Study on dipole layer formation and its origin at Al₂O₃/AlF_xO_y and Al₂O₃/AlN_xO_y multi-anion dielectric interfaces by considering anion areal density and valence differences

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Abstract

Dipole layer formation was experimentally observed at AlF_xO_y/Al_2O_3 interface. Molecular dynamic calculation of AlF_3/Al_2O_3 demonstrates a preferential migration of O from Al_2O_3 to AlF_3 which suggests anion migration due to the density difference could determine the direction of the dipole layer formed at this interface. However, charge separation due to the difference in the anion valences should also be taken into consideration. These factors may also explain the experimental results of Al_2O_3/AlN_xO_y systems.

1. Introduction

Incorporation of materials with high dielectric constants can reduce leakage current when capacitance is maintained [1]. It is also regarded as a promising strategy to manipulate the threshold voltage of MOSFETs with the dipole layer formed at high-k oxide/SiO₂ interfaces [2]. Even though the driving force of dipole layer formation at high-k oxide/SiO₂ interfaces is still not well understood, oxygen migration due to the oxygen areal density difference [2] has been widely accepted to be a possible origin. In this paper, we extended this concept to the Al-based-multi-anion dielectric stacks $(Al_2O_3/AlF_xO_y \text{ and } Al_2O_3/AlN_xO_y)$ by considering the total anion areal density as the key parameter instead of oxygen areal density. Note that the difference in anion areal densities ($\sigma(Al_2O_3) = 0.171 \text{ Å}^{-2}$, $\sigma(AlF_3) = 0.162 \text{ Å}^{-2}$, and $\sigma(AlN) = 0.132 \text{ Å}^{-2}$) is estimated using the unit volumes containing one anion which were calculated based on their crystallographic data. These interfaces are shared by a same kind of cations but different kinds of anions. Thus the difference in the anion valences is also expected to affect the dipole layer formation process in addition to the anion areal density difference. The total effects of those possible factors are discussed based on theoretical calculation and experiential results of Al₂O₃/AlF_xO_y as well as Al₂O₃/AlN_xO_y. 2. Experimental

After thermal growth of oxide on Si, AlN, AlF₃, and Al₂O₃ targets were sputtered to form four kinds of Al-based double dielectric stacks (**Fig.1**). The samples were annealed in 0.1% O₂ ambient under different temperatures (400-600 °C), followed by the deposition of Au gate electrode, to form MIS capacitors. As the final step, forming gas annealing at 400 °C was conducted. The V_{fb} values were extracted from the capacitance-voltage characteristics measured at 1 MHz. The compositions of the AlF_xO_y and AlN_xO_y were determined using X-ray photoelectron spectroscopy as Al₂FO_{2.5} for the structure with AlF_xO_y at bot-

tom, AlFO for the structure with AlF_xO_y on top, and $Al_2NO_{1.5}$ for AlN_xO_y .

3. Simulation Methods

The molecular dynamic (MD) simulation was performed using a commercial simulation package Fujitsu SCIGRESS ME. An AlF₃/Al₂O₃ interface model was constructed by stacking an amorphous AlF₃ block on an amorphous Al₂O₃ block ($7 \times 7 \times 5$ 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. This method has been reported to be effective to reproduce the dipole layer formation at high-k oxide/SiO₂ interfaces [3].



Fig. 1 Four kinds of Al-based double dielectric stacks to investigate the dipole-induced V_{fb} shift at Al₂O₃/AlF_xO_y and Al₂O₃/AlN_xO_y interfaces.

4. Results and Discussions

The CETs vs V_{fb} diagrams of $Al_2O_3/Al_2FO_{2.5}/SiO_2$ ($Al_2FO_{2.5}/SiO_2$ as the reference structure) and Al-FO/Al_2O_3/SiO_2 (Al_2O_3/SiO_2 as the reference structure) are shown in **Fig. 2**. The dipole-induced V_{fb} shift (indicated by ΔV) was observed after extrapolating the linear fittings to the CETs of the reference structures. The results indicates positive V_{fb} shift (~ + 0.15 V) at Al_2O_3 on Al_2FO_{2.5} interface and negative V_{fb} shift (~ - 0.5 V) of AlFO on Al_2O_3 interface. The negative dipole layer (dipole layers that shift V_{fb} negatively) formed at Al_2O_3 on AlF_xO_y interfaces are considered to be the results of two possible origins: oxygen migration from Al_2O_3 to AlF_xO_y because of the higher anion areal density of Al_2O_3 and intermixing originated charge exchange between F⁻ and O²⁻ anions (**Fig. 3**).



