Positive and Negative Dipole Layer Formation at High-k/SiO₂ Interfaces Simulated by Classical Molecular Dynamics

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Abstract

We show that the positive and negative dipole formation in metal-high-k gate stacks is explained by the imbalance between cation and anion migrations across the high- k/SiO_2 interface. A series of molecular dynamics simulations is carried out for Al₂O₃/SiO₂, MgO/SiO₂, and SrO/SiO₂ interfaces, which reproduce the experimentally observed flat band voltage (V_{FB}) shifts of these systems. At Al₂O₃/SiO₂ interface, a dipole layer is formed by the oxygen migration from Al₂O₃ side to SiO₂ one. Opposite dipole moment appears at MgO/SiO₂ and SrO/SiO₂ interfaces due to a preferential migration of metal cations in high-k oxide toward the SiO₂ layer. Thus, oxygen ion and metal cation migrations are both important to understand the origin of the V_{FB} shift in high-k gate insulator.

1. Introduction

The threshold voltage shift in the high-k/metal gate stack is known to be caused by the electric dipole layer formation at the high-k/SiO₂ interface [1]. Among several proposed mechanisms for the dipole layer formation, the oxygen ion migration model [2] is noteworthy due to its simplicity and potential to be applicable to wide variety of high-k materials. The direction and magnitude of the dipole was found to be a good correlation with the density difference of oxygen atoms between high-k oxide and SiO₂, which inspired the model of oxygen ion migration from higher-oxygen-density side to a lower-oxygen-density one [2]. In previous works, a part of the authors succeeded in reproducing the dipole layer formation at Al_2O_3/SiO_2 by classical molecular dynamics (MD) simulation [3, 4], in which the dipole layer was formed by the oxygen ion migration.

In this paper, we report on a MD simulation reproducing the dipole formation at MgO/SiO₂ and SrO/SiO₂ interfaces, both of which is known to be oriented oppositely from that at the Al₂O₃/SiO₂ interface. We have found that the metal cation migration is also important to understand the origin of the dipole layer.

2. Simulation Methods

The MD simulation was conducted by using the commercial software from Fujitsu Ltd., SCIGRESS. Fig. 1 shows the simulated high-k/SiO₂ interface model, which is constructed by sandwiching the amorphous high-k oxide block in between amorphous SiO₂ blocks. The high-k block and the SiO₂ block were prepared independently by melting crystalline structure at 4000 K. Next, these amorphous oxide blocks were connected to each other and annealed by the isothermal-isobaric MD calculation at 1000K at atmospheric pressure for 20ps. Finally it was cooled down to 300 K. The model size is 6.5nm × 6.5nm × 16.5nm. A three-dimensional periodic boundary condition was posed throughout the simulation. The MD simulation was performed by employing

Born-Mayer-Huggins potential defined by Eq. (1) together with the CIM parameter set [5] summarized in Table 1. In CIM parameter set, ionic charge is equal to the valence number. Other parameters were determined to reproduce crystalline oxide structures at atmospheric pressure.

3. Results and Discussion

Fig. 2 shows the charge density profiles across the highk/SiO₂ interface model. Here, we define the positive dipole as that oriented from the SiO₂ side to the high-k side. A positive dipole appears at the Al₂O₃/SiO₂ interface, whereas a negative dipole layer is formed at the MgO/SiO2 and SrO/SiO2 interfaces. The dipole orientation at Al₂O₃/SiO₂ and SrO/SiO₂ coincide with the prediction from the oxygen density difference [2], i.e., the oxygen density of Al₂O₃ is higher than that of SiO₂ and that of SrO is lower than that of SiO₂. In case of MgO/SiO₂ interface, it has been experimentally reported that a negative dipole is observed in spite of the oxygen density of MgO is higher than SiO₂ [6]. which is also reproduced in the present MD simulation. Fig. 3 shows the electrostatic potential profile. The build-in potential is +2.12V at Al_2O_3/SiO_2 , -2.07V at MgO/SiO_2 and -3.13V at SrO/SiO_2 interface. Though the build-in potentials are overestimated compared with the experimental V_{FB} shifts due to the large charge values of CIM parameter set [5], the direction of the potential shift agrees well with experimental results.

Fig. 4 shows the magnified images of the high-k/SiO₂ interfaces. At the Al₂O₃/SiO₂ interface, oxygen ions in Al₂O₃ preferentially migrate to SiO₂. Contrary, at the MgO/SiO₂ and the SrO/SiO₂ interface, both oxygen ions and the metal cations (Mg⁺, Sr⁺) migrate to the SiO₂ side, resulting in the formation of a silicate layer at the interface.

