Theoretical analysis of the Fermi level pinning in HfO₂/Si system induced by the interface defect states

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1. Introduction

The high-k gate dielectrics such as HfO₂ have been widely studied as the most promising candidate for replacing silicon dioxide in scaled CMOS. In the actual CMOS device application of HfO2 with poly-Si gate, the threshold voltage increase for p+poly Si gate on HfO₂ has been reported [1]. This is attributed to the effect of the Fermi Level Pinning (FLP) at the interface between the HfO₂ and p+poly-Si [1-2]. Up to now, two theoretical models are proposed to explain the FLP. One is the ab-initio calculations [1-3], showing that FLP occurs due to formation of the chemical bonds between Hf and Si atom as a result of deficit of oxygen atoms at the hetero-interface. The other attributes FLP to the dipole moments formation at the interface as a result of the charge transfer of oxygen vacancies in HfO₂ to the poly-Si layer, and estimates the threshold voltage shifts using the model calculation [4].

However, the detailed mechanism of the FLP remains unknown. This paper presents a new theoretical analysis to explain the mechanism of the FLP, based on the first principles calculations.

2. Methodologies

Throughout this work, we used the Projector Augmented Plane Wave (PAW) method with the local density functional theory corrected by the generalized gradient approximation [5-7]. The HfO₂/Si interface model structures are formed by using a new hypothetical crystal structure of HfO₂. This crystal structure C5 as shown in Fig.1(a) is found through the computational simulation in melting HfO₂ [8-10]. The lattice misfit at the HfO₂/Si interface structure is only 3% as illustrated in Fig.2(a). The number of atoms in our model systems ranges from 58 to 288. The vacuum layer is also present in our model to estimate the work function of HfO₂ properly. The surface layer of poly-Si is terminated by hydrogen atoms to simplify the analysis as shown in Fig.3(a).

3. Results and Discussion

First of all, it must be pointed out that the ratio of oxygen to metal atom at the ideal interface between Si and HfO₂ is 100%, whereas the same kind of the ratio at the interface of Si and SiO₂ (β -quartz) case is 50% as compared in Fig.2(a) and (b). At the SiO₂/Si interface, both Si and O atoms have the stronger covalent bonds than those of HfO₂/Si. Therefore, removing the oxygen atom at the interface never creates the interface state in the Si band gap because Si-Si dimer formation at the interface eliminates the interface states in the gap.

In Fig.3(a), we show the ideal interface model structure together with the dopant (As or B) site in poly-Si. The density of dopant atom is 1% in the poly-Si layer. In Fig.3(b), the total density of states (DOS) for this ideal interface structures is shown. The position of the Fermi level locates at the top of the valence bands. In Fig.3(c), the DOS for the As doped Si (n-type) case is shown. The Fermi level moves up and locates at the edge of the conduction bands. In the case of B doped Si (p-type), the DOS is illustrated in Fig.3(d). The Fermi level goes down and locates at the top of the valence bands. These figures clearly show that there is no FLP at the ideal interface structure for the HfO₂/Si.

We introduce the oxygen vacancy defect into the ideal interface as schematically shown in Fig.4(a) and relax the whole system to obtain the optimized structure as illustrated in Fig.4(b). The missing of the oxygen atom enhances the covalent bond energies between Si-1 and O-1 and between Si-2 and O-2, resulting in the bond length shrinkage between them. In Fig.5(a), we show the oxygen vacancy site and in Fig.5(b) we show the charge density corresponding to the defect state that appears in the band gap of Si. In Fig.5(c), the Fermi level locates at the defect induced interface state. In the case of the As doped Si, the Fermi level moves upward and locates at the edge of the conduction bands of Si as shown in Fig.5(d). This indicates that the FLP is not apparently observed for n-type doping. However, the Fermi level of the B-doped Si (p-type) case still remains near the interface state as illustrated in Fig.5(e). The FLP appears as a result of the missing of oxygen atom at the interface. In this calculation, 12.5% of the interface oxygen atoms are removed. It seems that there exists the covalent bond between the Hf and the Si atom near the vacancy defect (Fig.5(b)) which induces interface states and the FLP for p-type poly-Si gate. By analyzing wavefunction of the interface state, we conclude that this chemical bond is an accidental one and very difficult to be detected by XPS due to its weak bond energy.

The oxygen vacancy in the bulk HfO_2 layer creates the defect states below the top of the valence bands in this crystal interface model. The vacancy in the bulk HfO_2 never concerns the FLP phenomenon. In order to circumvent this

situation, the amorphous HfO_2/Si interface model structures are obtained by the melt and quench method [8-10]. In this model, the oxygen vacancy in the bulk HfO_2 , being located far away from the interface, creates the defect state in the conduction bands of Si. However, we cannot observe the FLP phenomenon by adding the B-dopant into Si layer, contrary to the prediction of Shiraishi et al.[4]. We think that the Shiraishi et al's model is applicable to the FLP of the $HfO_2/SiO_2/Si$ system. And we obtain the preliminary results for the FLP in $HfO_2/SiO_2/Si$ structures which can be interpreted by Shiraishi et al.'s scheme.

4. Conclusions

The mechanism of FLP is investigated using the first principles calculations. It is shown that the FLP originates from the oxygen vacancy defect at the interface. This defect induces the interface state below the conduction band minimum of Si. The resultant interface state shows a very weak bonding between the Si and the Hf atom near the oxygen vacancy.

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Fig. 1. A new hypothetical crystal structure of HfO_2 is shown in (a). The oxygen atom occupies the 3-fold-coordination site, whereas the Hf atom takes the 6-fold-coordination. In (b), the total energies of several typical HfO_2 structures are plotted as function of volumes. The new one C5 is stable in the low pressure phase.



Fig. 2. The atomic arrangements with nearby ideal interface structures are shown in (a) HfO_2/Si and (b) SiO_2/Si . The misfit of the lattice constants is 3% for the HfO_2/Si and 2.5% for the $SiO_2(\beta-quartz)/Si$ model system.



Fig. 3. The HfO₂/Si interface model is shown in (a). The interface is modeled by the vaccum/HfO₂/Si structure. The calculated DOS for non-doped case (b), n-type (c) and p-type case (d) are compared. The FLP does not appear for the ideal interface case.



(a) O^{0} -vacancy (b) bonding Fig. 4. The oxygen defect site at the interface is shown in (a). The oxygen vacancy enhances the bonding energies between Si-1 and O-1 and between Si-2 and O-2 as shown in (b), leading to the bond length shrinkage.



Fig. 5 The oxygen vacancy site is shown in (a). The charge density of the defect state is illustarated in (b). The local DOS of the nondoped (c), n-type case (d) and p-type case (e) are compared. The FLP appears in (e).