

Consideration on the Origin of Dipole Layer Formation at Dielectric Interfaces with Different Anions (Fluorine, Oxygen, and Nitrogen)

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[Motivation] A widely accepted explanation of the origin of dipole layer formation at high-k/SiO₂ is oxygen density difference [1]. To gain a further understanding of the origin, we have explored dipole layer formation at general dielectric interface by studying the V_{fb} shift of AlF_xO_y/Al₂O₃ interfaces [2], which shows a AlF_xO_y (-)/Al₂O₃ (+) dipole layer formation. In this report, we further clarify the driving force by calculating the displacements of all atoms at interface after molecular dynamic (MD) simulation of AlF₃/Al₂O₃. In addition, V_{fb} shifts of other dielectric systems with different anions (AlN_xO_y/Al₂O₃ and AlN_xO_y/AlF_xO_y) were experimentally studied to investigate other factors that affect the dipole layer formation in addition to anion density difference.

[Procedure] MD simulation was conducted on an amorphous AlF₃/Al₂O₃ structure (7×7×5 nm³ for both blocks). The hetero-oxide layer structure was annealed by the isothermal-isobaric MD calculation for 10 ps, thermostated at 1000 K by speed scaling with keeping the pressure at 1 atm. Finally, the structure was cooled down in 10 ps. For the experimental study, MOS capacitors with bilayer Al-based dielectrics were prepared by using several combinations of dielectric materials. ~ 5.4-nm-thick SiO₂ was formed on p-type Si substrates by thermal oxidation., followed by rf sputtering of AlF₃, Al₂O₃ and AlN targets to form Al₂O₃/AlN_xO_y and AlN_xO_y/AlF_xO_y stacks with different thicknesses. After PDA at 500 - 600 °C in 0.1% O₂, Au gate electrodes were deposited for making MOS capacitors. The composition of AlN-sputtered films after PDA was confirmed as Al₂NO_{1.5} by XPS.

[Results and Discussions] MD simulation of Al₂O₃/AlF₃ was performed and the calculated potential profile successfully reproduced the experimentally observed dipole direction, as shown in Fig. 1. The displacements of F⁻ and O²⁻ anions near interface were calculated as shown in Fig. 2. The positive and negative values mean migration from Al₂O₃ to AlF₃ and from AlF₃ to Al₂O₃, respectively. A preferential migration of O²⁻ anion from Al₂O₃ to AlF₃ was observed whereas the migration directions and distances of F⁻ anions were likely to be random. This result is consistent with the idea that the driving force of anions migration at the interface is determined by anion density difference even for multi-anion systems and that this driving force determines the dipole layer direction. We consider charge separation due to the inter-diffusion of anions with different valence numbers (F⁻ and O²⁻) which may enhance the dipole layer strength, could be another important factor to explain the relatively large negative V_{fb} shift (~ -0.5 V) experimentally observed at AlFO/Al₂O₃ which we have reported [2].

Other systems, Al₂O₃/Al₂NO_{1.5} and Al₂NO_{1.5}/Al₂FO_{2.5}, were also experimentally studied and the observed interface dipole strengths are compared with our previous reports on AlF_xO_y/Al₂O₃ systems, are shown in Fig. 3. For nitride interface we can hardly observe V_{fb} shift after extrapolating the fitting to the V_{fb} of the reference structure even though the anion densities are quite different ($\sigma(\text{Al}_2\text{O}_3) = 0.171 \text{ \AA}^{-2}$, $\sigma(\text{AlF}_3) = 0.162 \text{ \AA}^{-2}$, and $\sigma(\text{AlN}) = 0.132 \text{ \AA}^{-2}$). Although this could be the results of the opposite effect of the differences in the anion valences between N³⁻ and F⁻ to the anion density differences, it might indicate the limitation of the applicability of "anion density difference" model which works for the oxide/fluoride interface but not suitable to the interfaces with nitrides.

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[Ref] [1] K. Kita and A. Toriumi, *APL* **94**, 132902 (2009). [2] J. Fei et al, The 63rd JSAP Sping Meeting, 20p-S221-6 (2016).

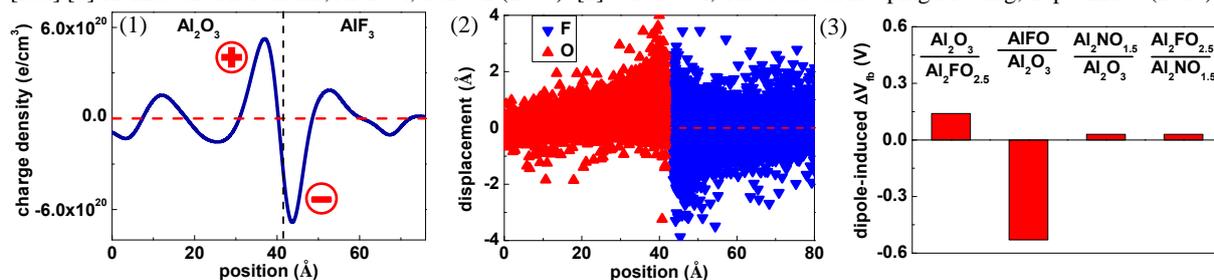


Fig. 1. Charge profile of Al₂O₃/AlF₃ structure after MD calculation, which shows an identical dipole direction as our experimental results on Al₂O₃/AlF_xO_y. 2. Perpendicular-to-interface displacements of F⁻ and O²⁻ at different positions. 3. Comparison of the interface dipole induced ΔV_{fb} of four Al-based dielectric interfaces which were extracted from the experimental results.