# Consideration on the interfacial dipole layer formation at non-SiO<sub>2</sub> oxide interfaces in the examples of MgO/Al<sub>2</sub>O<sub>3</sub> and HfO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>

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#### Abstract

Possible dipole layer formation at MgO/Al<sub>2</sub>O<sub>3</sub> and HfO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> interfaces has been demonstrated by the studying dipole-induced flatband voltage shift. When the large  $V_{\rm fb}$  shift at MgO/Al<sub>2</sub>O<sub>3</sub> shows a process dependence, the one at HfO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> is small in magnitude. The origin of dipole layer formation at these two interfaces will be further discussed based on molecular dynamics simulation results.

## 1. Introduction

Dipole layer formation which is regarded as a promising way to tune the threshold voltage of MOSFETs has been demonstrated at many high-k/SiO<sub>2</sub> interfaces [1]. However, study on dipole layer formation at gate dielectric interfaces in addition to the high-k/SiO<sub>2</sub> interfaces is quite limited. There is even a report suggesting that dipole layer formation could be unique at high-k/SiO2 interfaces because of the different structures between the high-k oxides and SiO<sub>2</sub>. To develop a strategy to fabricate a MOS capacitor with desirable V<sub>fb</sub>, understanding on the dipole layer formation at general dielectric interfaces is necessary. Therefore, in this work, we investigate the opportunity of dipole layer formation at non-SiO<sub>2</sub> oxide interfaces in the examples of MgO/Al<sub>2</sub>O<sub>3</sub> and HfO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> interfaces. Molecular dynamics (MD) simulation was on MgO/Al<sub>2</sub>O<sub>3</sub> to discuss the possible driving force of interface dipole layer formation .

# 2. Experimental and Simulation Methods

The MOS capacitors with tri-layer dielectrics consisting of thermally-grown SiO<sub>2</sub>, layer 1 and layer 2 and their references consisting of SiO<sub>2</sub> and layer 1 were fabricated. Layer 1 and 2 shown in **Table 1** were deposited by sputtering of oxide targets on p-Si substrates covered with thermal oxides. Post deposition annealing (PDA) 1 and 2 were conducted in 0.1% O<sub>2</sub> ambient after the deposition of each layer for 5 mins. The final step was deposition of Au gate electrodes and Al back-side electrodes to form MOS capacitors. The flatband voltages were determined from the capacitance-voltage characteristics measured at 1 MHz.

**Table 1** List of dielectrics and PDA temperatures.  $\sim 0.5$  nm  $Al_2O_3$ was capped on MgO to prevent moisture effect for Sample 1.

	Layer 1	PDA 1	Layer 2	PDA 2
	(bottom)	$T(\mathcal{C})$	(top)	$T(\mathcal{C})$
Sample 1	$Al_2O_3$	w/o, 600,	MgO	600 or
Reference 1		700, or 800	-	800
Sample 2 Reference 2	$Al_2O_3$	-	HfO <sub>2</sub> -	600

The molecular dynamic (MD) simulation was performed

following a standard condition [2]. An MgO/Al<sub>2</sub>O<sub>3</sub> interface was constructed by stacking an amorphous MgO block on an amorphous Al<sub>2</sub>O<sub>3</sub> block ( $7 \times 7 \times 5 \text{ nm}^3$  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 from 1000 to 300 K in 30 ps and maintained at 300 K for another 10 ps.

# 3. Results and Discussions

3.1 Dipole layer formation at MgO/Al<sub>2</sub>O<sub>3</sub>



**Fig. 1.** CV curves and CETs vs  $V_{fb}$  diagram of  $Al_2O_3(cap)/MgO/Al_2O_3/SiO_2$  stacks annealed at 800 °C (PDA 2).

A positive  $V_{fb}$  shift (~ + 0.3 V) was observed for MgO/Al<sub>2</sub>O<sub>3</sub> annealed at 600 °C (PDA 2) (not shown). However, a negative  $V_{fb}$  shift (~ - 0.5 V) at MgO/Al<sub>2</sub>O<sub>3</sub> is observed for the same structure annealed at 800 °C. The negative  $V_{fb}$  shift is determined from the CETs vs  $V_{fb}$  diagram of MgO/Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> stack annealed at 800 °C (PDA 2) (**Fig. 1**). The dipole-induced  $V_{fb}$  shift (indicated by  $\Delta V$ ) was observed after extrapolating the linear fitting to the CETs of the reference structure. As shown in **Fig. 2**, the positive  $V_{fb}$  shift was reduced to zero when PDA 1 (annealing before the deposition of MgO) was conducted. This implies that poor quality of Al<sub>2</sub>O<sub>3</sub> could induce an anomalous  $V_{fb}$  shift. But the negative  $V_{fb}$  shift, which is activated by higher temperature PDA 2, was not sensitive to the temperature of PDA 1.



Fig. 2. Process-dependent  $\Delta V_{dipole}$  at  $M_{gO}/Al_2O_3$  when the interfaces were annealed at 600 and 800 °C.



**Fig. 3.** Mg/(Mg+Al) ratios at different estimated depths in the  $MgO/Al_2O_3/SiO_2$  stacks annealed at 600 and 800 °C.

