Reliability-aware Germanium Gate Stack Formation by GeO_2 Network Modification

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[Introduction] Ge gate stack formation has been intensively investigated and several successful demonstrations on MOSFET application have been made by high quality GeO_2-based gate dielectrics on Ge [1-4]. However, it is concerned about the device reliability that the promising initial properties of the Ge stacks might be degraded over time at electric stress field (E_{stress}) [5]. This work is to provide a guideline to keep reliability robustness as well as initial good performance in Ge gate stacks through a structural understanding on GeO_2-based dielectrics.

[Experiment] After HF-last cleaning, (4.5 nm) GeO_2/Ge stacks (EOT=3 nm) were prepared by high pressure oxidation (HPO) [1] of both p and n-Ge(111) substrates. (4 nm) M_2O_3 doped GeO_2/Ge (M-GeO_2, M for Al, Sc and Y) stacks (EOT=2 nm) were also prepared by co-sputtering of GeO_2 and M_2O_3 targets [4]. Y, Sc or Al doping was controlled to be 10%. Au and Al were deposited for the gate electrode and substrate contact of MOSCAPs, respectively. The constant E_{stress} experiments of both polarities were carried out at room temperature (RT) by applying positive and negative gate voltages (V_G) on n and p-Ge MOSCAPs, respectively. Note that, in this work, the E_{stress} is defined as V_G/EOT for a fair comparison of various dielectrics.

[Results and discussion] All the HPO-GeO_2 and M-GeO_2/Ge stacks show promising initial properties with low D_{it} values on the order of 10^{11} $ev^{-1}cm^{-2}$ throughout the Ge band gap (data not shown). E_{stress} with various fields was applied on the stacks and trap density (N_t) was estimated from the V_{FB} shift by the following equation [6]:

$$N_t = C_{ox}\Delta V_{FB}/q \quad (1)$$

Here, C_{ox} is the capacitance of the gate oxide and q is the electron charge. **Fig. 1** shows electron trap density in HPO-GeO_2 and M-GeO_2/n-Ge stacks as a function of positive E_{stress} calculated by equation (1). It is found that both HPO-GeO_2 and M-GeO_2/Ge stacks show low N_t at low E_{stress} (4 MV/cm). This low N_t is attributable to the low pre-existing N_t in the as prepared gate stack since the V_{FB} shift saturated over long stress time. While at the high E_{stress}, HPO-GeO_2/Ge stack is drastically degraded by newly generation traps. Among the M-GeO_2/Ge stacks, trap generation is preferentially reduced in Y and Sc cases (symmetrically for positive and negative E_{stress}, data not shown), while Al doping cannot suppress trap generation. The different trap generations in HPO-GeO_2 and M-GeO_2/Ge stacks are understandable by combining the GeO_2 structural knowledge [3, 4, 7] with the thermochemical model of dielectric degradation [5]. In detail, the single bond strength and coordination number of metal-oxygen (M-O) bond are the critical material parameters for the bond breaking and ion displacement at E_{stress}, respectively [5]. GeO_2 has a weak Ge-O bond and a low average coordination number (N_{av}) of 2.67 [7], which make it highly susceptible to bond breaking and ion displacement at high E_{stress} as schematically shown in **Fig. 2(a)**. On the other hand, small amount of Y or Sc doped GeO_2 forms a modified random network (MRN) [3, 4] and increases the N_{av} to about 3 (not for Al), which is expected to suppress the ion displacement and trap generation. It is notable that the stronger reliability of Y or Sc-GeO_2 than that of HPO-GeO_2 is consistent with their higher thermal stability [4] from a kinetic viewpoint as described in **Fig. 2(b)**. Both reliability and thermal degradations involve the configuration change from initial oxides to defect site. Network modification by Y or Sc is an effective approach to suppress GeO_2 degradation in both cases from the energy viewpoint

[Conclusion] A proper N_{av} is the critical parameter for achieving both promising initial property and long term reliability in Ge gate stacks. Y or Sc-GeO_2 demonstrates the manipulation of N_{av} by network modification.

[Reference] [1] C. H. Lee *et al*, *IEEE TED*. **58**, 1295 (2011). [2] S. Takagi *et al*., *IEDM*, 372 (2012). [3] C. Lu *et al*., *APL*, **104**, 092909 (2014). [4] C. Lu *et al*., *JAP*, **116**, 174103 (2014). [5] J. W. McPherson *et al*., *IEEE TED*, **50**, 1771 (2003). [6] S. M. Sze *et al*., *Physics of Semiconductor Devices* (Wiley, NJ, 2007). [7] G. Lucovsky, *J. Vac. Sci. Technol*. A **1**, 1553 (2001).

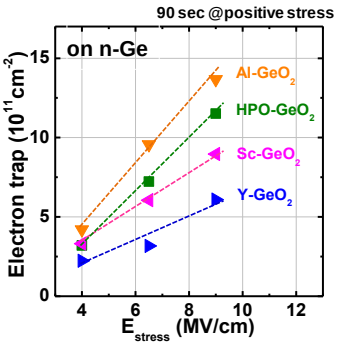

Fig. 1 Electron trap density generated in HPO-GeO_2 and M-GeO_2/Ge stacks as a function of E_{stress} for 90 sec.

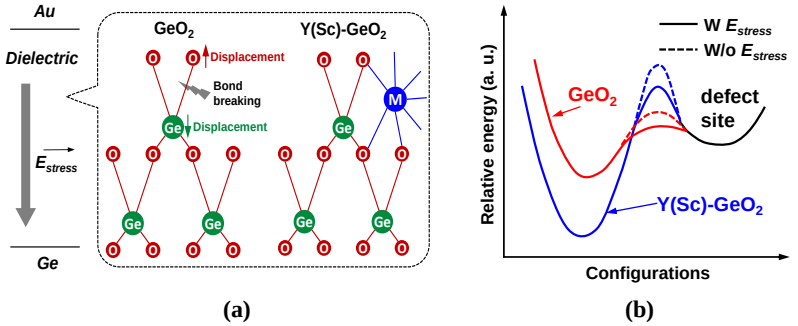

Fig. 2(a) Schematic of Y(Sc)-GeO_2 MRN structure and its impact on the ion displacement. **(b)** Schematic of energy diagram for the dielectric degradation by E_{stress} or by thermal decomposition (GeO desorption).