p -Ge MISCAP with 10-atm HPOA.