Thermodynamic selection of the desirable doping materials in GeO$_2$

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[Introduction] The formation of high-quality GeO$_2$/Ge interface is regarded as one of the best solutions for realizing high-performance Ge CMOS [1-3]. Recently, we demonstrated that a suitable metal oxides doping into GeO$_2$ (M-GeO$_2$) can drastically improve the thermal stability and water resistance of GeO$_2$/Ge stack without the degradation of the interface [4]. However, a systematic selection of desirable doping oxides is yet to be carried out. In this work, a criterion on the selection of doping material is given from thermodynamic viewpoint.

[Experiment] After p-Ge substrates were chemically cleaned with methanol, HCl, and HF solutions, Y-GeO$_2$ and Hf-GeO$_2$ was deposited on Ge by co-sputtering GeO$_2$ target with Y$_2$O$_3$ or HfO$_2$ target, respectively. Post deposition annealing was carried out at 500 °C in N$_2$ ambient for 30 sec. The atomic percentage of Y or Hf in GeO$_2$ was controlled to be 10% among the metallic atoms by sputtering power and confirmed by XPS measurements. Au and Al were deposited by vacuum evaporation for the gate electrode and substrate contact of the MOSCAPs, and the capacitance-voltage (C-V) were measured at room temperature (RT).

[Results and discussion] Fig. 1 shows the bidirectional C-V curves of Y-GeO$_2$/Ge and Hf-GeO$_2$/Ge MOSCAPs measured at RT. No hysteresis and frequency dispersion is observed in Y-GeO$_2$/Ge stack, indicating a low interface states density (D$_\text{it}$), while the C-V curve of Hf-GeO$_2$/Ge stack has large hysteresis, which is attributable to a huge amount of D$_\text{it}$. To investigate the origin of different interface properties in Y-GeO$_2$/Ge and Hf-GeO$_2$/Ge stacks, the bonding configurations in both gate stacks were characterized by XPS. Fig. 2(a) shows the Ge 3d core level spectra of Y-GeO$_2$/Ge and Hf-GeO$_2$/Ge stacks. The Ge 3d spectrum of a bare Ge substrate is also shown for comparison (dotted line). The chemical shift of Y-GeO$_2$ and Hf-GeO$_2$ is 2.95 and 3.1 eV with respect to Ge substrate peak, respectively, which is lower than that of pure GeO$_2$. This lower chemical shift of Y-GeO$_2$ and Hf-GeO$_2$ is originated from the second-nearest-atom effect of Y and Hf atoms through O-M bond configuration. It is worth noting that Ge-Hf metallic bond formation is also observed in Hf-GeO$_2$/Ge stack at a lower binding energy with respect to Ge substrate peak, while no Ge-Y bond is found in Y-GeO$_2$/Ge stack.

The difference of bond configurations in Y-GeO$_2$/Ge and Hf-GeO$_2$/Ge stacks is schematically shown in Fig. 2(b). The degradation of Hf-GeO$_2$/Ge interface is attributable to the Hf-Ge bond, which is consistent with the first principle calculation [5]. The different bond configuration of Y and Hf are explainable from different Gibbs free energy for germanidation. Within the accuracy of reference and thermodynamic database [6,7], it is calculated as

$$\text{HfO}_2 + 3\text{Ge} = \text{HfGe}_3 + \text{GeO}_2 \quad \Delta G = -27 \text{ kcal/mol} \quad (1)$$

$$\text{Y}_2\text{O}_3 + 3.5\text{Ge} = 2\text{YGe} + 1.5\text{GeO}_2 \quad \Delta G = 152.8 \text{ kcal/mol} \quad (2)$$

Hf-Ge metallic bond is easier to form due to the negative Gibbs free energy for germanidation, while the formation of Y-Ge bond is relatively hard from the thermodynamic viewpoint.

[Conclusion] A positive Gibbs free energy for germanidation is required for a desirable doping metal oxide in GeO$_2$ in order to prevent the Ge-M metallic bond formation.


Fig. 1 Bidirectional C-V curves of Y-GeO$_2$/Ge and Hf-GeO$_2$/Ge gate stack measured at room temperature.

Fig. 2(a) Ge 3d core level spectra of Y-GeO$_2$/Ge and Hf-GeO$_2$/Ge measured by XPS, the Ge-Hf metallic bond is found. (b) Schematic of the bond configurations in Y-GeO$_2$/Ge and Hf-GeO$_2$/Ge stacks.