

Theoretical Analysis of Oxygen Diffusion in monoclinic HfO_2

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1. Introduction

Recently, HfO_2 (hafnia) grown on Si substrates is widely studied as a potential candidate for replacing silicon dioxide as the gate dielectrics in scaled CMOS. At the interface between Si and hafnia, the interfacial layer has been formed. And this layer thickness increases by the post thermal annealing after the deposition process [1]. This fact indicates that atomic oxygen diffuses through hafnia. Foster et al. reported the interstitial oxygen diffusion in hafnia using the ultra-soft pseudopotential method [2]. They concluded that the O^{2-} diffuses in the bulk HfO_2 . In this report, we present the detailed analysis of the interstitial oxygen (O^{2+} , O^0 , O^{2-}) diffusion in hafnia using the first principles method with all electrons method. And we report the whole view of the diffusion process of oxygen with different charge states in hafnia.

2. Methodologies

Throughout this work, we used the Projector Augmented Plane Wave method (PAW) with the local spin density functional theory corrected by the generalized gradient approximation [3-5]. As for the Brillouin zone integration, one k-point sampling was employed. We used 250 eV for the cut off energy. In order to search for the diffusion path and the barrier height, we used the improved Nudged Elastic Band theory (NEB) [6]. We have used the $2 \times 2 \times 2$ multiple of the monoclinic HfO_2 crystal structure as the model for the bulk high-k film as shown in Fig. 1. Various charge states ($2+$, neutral and $2-$) of the interstitial oxygen are taken into account to study its diffusion path.

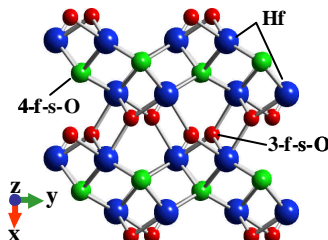


Fig. 1 The unit cell of the bulk monoclinic HfO_2 is shown. Oxygen atoms are classified by the 4-fold-sites or 3-fold-sites according to the number of the nearest neighbor Hf atoms.

3. Results and Discussion

First of all, it should be noted that the oxygen molecule

does not exist stably in bulk hafnia. This is different from the situation of SiO_2 case. There only exists metastable O_2 state. This molecule dissociates into two O atoms. And each oxygen atom couples with the 3-fold-site oxygen and forms the dimer structure. The dissociation energy barrier is only 5 meV for neutral O_2 molecule. The total energy of this state is lower than the metastable state by 1eV. This fact is valid for any charge states of the oxygen molecule, being different from the previous report [2].

In Fig. 2(a)-(c), we showed the stable position of the interstitial oxygen with the different charge states in hafnia. In hafnia, metal atoms are positively charged whereas oxygen atoms are negatively charged due to the fact that the centers of the 5d- and 6s-bands locate at higher position than those of the 2s- and 2p-bands of oxygen. The interstitial O^{2+} forms a trimer with the two neighboring 3-fold-sites oxygen atoms. This is because the interstitial oxygen lacks of two electrons in this case. Therefore, the additional oxygen couples with the two neighboring oxygen atoms. The wave function components analysis clearly shows the bonding among them. And the neutral interstitial O^0 atom forms the dimer coupled with the one nearest neighbor 3-fold-site oxygen atom. Contrary to the previous ones, the O^{2-} forms new 3-fold site among Hf

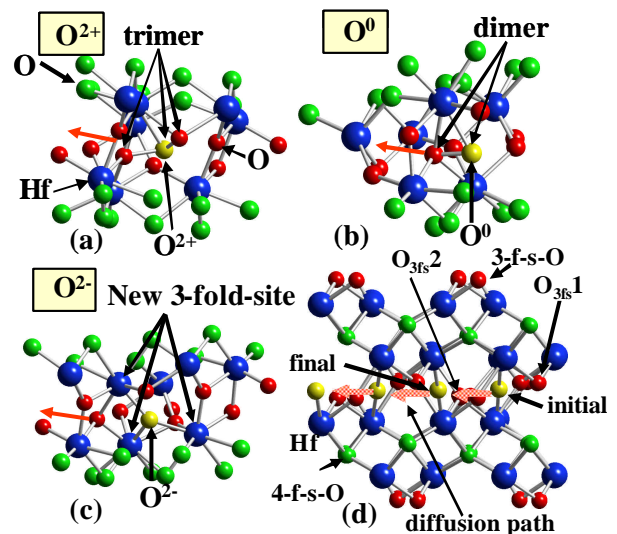


Fig. 2 The stable position of the interstitial oxygen for the corresponding charge states O^{2+} (a), O^0 (b) and O^{2-} (c). Diffusion path is schematically illustrated in (d).

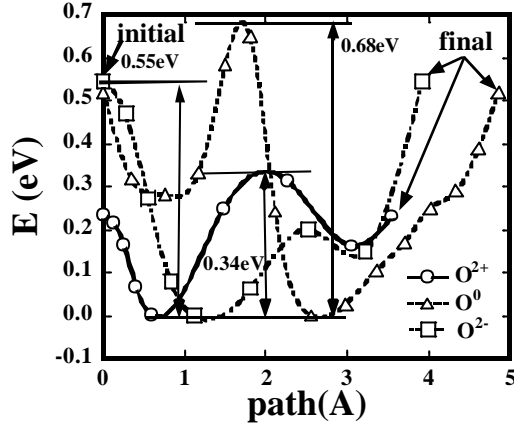


Fig. 3 The energy along the diffusion path are illustrated as a function of diffusion length for 3 charge states of the interstitial oxygen. The barrier height energy of the diffusion are also shown.

atoms. As this oxygen atom is already negatively charged, there appears the repulsive Coulomb force between the added atom and the neighboring oxygen atom.