Fig. 2 CETs vs V_{tb} diagrams of $Al_2O_3/Al_2FO_2.5/SiO_2$ and $Al-FO/Al_2O_3/SiO_2$ stacks to determine the dipole-induced V_{tb} shift.

MD simulation was employed to understand which could be the actual factor that determines the dipole layer formation process. Formation of a dipole layer with an identical direction with experiments is reproduced at the simulated Al₂O₃/AlF₃ interface (Fig. 4(a)). Fig. 4(b) shows the perpendicular-to-interface displacements of individual F and O atoms at different positions of the initial blocks. Note that a positive value means migration from Al₂O₃ to AlF₃ and a negative value means migration with the opposite direction. Even though the enhanced migration of atoms just after attachment of the two blocks in the initial stage of the simulation may result in overestimation of the displacements at the interface, a strong tendency of O anion migration from Al₂O₃ to AlF₃ is clearly observed while the migration directions and distances of F anions are likely to be random, which is also supported by calculating the displacement distribution of anions near Al₂O₃/AlF₃ interface (region between the two green lines in Fig. 4(b)), as shown in Fig. 4(c). The cations in AlF₃ and Al₂O₃ actually followed the same tendency, however the average migration distances were smaller than those of the anions (data no shown), which was insufficient to compensate the unbalanced charges caused by anion migration. The results support the idea that anions migrate from high anion areal density side to low areal density side, which is useful in explaining the direction of the dipole layer. However, the relatively small anion areal density difference (< 10%) does not seem to be enough to cause the large experimentally observed negative V_{fb} shift (~ - 0.5 V) at AlFO on Al₂O₃ interface, the difference in the charges of the anions which would enhance the dipole in this system further, should also contribute when some extent of intermixing is expected.



Fig. 3 Possible origins of dipole layer formation due to anion density and valence differences at Al_2O_3/AlF_3 .



Fig. 4(a) Charge profile of $Al_2O_3/AlF_3/Al_2O_3$ structure after MD calculation. (b) Perpendicular-to-interface displacements of F and O atoms at different positions and (c) ratios of F and O near the interface (between the two green solid lines in (b)) that had different displacements. Another system, Al_2O_3/AlN_xO_y , was also experimentally

studied. The dipole-induced $V_{\rm fb}$ of $Al_2O_3/Al_2NO_{1.5}/SiO_2$ and Al₂NO_{1.5}/Al₂O₃/SiO₂ was extracted after plotting the CETs vs V_{fb} diagrams (Fig. 5). We can hardly observe a dipole-induced V_{fb} shift at Al₂NO_{1.5} on Al₂O₃ interface in Fig. 5(a) while Fig. 5(b) indicates no or a weakly positive dipole layer (indicated by ΔV) at Al₂O₃ on Al₂NO_{1.5} interface. The above result implies that at least a negative dipole layer did not form at Al2O3/Al2NO1.5 and this does not conflict with our considerations about the origins of the dipole layer formed at Al₂O₃/AlF_xO_y. If only the anion valence difference had been considered, a negative dipole layer should have existed at Al₂O₃ on Al₂NO_{1.5} after some extent of intermixing. Therefore oxygen migration from Al₂NO_{1.5} to Al₂O₃ which tends to induce a positive dipole layer could have certain effect on the Al₂O₃ on Al₂NO_{1.5} interface. This is natural if we consider the necessity of structure relaxation when the interface is formed. Thus the total effect of anion areal density and valence differences result in no or weakly positive dipole layer formation at Al₂O₃/Al₂NO_{1.5} (Fig. 6).



Fig. 5(a) CETs vs $V_{\rm fb}$ diagram of Al₂NO_{1.5}/Al₂O₃/SiO₂ and the reference structure (Al₂O₃/SiO₂). (b) $V_{\rm fb}$ vs CET diagram of Al₂O₃/Al₂NO_{1.5}/SiO₂ and the reference structure (Al₂NO_{1.5}/SiO₂).



Fig. 6 Opposite effects of anion areal density valence differences, the total effect of which may lead to weak or no dipole layer formation. 5. Conclusions

The dipole layer formation at AlF_xO_y (AlFO and $Al_2FO_{2.5}$)/ Al_2O_3 was experimentally observed. The MD calculation suggests oxygen migration originated from anion areal density difference could be the reason for such dipole layer formation, even though the effect of anion valence difference should also be considered to explain the large negative V_{fb} shift. The experimental results of no or weakly positive V_{fb} shift at Al_2O_3 on $Al_2NO_{1.5}$ are also explainable by the consideration of the same factors on dipole layer formation.

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