Extended Abstracts of the 2017 International Conference on Solid State Devices and Materials, Sendai, 2017, pp525-526

Role of Y-doping into GeO_2 in Ge gate stack reliability

Xiaoyu Tang[1, 2] and Akira Toriumi[1]
[1]Department of Materials Engineering, The University of Tokyo, Tokyo 113-8656, Japan
[2]School of Electronic Science and Engineering, Nanjing University, Nanjing, 210093, P. R. China
e-mail: toriumi@material.t.u-tokyo.ac.jp

***Abstract* — This paper discusses the difference between GeO_2/Ge and Y-doped GeO_2/Ge from the gate stack reliability viewpoint. The results show that GeO_2/Ge is fragile against electric bias stress, which means that superior initial characteristics of GeO_2/Ge gate stacks cannot ensure good reliability. This is critically important for the assessment of new channel materials gate stacks.**

I. Background and Objective

Ge is one of the promising candidates to replace Si in terms of high electron and hole mobility. A well-behaved gate stack is the first target to achieve Ge advantages. We have demonstrated very good gate stack properties using high pressure O_2 oxidation [1] and/or doped GeO_2 such as Y-doped GeO_2 [2]. In fact, GeO_2/Ge stacks are investigated world-wide for achieving high performance Ge FETs. It is, however, not always true that excellent initial gate stack properties may assure the long term reliability. We preliminarily studied about the trapping properties in GeO_2 and doped-GeO_2, and found an appreciable difference between them [3]. In this work, we have extended it in more detail to understand the reliability differences among those films. We think this is the most important in Ge gate stack technology.

II. Experiment

GeO_2 was thermally grown in high-pressure O_2 (HPO: 50 atm at room temperature) at 550ºC, while doped GeO_2 was deposited by co-sputtering on Ge, followed by PDA in N_2 at 500ºC. In this work, 10% Y_2O_3-doped GeO_2 (YGO) was investigated. Au and Al were evaporated for the gate electrode and back contact, respectively. GeO_2 and YGO on p-type Ge (111) substrate were electrically stressed under different electric fields, and then V_{FB} shift was evaluated as a function of stress-time.

III. Results and Discussion

All samples of HPO-GeO_2 and YGO on Ge showed good initial C-V characteristics as reported [1, 2]. Initial characteristics in HPO-GeO_2/Ge were slightly better those in YGO/Ge in the present experiments.

1) <u>Bias stress effects on V_{FB}</u>

Positive bias stresses were applied on Au/GeO_2/Ge and Au/YGO/Ge stacks under E_{stress}=(V_g-V_{FB}-2ϕ_F)/EOT. In case of Ge gate stacks, even positive applied voltage on p-Ge is effectively biased thanks to easy inversion formation at room temperature. **Fig. 1 (a)** and **(b)** show

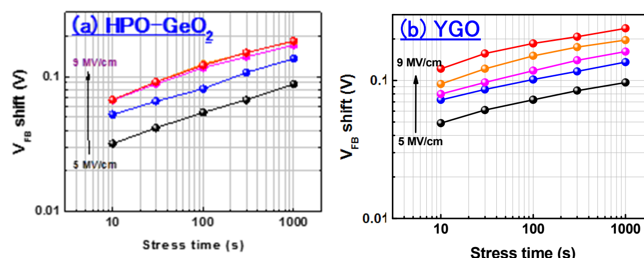

Fig. 1 V_{FB} shift as a function of stress time under positive gate bias conditions for Ge gate stacks with **(a)** HPO-GeO_2 and **(b)** YGO on Ge.

that V_{FB} shifts in both GeO_2/Ge and YGO/Ge behave as the power law, $\Delta V_{FB} = \alpha t^n$. It is more interestingly found that n in GeO_2 is higher (2x) than that in YGO as shown in **Fig. 2**, which indicates that the degradation speed in GeO_2 is much faster than in that in YGO, though initial C-V characteristics were almost the same.

In negatively biased case, GeO_2 was broken down at medium field, while YGO was survived up to 10 MV/cm. This fact also suggests YGO/Ge is much better than GeO_2/Ge.

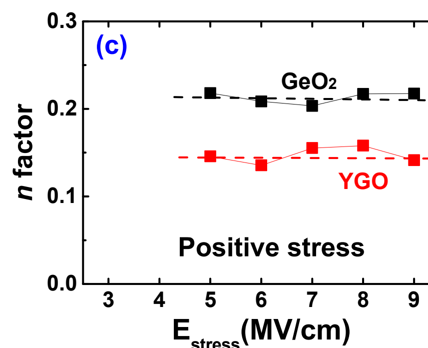

Fig. 2 n-factor in case that ΔV_{FB} is expressed in αt^n. n in GeO_2 is $x2$ higher than that in YGO. This fact means the much faster degradation in GeO_2/Ge gate stacks.

2) <u>Recovery test</u>

By applying the opposite electric field (positive bias) after the negative stressed gate stacks on YGO, V_{FB} were recovered dependent on the electric field, as shown in **Fig. 3**. More interestingly it was recovered to almost the initial V_{FB} under the opposite and same electric field as the initial electric field.

This fact suggests just trapping/detrapping process and no YGO network change. Traps generated in the stress are not permanent one but reversible, while traps in HPO-GeO_2/Ge were not the case (data not shown).

