

Considering Possible Descriptors for Dipole Moment at High-k/SiO₂ Interfaces

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Abstract

We investigate the relationship between the dipole moment (DM) and several parameters to find which of these parameters is a better descriptor of the dipole layer formation in high-k/SiO₂ interfaces. A series of molecular dynamics simulations is carried out for 1300 different high-k/SiO₂ structures, made from various mixes of Al, Mg, Ti and Sr oxides, and the obtained DMs are plotted against the oxygen density, the cation charge, and the coordination number. Oxygen density shows a big area that strongly disagrees with the expectations of the Oxygen Density Difference Accommodation Model. Cation charge shows a high correlation coefficient, but the existence of same-charge/different-DM samples is an issue. The coordination number was introduced to solve that, but it shows worse results overall.

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 a wide variety of high-k materials. According to this model, the direction and magnitude of the dipole is correlated to the oxygen density difference between both materials, which causes the oxygen atoms from the higher-density material to migrate to the lower-density material, creating the dipole through charge relocation. [2]. In previous works, part of the authors successfully reproduced the dipole layer formation at Al₂O₃/SiO₂, MgO/SiO₂ and SrO/SiO₂ through classical molecular dynamics (MD) simulation [3], where the dipole layer was found to be formed by both the oxygen ion migration (Al₂O₃) and the cation migration (MgO and SrO).

In this work, we built a large sample size of multicomponent oxides through MD simulation and have considered several parameters (oxygen density, cation charge and coordination number) that could act as definers of the direction and magnitude of the dipole moment. Plotting the dipole moment against these parameters, we have found that the metal cation related parameters have a higher correlation to the dipole moment.

2. Simulation Methods

The MD simulation was conducted by using the commercial software from Fujitsu Ltd., SCIGRESS. The high-k block and the SiO₂ block were prepared separately by melting the crystalline structure at 4000 K. Next, the amorphous structures were connected to each other and annealed by the isothermal-isobaric MD calculation at 1000K and atmospheric pressure for 20ps, and cooled down to 300 K. The model size is 7 nm × 7 nm × z nm (z depends on the density of the high-k oxide, all samples have ~40000 atoms). The MD simulation was performed by employing Born-Mayer-Huggins potential defined by Eq. 1 together with the CIM (Completely Ionic Model) parameter set [4] (Table 1). This parameter set defines the ionic charge as the valence number. atmospheric pressure.

3. Results and Discussion

Fig. 1 shows the correlation between the dipole moment and the oxygen density. Oxygen density is represented as normalized oxygen density (NOD) with respect to SiO₂. First observed issue is the correlation factor ($r = 0.680$), which is considerably low. Adding to that, the Al, Mg, Sr and Ti pure oxides are clearly not arranged linearly. Most importantly, according to the oxygen density difference accommodation model, samples with $NOD < 1$ should always present negative dipoles, while samples with $NOD > 1$ should be positive. This seems to be true in the $NOD > 1$ zone, but the red-dotted area shows a huge sample size that clashes with the expectations set by the oxygen density difference accommodation model. This leads us to think that the oxygen density, at least by itself, is not a good definer of the direction and magnitude of the dipole moment.

Next, as seen in Fig. 2, we investigated the correlation between the dipole moment and the cation charge, defined as the mean valence number of the cations. In this case, the correlation factor ($r = 0.841$) is much higher than that of the normalized oxygen density, and the pure oxides are arranged linearly. However, several points with the same mean valence value and different dipole moment are found in the plot, meaning that, albeit the relationship seems linear, it is impossible to accurately correlate the cation charge to the dipole moment. Additionally, even though the sample size can be considered large (1300 different compounds), the actual number of different species used is limited, as only Al, Mg, Ti and Sr were used. Adding more species could result in a lower correlation coefficient.

With all that, the cation charge shows encouraging results towards finding a good definer of the dipole moment, but it is clearly not good enough on its own. Next, the coordination number was introduced as a possible parameter that might overcome the issues found with the cation charge.

Fig. 3 shows the dipole moment plotted against the coordination number Z_{ij} (Eq. 2a). Compared to the cation charge, the distribution has lost linearity, and there is a higher dispersion of data in the positive dipole area. To solve this, several modifications to the coordination number equation were contemplated.

Fig. 4 and Fig. 5 plot the dipole moment against the coordination numbers X_{ij} (Z_{ij}/r , Eq. 2b) and Y_{ij} ($Z_{ij} \cdot r$, Eq. 2c), respectively. The former shows better results, although still far from the ones obtained for the cation charge. Therefore, we are still trying to find a better fit.

4. Conclusion

We have built a large sample size of multicomponent high-k/SiO₂ structures through MD simulation to obtain their dipole moment. The proposed defining factors for the dipole formation showed that cation related parameters seem to have a better correlation to the dipole direction and magnitude, although charge itself is not accurate enough.

Lastly, the coordination number does not show improvement over the cation charge, although Y_{ij} shows promising results.