In Fig.2(d), the diffusion path of the interstitial oxygen atom is schematically illustrated by big arrows. The interstitial oxygen atom with any charge state propagates along the path connected with 3-fold-sites oxygen atoms. In Fig.3, energy dependence along the diffusion path is plotted against the diffusion length. We obtain 0.34(2+), 0.68(neutral) and 0.55 eV (2-) as the barrier height energy for the interstitial oxygen atom. We also checked the diffusion path by using the simulated annealing method.

In Fig.4(a), we plotted the oxygen vacancy formation energy for several charge states as a function of the chemical potential (E_f) [7]. This figure shows that the most stable vacancy state is V_3^{2+} . The V_3^{2+} state is made by removing the doubly charged oxygen atom at 3-fold-site from the system. Therefore, its charge state is 2+.

As for the interstitial defects, 3 charge states (2+, neutral and 2-) are possible depending on E_f of the system as shown in Fig.4(b). The E_f is the quantity that measures

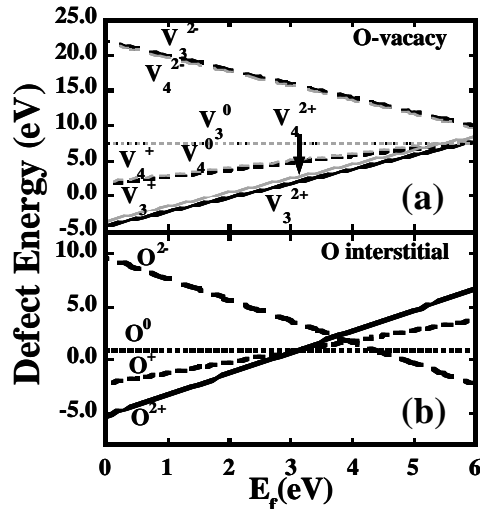


Fig. 4 The formation energies of the oxygen vacancy (a) and those of the interstitial oxygen (b) with several charge states are illustrated as function of the chemical potential.

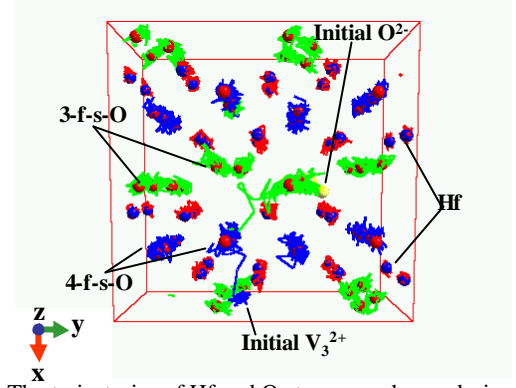


Fig. 5 The trajectories of Hf and O atoms are shown during 4 ps under the simulated annealing method using PAW.

the potentiality of additional electrons in the cell. Therefore, as E_f increases, the most stable charge state of the interstitial oxygen changes from 2+, neutral to 2- state. As for the O^+ state, two O^+ states can be decayed into O^{2+} and O^0 states [7].

In hafnia, there are lots of oxygen vacancies and those charge states are 2+ state. If there exists an interstitial O^{2-} atom, this atom interacts with the V_3^{2+} . As this attractive Coulomb interaction is a long range order, there might occur a pair annihilation between O^{2-} and V_3^{2+} . We simulated the defect pair annihilation process using the simulated annealing method. As O^{2-} and V_3^{2+} were initially placed in the same cell, then at finite temperature the O^{2-} atom propagated and kicked the 4-fold-site oxygen. Then this oxygen atom moved and occupied the vacancy site. In Fig.5 we showed the trajectories of the whole diffusion process.

4. Conclusions

In hafnia, the charge state of the interstitial oxygen atom can take 3 charge states depending on E_f . However, the O^{2-} does not contribute the diffusion process in hafnia because of the pair annihilation process between O^{2-} and V^{2+} defect pair. In the higher range of E_f , O^0 might contribute. And for the lower range of E_f , we think that the actual experimental situation satisfies this condition, the O^{2+} only contributes to the diffusion process in hafnia.

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References

- [1] T.Nabatame, T.Yasuda, M.Nishizawa, M.Ikeda, T.Horikawa and A.Toriumi, Extended Abstracts of SSDM 2002, p.64.
- [2] A.S.Foster, A.L.Shluger, and R.M.Nieminen, Phys.Rev.Lett. 89, 225901(2002) and A.S.Foster,F.L.Lopez Gejo, A.L.Shluger, and R.M.Nieminen, Phys.Rev.B65,174117(2002).
- [3] G.Kresse and J. Hafner,Phys.Rev.B47,558(1993) and G.Kresse, TUW,Thesis(1993).
- [4] P.E. Blöchl, Phys. Rev. B **50**, 17953 (1994).
- [5] G.Kresse and D.Joubert, Phys.Rev.B59,1758(1998).
- [6] G.Henkelman and H. Jonsson, J.C.P.,Vol 113,9978(2000).
- [7] A.Eichler, Phys. Rev. B64, 174103(2001).