However, there are two possible explanations for this negative V<sub>fb</sub> shift: ionic migration limited just at MgO/Al<sub>2</sub>O<sub>3</sub> interface and Mg diffusion to the near SiO<sub>2</sub> region. So physical characterization to measure the Mg concentration at different depth of the stacks was carried out to investigate the Mg diffusion extent. For sample fabrication, 4 nm-MgO/5 nm-Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>/Si stacks were prepared and annealed at 600 or 800 °C for 5 min. Mg/(Mg+Al) ratios were determined by XPS with a TOA  $=45^{\circ}$  when plasma etching was performed. Fig. 3 shows the Mg/(Mg+Al) ratios of the two stacks at different depths. It shows that there is only small change in the profiles between 600 and 800 °C annealed stacks. The ratio drops to 20% when the top MgO layer was almost removed for the 800 °C annealed stack. The result indicates the limited migration of ions at MgO/Al<sub>2</sub>O<sub>3</sub> should be the cause of negative dipole layer formation, rather than the Mg diffusion to the bottom SiO<sub>2</sub> interface.

**Table 2** Average displacement of each ion species at the simulated  $Al_2O_3/M_8O$  interface (within ~1 nm).

	Al	$O(Al_2O_3)$	Mg	O (MgO)
Average dis- placement (Å)	+1.30	+1.29	-0.16	-0.11

MD simulation was performed on MgO/Al<sub>2</sub>O<sub>3</sub> interface to investigate the relationship between interface atomic migration and charge separation. A charge separation with the same direction as the one to cause the negative  $V_{fb}$  shift after 800 °C annealing was observed. The average displacements (perpendicular-to-interface position differences after and before the MD simulation) of ions at near interface region (within the region ~ 1 nm around interface) were calculated and shown in Table 2. Note that the positive and negative values mean the migration from Al<sub>2</sub>O<sub>3</sub> to MgO and that to the opposite direction. It indicates charge-balanced migration of Al<sup>3+</sup> and O<sup>2-</sup> in Al<sub>2</sub>O<sub>3</sub> because of the comparable average displacements. However, the average displacement of  $Mg^{2+}$  was much larger than that of  $O^{2-}$  in MgO. Therefore the unbalanced ionic motion in MgO could be responsible to the negative dipole layer formation at MgO/Al<sub>2</sub>O<sub>3</sub>. Such dominant cation migration effect on dipole layer formation, which is not expected in the oxygen density difference model, would be due to the reactivity of MgO/Al<sub>2</sub>O<sub>3</sub> interface [3]. The dominant effect of Mg cation in dipole layer formation is consistent with our reports on the reactive MgO/SiO<sub>2</sub> interface [4]. 3.2 Dipole layer formation at  $HfO_2/Al_2O_3$ 

Next, the CV curves and CETs vs  $V_{fb}$  diagram of HfO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> stack annealed at 600 °C were investigated as shown in **Fig. 4**. A negative dipole induced  $V_{fb}$  shift of ~ -0.07 V is observed at HfO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>. Even though the magnitude is quite small, the direction of the  $V_{fb}$  shift is explainable by the oxygen migration due to the oxygen density difference [5]. At this non-reactive interface, it is reasonable that oxygen migration should play a dominant role [2]. The weak dipole should be because of a smaller driving force of oxygen migration than that of high-k/SiO<sub>2</sub> interfaces.



Fig. 4. CV curves and CETs vs  $V_{fb}$  diagram of  $HfO_2/Al_2O_3/SiO_2$  stacks annealed at 600 °C (bottom).

# 4.3 Difference in the origin of dipole layer formation at high-k/high-k and high-k/SiO<sub>2</sub> interfaces

The above results suggest that dipole layer formation at high-k/high-k interface is not that different from high-k/SiO<sub>2</sub> interface [2, 4]. However, the observation that negative dipole layer formation at MgO/Al<sub>2</sub>O<sub>3</sub> requires activation at higher temperature could be due to the higher activation energy of reaction between MgO and Al<sub>2</sub>O<sub>3</sub> than that between MgO and SiO<sub>2</sub> [3, 6]. The weak dipole layer formed at HfO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> with such large areal oxygen density difference (>15%) could be because of a smaller driving force to displace oxygen at ionic/ionic interface than at ionic/covalent interface [5].

## 4. Conclusions

Possible dipole layer formation has been experimentally demonstrated at non-SiO<sub>2</sub> oxide interface in the examples of MgO/Al<sub>2</sub>O<sub>3</sub> and HfO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>. The dipole-induced V<sub>fb</sub> shift at MgO/Al<sub>2</sub>O<sub>3</sub> has a process dependence. The negative V<sub>fb</sub> shift could be the result of unbalanced cation and anion migration in MgO activated at higher temperature. The small negative V<sub>fb</sub> shift at HfO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> is explainable by oxygen migration due to the oxygen density difference when the driving force could be smaller.

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**References:** [1] N. Mise et al. IEDM Tech. Dig., 2007, p. 527. [2] K. Shimura et al., *JJAP*, **55**, 04EB03 (2016). [3] E. B. Watson and J. D Price, *Geochimica et Cosmochimica Acta*, **66**, 2123 (2002). [4] J. Fei and K. Kita, *JJAP*, **55**, 04EB11 (2016). [5] K. Kita and A. Toriumi, *APL*, **94**, 132902 (2009). [6] G. W. Brindely and R. Hayami, *Philosophical Magazine*, **12**, 505 (2006).