This reversible process exhibits the nature of traps generated by the electrical stress in YGO stacks.

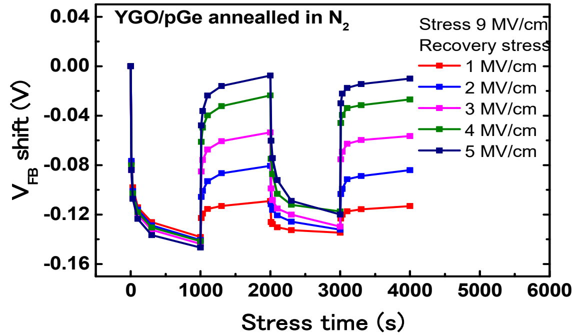

Fig. 3 (a) V_{FB} shift and recovery measurements for positive bias stresses on negatively stressed YGO/Ge stacks. The first negative stress was under 9 MV/cm. V_{FB} shifts in positive bias stresses on negatively stressed YGO/Ge stacks are recovered toward the initial value dependent on the positive stress field.

3) Structural consideration of GeO_2

GeO_2 has more flexible O-Ge-O bond angle in addition to a smaller Ge-O bonding energy than SiO_2 counterpart. This means that GeO_2 should be more fragile against energetic electron injection. YGO/Ge stack shows more robust characteristics under electric stress. This is due to the more rigid network formation in YGO thanks to a higher coordination number of Y in YGO. Thus, it is suggested that the network flexibility may be slightly reduced, but that O-Ge-O bond is not easily reconstructed. Namely, the local bond breaking in YGO will not trigger the fatal deterioration, as schematically shown in **Fig. 4** [4].

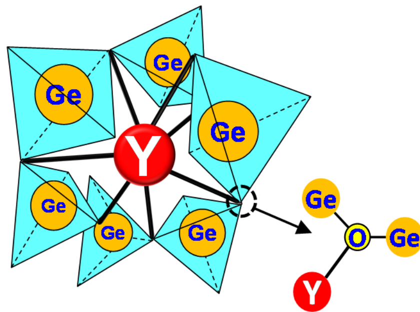

Fig. 4 Schematic image of Y-doped GeO_2 network. This change considerably affects the gate stack reliability, because the network structure of GeO_2 is topologically toughened by Y-doping.

The GeO_2/Ge interface and bulk GeO_2 have been significantly improved by suppressing the GeO desorption by HPO thermodynamically. However, GeO_2 is intrinsically fragile against the network modulation. Resultantly, the GeO_2 tetrahedron unit becomes unstable by a Ge-O bond breaking in the network and permanent defects are generated. Meanwhile, in YGO case, even though there are more pre-existing traps (in the present experiments), trap generation and permanent trap formation are considerably suppressed. The flexibility in the network structure of dielectric films enables to achieve excellent gate stacks at the initial state, while it makes the network structure weak against the external stress. On the other hand, since the SiO_2/Si system is not so flexible with higher Si-O bonding energy, H-passivation by FGA is needed to disable so many dangling bonds which are initially existing, particularly, at the interface. This difference suggests the key guideline to achieve reliable gate stacks. **Fig. 5** schematically compares GeO_2/Ge with SiO_2/Si. Namely, to stabilize the gate stacks, hydrogen is the key in SiO_2/Si, while an appropriate cation doping such as Y is mandatory.

It is generally considered that metal doping into GeO_2 might generate gap states, but in case of GeO_2, appropriate metal can strengthen the network structure. This is a great advantage of YGO in addition to the oxygen potential control of dielectric films [5].

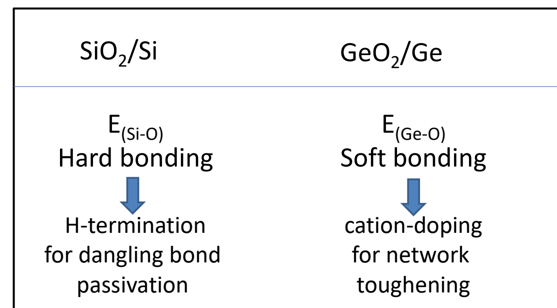

Fig. 5 Comparison between SiO_2/Si and GeO_2/Ge. $E_{(Si-O)}$ and $E_{(Ge-O)}$ are bonding energies of Si-O and Ge-O, respectively. The network toughness of the dielectric film is critically important for assessing the reliability. Note that SiO_2 and GeO_2 are in principle with the same network structure, but that technical challenges are quite different.

IV. Conclusions

The results obtained in this study present several important messages, in addition to the fact that initial gate stack properties do not assure the Ge gate stack reliability. Two critical points should be emphasized in Ge gate stacks. GeO_2 is regrettably not a good candidate for Ge gate stack from the reliability viewpoint. Y-doping is so effective for enhancing the network toughness of GeO_2. Thus, to design high performance Ge gate stacks, the network toughness as well as the oxygen potential control should be taken into consideration.

Acknowledgment

This work was partly supported by Grant-in-Aid for Scientific Research (A).

References

[1] C. H. Lee et al., *APEX* **5**, 114001 (2012).
[2] C. Lu et al., *APL* **104**, 092909 (2014).
[3] C. Lu et al., *APEX* **8**, 021301(2015).
[4] C. H. Lee et al., IEDM 2013.
[5] C. Lu et al., IEDM 2015.