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## Network modification of GeO<sub>2</sub> by trivalent metal oxide doping

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**[Introduction]** The proper intermixing between high-k metal oxide and  $GeO_2$  is believed to be a basic criterion to achieve good interface passivation for Ge [1]. Based on the thermodynamic understanding, a successful demonstration has been made by Yttrium-doped GeO<sub>2</sub> (Y-GeO<sub>2</sub>), which drastically improved the thermal stability and water resistance of  $GeO_2/Ge$  gate stack without the degradation of the interface [2, 3]. In this work, a systematic comparison of the material properties is carried out among different trivalent metal oxide doped GeO<sub>2</sub> (M-GeO<sub>2</sub>).

[Experiment] After p-Ge substrates were chemically cleaned with methanol, HCl, and HF solutions, different M-GeO<sub>2</sub> (M for Al, Sc or Y) was deposited on Ge by co-sputtering GeO<sub>2</sub> target with M<sub>2</sub>O<sub>3</sub> target, respectively. Post deposition annealing was carried out at 500 °C in N2 ambient for 30 sec. The percentages of M atoms in GeO<sub>2</sub> were controlled to be 10% among the metallic atoms by sputtering power and confirmed by XPS measurements. GeO desorption from M-GeO<sub>2</sub>/Ge stacks were measured by thermal desorption spectrum (TDS). The water etching rate of M-GeO<sub>2</sub> were estimated by immersion in deionized water (DIW), followed by XPS measurements of the thickness reduction.

**[Results and discussion]**  $GeO_2/Ge$  stack is thermally unstable, while M doping is expected to improve its thermal stability. Fig. 1(a) shows the TDS peak temperature corresponding to GeO (m/z=90) as a function of initial M-GeO<sub>2</sub> thickness. Desorption of GeO from GeO<sub>2</sub>/Ge is shown for comparison [4]. All the M-GeO<sub>2</sub>/Ge stacks show higher GeO desorption temperature than GeO<sub>2</sub>/Ge stack for each thickness of respective films, which is consistent with the thermodynamic expectation that M doping can lower the oxygen potential of M-GeO<sub>2</sub>. It is notable that Y and Sc are particularly strong in terms of suppressing GeO desorption, while the effect Al is relatively weak. The prominent effect of M doping is also reflected in the stronger water resistance of M-GeO<sub>2</sub>. Fig. 1(b) shows the DIW etching rate of M-GeO<sub>2</sub> estimated by XPS. The etching rate of pure GeO<sub>2</sub> is also shown for comparison. All the M-GeO<sub>2</sub> show lower DIW etching rate than pure GeO<sub>2</sub>. It is interesting to see that Y and Sc are also stronger than Al in terms of decreasing the water etching rate of M-GeO<sub>2</sub>.

The network modification model offers an explanation on both improvements of water resistance and thermal stability of M-GeO<sub>2</sub>. Trivalent metal oxide doping exists as M cation in the GeO<sub>2</sub> network, bonded to the nearest oxygen atoms as schematically shown in Fig. 2. The additional M-O bonds in the M-GeO<sub>2</sub> strengthen the network and improve the material properties, which is thermodynamically consistent with oxygen potential lowering in M-GeO<sub>2</sub>. The M-O bonding number is determined by the ratio of the M cation radii to the  $O^{2-}$  anion radii [5]. Y and Sc have large cation radius (0.9 and 0.745 Å, respectively [6]), which enable them to have 6-7 M-O bonds. On the other hand, Al has only 4 M-O bonds due to its relatively small cation radii (0.535 Å [6]). The higher M-O bonding number explains the particularly strong effect of Y and Sc on the improvement of water resistance and thermal stability.

[Conclusion] Water resistance and thermal stability of GeO<sub>2</sub> were improved by trivalent metal oxide doping, particularly Y and Sc. These improvements are attributable to the network modification of GeO<sub>2</sub> by doping.

[Reference] [1] Y. Kamata, Materials today, 11 (2008) 30. [2] C. H. Lee et al., VLSI symp., T28, (2013). [3] C. Lu et al., SSDM, (2013). [4] S. K. Wang et al., JAP, 108 (2010) 054104. [5] J. Wang et al., J. Non-Cryst. Solids, 163 (1993) 261. [6] R. D. Shannon, Acta Cryst. A32, (1976) 751.





Fig. 1(a) TDS peak temperature corresponding to GeO (m/z=90) as a function Fig. 2 Schematic of network of initial M-GeO<sub>2</sub> and GeO<sub>2</sub> thickness. (b) DIW etching rate of M-GeO<sub>2</sub> and modification of GeO<sub>2</sub> by doping pure GeO<sub>2</sub>. M doping reduces the etching rate, particularly Y and Sc.

trivalent oxide  $(M_2O_3)$ .