AlF_xO_y/Al_2O_3 MOS キャパシタにみられる異常なフラットバンド電圧シフト
ー 異なる陰イオンで構成された絶縁膜界面のダイポール層 ー

Anomalous Flatband Voltage Shift of AlF_xO_y/Al_2O_3 MOS Capacitors: Dipole Layer Formation at Dielectric Interfaces with Different Anions

東京大学大学院工学系研究科マテリアル工学専攻，費嘉陽，喜多浩之
Department of Materials Engineering, The Univ. of Tokyo, °Jiayang Fei and Koji Kita
E-mail: jiayang@scio.t.u-tokyo.ac.jp

[Motivation] The dipole layer formed at high-k/SiO_2 has been recognized as a promising way to adjust the threshold voltage of MOSFETs. To reasonably explain the directions and magnitudes of dipoles for various high-k/SiO_2 systems, the anion (= oxygen ion) density difference at the interface has been pointed out to be the most important factor[1], even though the role of cation migration should be also taken into account for the cases of reactive systems[2,3]. In this study we investigated the flatband voltage shift caused by an Al_2O_3/AlF_xO_y interface, due to the dipole layer formation at the dielectric interface of common cations but different anions (O^- and F^-), to clarify that the previous model can be extended to the multi-anion systems.

[Procedure] ~ 5.4-nm-thick SiO_2 was formed on p-type Si substrates by thermal oxidation. Then an AlF_3 or Al_2O_3 target was rf sputtered to form Al_2O_3/AlF_xO_y stacks with different thicknesses. After PDA at 500 ℃ in 0.1% O_2, Au gate electrodes were deposited for making MOS capacitors. The AlF_3-sputtered films after PDA contained significant amount of oxygen (F/(F+O)~0.51) as confirmed by XPS.

[Results and Discussions] The change of flatband voltage (V_{fb}) of the $Al_2O_3/AlF_xO_y/SiO_2$ stacks by changing the Al_2O_3 thickness while the AlF_xO_y thickness was fixed as 6 nm is shown in the figure. The flatband voltage of AlF_xO_y/SiO_2 was used as the reference point. The offset (ΔV) observed by extrapolating the slope to zero-Al_2O_3-thickness indicates a possible existence of a dipole layer to induce positive ΔV_{fb} at the Al_2O_3/AlF_xO_y interface with a magnitude of ~ 0.15 V.

Since the two dielectric layers share the same kind of cation, we attribute the formation of the dipole layer to the charge separation caused by anion migration at the interface. There are two possible factors to determine how the charge separation occurs by anion migration: anion number density difference and the valence difference between O and F anions. The volume of AlF_3 unit structure containing one anion is calculated to be 16.4 $Å^3$[4] while it is 14.2 $Å^3$ for Al_2O_3[1]. So, we speculate that the anion density of Al_2O_3 should be a few % higher than the AlF_xO_y layer, if we take into account of our film composition. In the analogy to oxygen density model[1] the interface relaxation would induce anion migration from Al_2O_3 to AlF_xO_y side which can explain the direction of the observed dipole. In addition, the difference in the valence of the anions can be another factor. Since one O anion is 2- charged and one F anion is 1- charged, mutual diffusion will result in the charge separation with negative charges on the AlF_xO_y and positive charges on the Al_2O_3 side, which also explains the observed dipole direction.

Acknowledgement: This work was partly supported by JST Adaptable & Seamless Technology Transfer Program through Target-driven R&D (A-STEP) FS stage, and by JSPS KAKENHI.

[Reference] [1] K. Kita and A. Toriumi, *APL* **94**, 132902 (2009). [2] J. Fei and K. Kita, SSDM2015, N-4-2, Sapporo. [3] 功刀ら，第 76 回応物学会秋季学術講演会，13A-4C-7 (2015). [4] A. Le Bail et al. *J. Solid State Chem*. **77**, 96, 1988.

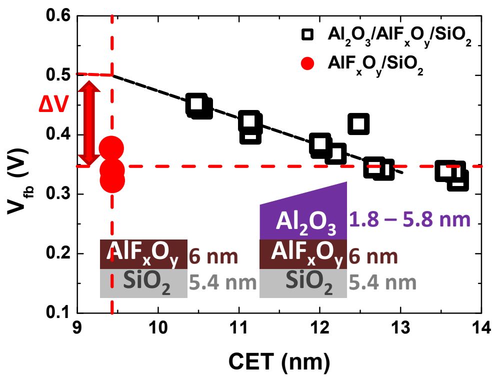

Fig. Thickness dependence of the V_{fb} of $Al_2O_3/AlF_xO_y/SiO_2$ and AlF_xO_y/SiO_2 stacks.