Positive and Negative Dipole Layer Formation at High-k/SiO$_2$ 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 Al$_2$O$_3$/SiO$_2$, MgO/SiO$_2$, and SrO/SiO$_2$ interfaces, which reproduce the experimentally observed flat band voltage ($V_{FB}$) shifts of these systems. At Al$_2$O$_3$/SiO$_2$ interface, a dipole layer is formed by the oxygen migration from Al$_2$O$_3$ side to SiO$_2$ one. Opposite dipole moment appears at MgO/SiO$_2$ and SrO/SiO$_2$ interfaces due to a preferential migration of metal cations in high-k oxide toward the SiO$_2$ 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/SiO$_2$ 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 SiO$_2$ which 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$_2$O$_3$/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/SiO$_2$ and SrO/SiO$_2$ interfaces, both of which is known to be oriented oppositely from that at the Al$_2$O$_3$/SiO$_2$ 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/SiO$_2$ interface model, which is constructed by sandwiching the amorphous high-k oxide block in between amorphous SiO$_2$ blocks. The high-k block and the SiO$_2$ 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 $\times$ 6.5nm $\times$ 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 high-k/SiO$_2$ interface model. Here, we define the positive dipole as that oriented from the SiO$_2$ side to the high-k side. A positive dipole appears at the Al$_2$O$_3$/SiO$_2$ interface, whereas a negative dipole layer is formed at the MgO/SiO$_2$ and SrO/SiO$_2$ interfaces. The dipole orientation at Al$_2$O$_3$/SiO$_2$ and SrO/SiO$_2$ interfaces coincide with the prediction from the oxygen density difference [2], i.e., the oxygen density of Al$_2$O$_3$ is higher than that of SiO$_2$ and that of SrO is lower than that of SiO$_2$. In case of MgO/SiO$_2$ interface, it has been experimentally reported that a negative dipole is observed in spite of the oxygen density of MgO is higher than SiO$_2$ [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$_2$O$_3$/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/SiO$_2$ interfaces. At the Al$_2$O$_3$/SiO$_2$ interface, oxygen ions in Al$_2$O$_3$ preferentially migrate to SiO$_2$. Contrary, at the MgO/SiO$_2$ and the SrO/SiO$_2$ interface, both oxygen ions and the metal cations (Mg$^+$, Sr$^+$) migrate to the SiO$_2$ 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 $k(r)$ 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/SiO$_2$ interface. The total CMM of Al$_2$O$_3$/SiO$_2$ is +1.93 e$^-$ nm, which is mainly caused by the positive CMM component of Al$_2$O$_3$ side due to the predominant migration of O$_{Al}$ (oxygen ion in Al$_2$O$_3$) toward SiO$_2$ layer. In case of MgO/SiO$_2$, the CMM component of MgO decreases from that of Al$_2$O$_3$, owing to the enhanced migration of metal cation (Mg$^+$). In case of the SrO/SiO$_2$, 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 SiO$_2$ and high-k oxides.
4. Conclusion
We have reproduced qualitatively the positive and negative V_{FB} shifts at high-k/SiO_2 interfaces by means of classical MD simulation, including the negative V_{FB} shift of MgO/SiO_2 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
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References

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

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 force of 6.948 kJ Å^{-1} mol^{-1}.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>O</th>
<th>Si</th>
<th>Al</th>
<th>Mg</th>
<th>Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>( q[\Theta] )</td>
<td>-2</td>
<td>4</td>
<td>3</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>( \bar{A}[\AA] )</td>
<td>1.626</td>
<td>1.012</td>
<td>1.064</td>
<td>1.161</td>
<td>1.632</td>
</tr>
<tr>
<td>( B[\bar{A}] )</td>
<td>0.085</td>
<td>0.080</td>
<td>0.080</td>
<td>0.080</td>
<td>0.080</td>
</tr>
<tr>
<td>( C[\bar{A}^2/(kJ/mol)^2] )</td>
<td>20</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>15</td>
</tr>
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</table>

Table 1 Potential parameters of Eqn. (1).

<table>
<thead>
<tr>
<th>Oxide</th>
<th>SiO_2</th>
<th>Al_2O_3</th>
<th>SrO</th>
</tr>
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<td>( N_{\text{atom}} / \text{nm}^2 )</td>
<td>23.68</td>
<td>32.56</td>
<td>19.95</td>
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<td>( N_{\text{atom}} / \text{nm}^2 )</td>
<td>34.98</td>
<td>42.84</td>
<td>22.69</td>
</tr>
<tr>
<td>( N_{\text{atom}} / \text{nm}^2 )</td>
<td>35.25</td>
<td>43.09</td>
<td>22.86</td>
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<td>43.09</td>
<td>22.86</td>
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</tbody>
</table>

Table 2 CMM for each species, net CMM in oxide, and total CMM value of each high-k/SiO_2 interface.