**AlF₃Oₓ/Al₂O₃ 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 — 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 —**

Anomalous Flatband Voltage Shift of AlF₃Oₓ/Al₂O₃ MOS Capacitors: Dipole Layer Formation at Dielectric Interfaces with Different Anions

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**Motivation** The dipole layer formed at high-k/SiO₂ 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/SiO₂ systems, the anion (= oxygen ion) density difference at the interface has been pointed out to be the most important factor, even though the role of cation migration should be also taken into account for the cases of reactive systems. In this study we investigated the flatband voltage shift caused by an Al₂O₃/AlFₓOᵧ 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-mm-thick SiO₂ was formed on p-type Si substrates by thermal oxidation. Then an AlF₃ or Al₂O₃ target was rf sputtered to form Al₂O₃/AlFₓOᵧ stacks with different thicknesses. After PDA at 500°C in 0.1% O₂, Au gate electrodes were deposited for making MOS capacitors. The AlF₃-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 (Vfb) of the Al₂O₃/AlFₓOᵧ/SiO₂ stacks by changing the Al₂O₃ thickness while the AlFₓOᵧ thickness was fixed as 6 nm is shown in the figure. The flatband voltage of AlFₓOᵧ/SiO₂ was used as the reference point. The offset (∆V) observed by extrapolating the slope to zero-Al₂O₃-thickness indicates a possible existence of a dipole layer to induce positive ∆Vfb at the Al₂O₃/AlFₓOᵧ 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 AlF₃ unit structure containing one anion is calculated to be 16.4 Å³, while it is 14.2 Å³ for Al₂O₃. So, we speculate that the anion density of Al₂O₃ should be a few % higher than the AlFₓOᵧ layer, if we take into account of our film composition. In the analogy to oxygen density model, the interface relaxation would induce anion migration from Al₂O₃ to AlFₓOᵧ 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 AlFₓOᵧ and positive charges on the Al₂O₃ side, which also explains the observed dipole direction.

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![Fig. Thickness dependence of the Vfb of Al₂O₃/AlFₓOᵧ/SiO₂ and AlFₓOᵧ/SiO₂ stacks.](image-url)