To clarify the most contributed ion species to the electric dipole, we estimated the charge migration moment (CMM) for each species, which is defined as Eq. (2). As illustrated in Fig. 5, CMM is the integration of the differential atom density profile n(r) from the initial step function distribution $\theta(r)$ multiplied by the distance r from the interface. The origin of r is set such that $n(0) = \bar{n}/2$, where \bar{n} is the ion density of bulk region.

Table 2 shows the CMM of each high-k/SiO₂ interface. The total CMM of Al₂O₃/SiO₂ is +1.93 e \cdot nm, which is mainly caused by the positive CMM component of Al₂O₃ side due to the predominant migration of O_{Al}⁻ (oxygen ion in Al₂O₃) toward SiO₂ layer. In case of MgO/SiO₂, the CMM component of MgO decreases from that of Al₂O₃, owing to the enhanced migration of metal cation (Mg⁺). In case of the SrO/SiO₂, the CMM component of high-k side further decreases, which means that the metal cations (Sr⁺) migrate comparable to the oxygen ions O_{Sr}⁻.

These results mean that the dipole layer formation at high- k/SiO_2 interface should be explained by not only the oxygen ions but also the metal cations in SiO₂ and high-k oxides.

4. Conclusion

We have reproduced qualitatively the positive and negative V_{FB} shifts at high-k/SiO₂ interfaces by means of classical MD simulation, including the negative V_{FB} shift of MgO/SiO₂ which cannot be explained by the oxygen density difference accommodation model. The origin of the dipole layer formation is analyzed in terms of the charge migration moment (CMM). The results show that the metal cation migration is also important to understand the origin of the dipole layer.

Acknowledgments

6.5nm

1 (a)

Charge density [10²¹.e/cm³]

-1

2

3.5

Electrical potential [V]

Al₂O₃/SiO₂ MgO/SiO₂

- SrO/SiO₂

CMM =

■<u>SiO</u>₂ <u>→high-k</u>

 $\theta(r) = \begin{cases} 0 \ (r > 0) \\ \overline{n} \ (r < 0) \end{cases}$

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high-k

🔵 Sr

SiO

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$$V(r_{ij}) = \frac{q_i q_j}{r_{ij}} - \frac{C_i C_j}{r_{ij}^6} + f(B_i + B_j) \exp\left[\frac{A_i + A_j - r_{ij}}{B_i + B_j}\right]$$

Equation (1) Interatomic potential function of Born-Mayer-Huggins type. The first term is the Coulombic interaction. The second is van der Waals' potential. The last term describes the short range repulsion. f is a standard



AL₀

Fig. 4 Magnified images of (a) Al₂O₃/SiO₂ interface, (b) MgO/SiO₂ interface, and (c) SrO/SiO₂ interface.

MgO

SiO

Sr_O

SiO.



Fig. 5 Atom density profiles across the high-k/SiO₂ interface to calculate CMM. (a) Si ion and (b) metal ion in high-k material.

	200-
Equation (2) Definition of the Charge Migration Moment	0
CMM). r means the distance from z-position($r = 0$)	5.6
where the atom density is half of the bulk density \bar{n} .	5.0
CMM is integration of the differential atom density	
profile $n(r)$ from the initial step function distribution $\theta(r)$	

 \blacksquare high-k \rightarrow SiO₂

 $\theta(r) = \begin{cases} \bar{n} & (r > 0) \\ 0 & (r < 0) \end{cases}$

6

 $\int_{0}^{\infty} qr\{n(r) - \theta(r)\}dr$

z [nm]

Fig. 3 Potential profile across high-k/SiO₂ interfaces.

multiplied by the distance r from the interface.

Table 2 CMM for each species, net CMM in oxide, and total CMM value of each high-k/SiO2 interf	ace.
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Oxide	SiO ₂		Al ₂ O ₃		SiO ₂		MgO		SiO ₂		SrO	
Ion species	Si ⁺	Osi	Al^+	O _{Al}	Si ⁺	O _{Si} ⁻	Mg^+	O _{Mg} ⁻	Si ⁺	Osi	Sr^+	O _{Sr} -
CMM for each species	+19.95	-23.96	-21.75	+27.69	+18.14	-23.68	-24.74	+28.86	+24.53	-26.99	-16.19	+16.38
Net CMM in oxide [e•nm]	-4.	01	+5.94		4 -5.54		+4.12		-2.46		+0.19	
Total CMM [e•nm]	+1.93			-1.42			-2.27					