Acknowledgments

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References

[1] A. Toriumi and T. Nabatame, High Permittivity Gate Dielectric Materials, ed. by S. Kar, Springer (2013) 263.

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

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 force of $6.948 \text{ kJ } \text{Å}^{-1} \text{ mol}^{-1}$.

$$a) \quad Z_{ij}(r) = \sum_n \frac{N_j}{V} g_{ij}(n \cdot \Delta r)$$

$$b) \quad X_{ij}(r) = \sum_n g_{ij}(n \cdot \Delta r) \times \frac{1}{r}$$

$$c) \quad Y_{ij}(r) = \sum_n g_{ij}(n \cdot \Delta r) \times r$$

Equation (2) Coordination number (a) non-modified, (b) 1/r modified and (c) r modified. g_{ij} is the radial distribution function.

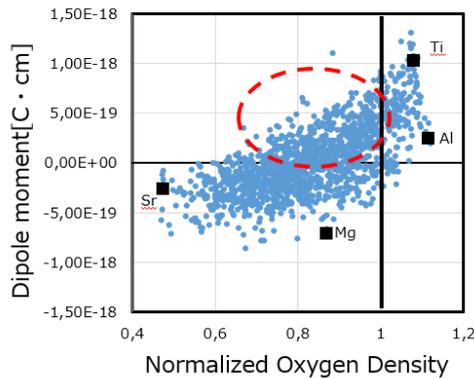


Fig. 1 Dipole moment VS oxygen density, normalized around SiO_2 OD ($R = 0.680$).

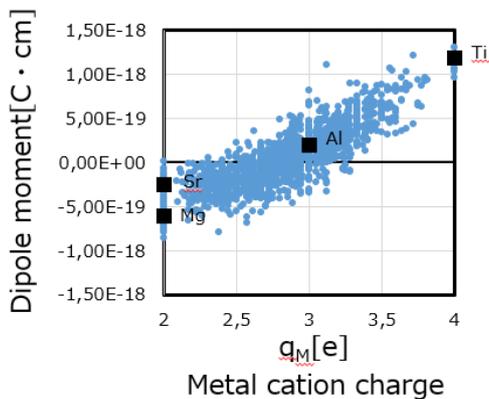


Fig. 2 Dipole moment VS cation charge ($R = 0.841$).

[2] K. Kita and A. Toriumi, APL 94, (2009) 132902.

[3] K. Shimura et al, Jpn. J. Appl. Phys. 55, (2016) 04EB03

[4] F. Yonezawa, Molecular Dynamics Simulations, Springer-Verlag (1990) 93.

[5] C-Y. Su et al., Thin Solid Films 520, (2012) 4908.

[6] S. Y. Lee et al., ECS Trans. 58, (2010) 53.

	Al	Mg	Ti	Sr
q	3	2	4	2
A	1.084	1.161	1.235	1.632
B	0.08	0.08	0.08	0.08
C	0	2	0	15
dipole	+	-	+	-

Table 1. CIM parameter set.

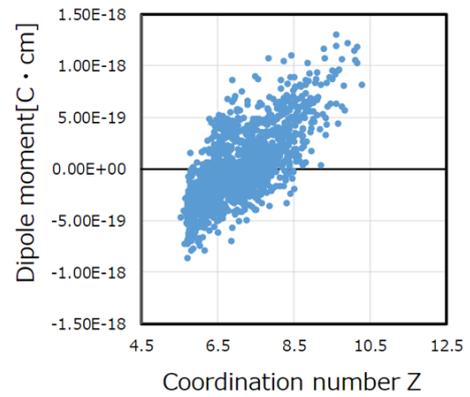


Fig. 3 Dipole moment VS coordination number Z_{ij} ($R = 0.734$).

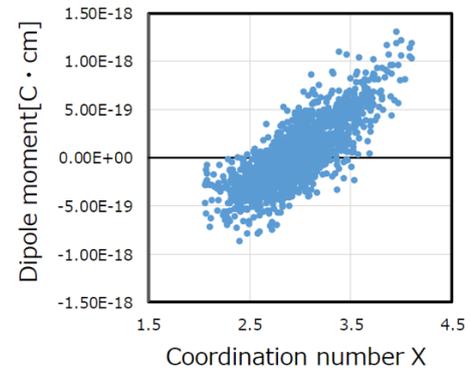


Fig. 4 Dipole moment VS coordination number X_{ij} ($R = 0.794$).

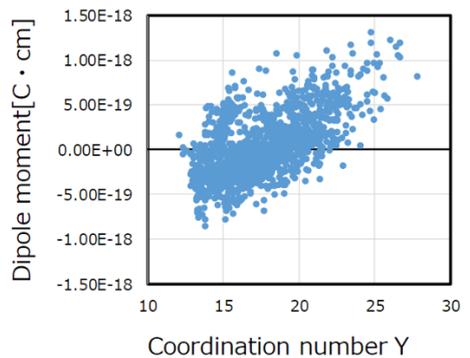


Fig. 5 Dipole moment VS coordination number Y_{ij} ($R = 0.604$).