Atomic Level Insight into the Variation and Tunability of Band Alignment between Si and Amorphous SiO_2/HfO_2

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The band alignment between silicon and high-k dielectrics, which is a key factor in device operation and reliability, still suffers from uncontrolled fluctuations and ambiguous understanding. In this study, by conducting atomic-level *ab initio* calculations on realistic $Si/SiO_2/HfO_2$ stacks, we reveal the physical origin of band alignment fluctuations, i.e., the oxygen density-dependent interface and surface dipoles, and demonstrate that band offsets can be tuned without introducing other materials. This is instructive for reducing the gate tunneling current, alleviating device-to-device variation, and tuning the threshold voltage. Additionally, this study indicates that significant attention should be focused on model construction in emerging atomistic studies on semiconductor devices.

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Ultra-scaled transistors require the gate dielectric to have a high dielectric constant, large band gap, and tunable band offset with the channel material. Furthermore, HfO_2 is one of the most widely used dielectric materials because of its superior dielectric constant (∼25) and intriguing ferroelectricity.[1–5] Additionally, ferroelectricity can be engineered and stabilized via interfacial charge transfer and hole doping.[6–10] Nevertheless, the band gap of HfO_2 (∼5.8 eV) is not outstanding. Moreover, the band offsets between HfO_2 and Si have been experimentally reported to fluctuate significantly. The conduction band offset (CBO) can range from 1.1 to 2.2 eV, and the valence band offset (VBO) spans a range from 2.5 to 3.4 eV.[11–22] These types of large fluctuations inevitably result in device-to-device variations and are a severe problem for integrated circuits. Additionally, a CBO as small as 1.1 eV can be detrimental to an n-type MOSFET owing to electron tunneling. Thus, the exploration of ways to suppress the band offset variation is very important. Besides, the band offsets are closely related to the threshold voltage ($V_{\rm th}$),[23–25] and it is desirable to tune $V_{\rm th}$ regularly by controlling the band offsets.

The long-standing questions are why band alignment varies significantly and how to tune it in practice. In recent years, many pioneering studies have attempted to answer these questions. Sharia *et al.* built a series of crystalline SiO_2/HfO_2 interfaces and demonstrated that the band offsets were strongly correlated with the coordination of interfacial oxygen atoms and interface dipoles.[26] Bersch *et al.* investigated the full $Si/SiO_2/HfO_2$ stack at experiment and narrowed the band offset range by considering the effect of charging.[27] Broqvist reported the influence of the interface dipole on the band alignment at the Ge/GeO_2 interface.[28] A photoemission study conducted by Fujimura *et al.* confirmed the presence of an electrical dipole.[29] For the origin of the interface dipole, Kirsch *et al.* proposed an electronegativity model by comparing the effect of different doping elements,[30] whereas Kita *et al.* proposed an areal density model by correlating the dipole direction and magnitude with the areal density of oxygen atoms in different oxides and concluded that the dipole formation was due to oxygen movement as opposed to electronegativity difference.[31] This type of discrepancy requires further investigation. For dipole modulation, rare-earth element doping and a TiO_2 interlayer between SiO_2 and HfO_2 are both useful,[30,32] but strategies based on pure $Si/SiO_2/HfO_2$ have rarely been observed.

Hence, the origin of the interface dipole remains ambiguous, and the tunability of the dipoles without inducing other materials has not been highlighted. Here, we conduct *ab initio* calculations on a series of amorphous $Si/SiO_2/HfO_2$ interfaces to clarify the origin of the interface and surface dipoles and further verify the regular tunability of dipoles and band alignment solely by varying the interface environment.

To explore the effects of the areal density and electronegativity, two groups of $Si/SiO_2/HfO_2$ models were constructed; the difference was that the number of oxygen dangling bonds (O-) at the SiO_2 surface was 12 and 6, respectively. Here, the O dangling bonds are not oxy-

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gen vacancies and are passivated by Hf atoms after HfO_2 deposition. These two concentrations were chosen because they are sufficiently different for a very clear comparison of band offsets; other concentrations in between will have band offsets in between. To guarantee the statistical validity of the results, six models were prepared for each group, and their differences were determined by the random velocity at the beginning of the melt-quench dynamical simulations. The Si/SiO_2 interface was prepared by Monte Carlo bond-switching simulations, which have been proven to be more advantageous than molecular dynamics (MD) simulations for building amorphous SiO_2.[33] Owing to their amorphous nature, the local structures of different SiO_2 materials can differ significantly. We selected two models with different amounts (12 and 6) of oxygen atoms at a plane that is about 0.9 nm away from the bulk Si, and cut the plane for HfO_2 deposition. HfO_2 deposition was carried out by molecular dynamics (MD) simulations using a melt-quench procedure. A crystal HfO_2 slab was first prepared and placed on top of the SiO_2, as shown in Fig. 1(a) and 1(b), and melted for 50 ps at 5000 K to obtain a completely disordered system, as shown in Fig. 1(c). The temperature was gradually reduced to room temperature within 500 ps to generate a stable structure, as shown in Fig. 1(d). This structure will be further relaxed using first-principles calculations. The constructed models are as large as 16.13 Å × 16.13 Å × 48.00 Å, and contain more than 630 atoms.

The MD simulation was conducted using the force field developed by Broglia *et al.*,[34] which can produce a good radial distribution function and coordination number for HfO_2.[34,35] The first-principles calculations were conducted using the plane-wave package, PWmat, which was compiled using a GPU architecture for acceleration.[36,37] The SG15 norm-conserving pseudopotentials were adopted with an energy cutoff of 50 Ry, and the PBE functional was used for structural relaxation with a force convergence criterion of 0.05 eV/Å. To obtain accurate band gaps and band alignments, the hybrid HSE functional was used for electronic structure calculations of all large models. The Gamma k-point was sampled considering the largeness of the supercells and large number of atoms in each model.

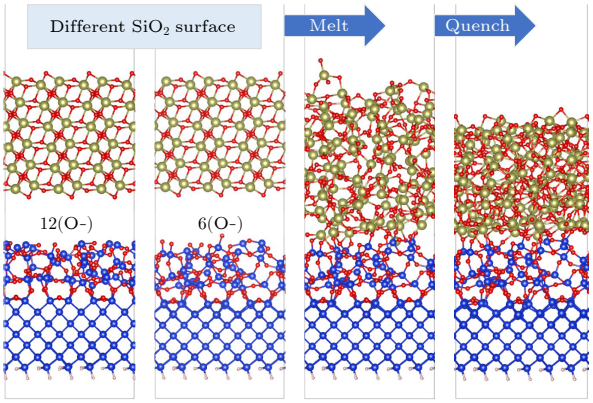

Fig. 1. The process of constructing different amorphous $Si/SiO_2/HfO_2$ interfaces. The number (density) of oxygen dangling bonds (O-) at SiO_2 surface is critical.

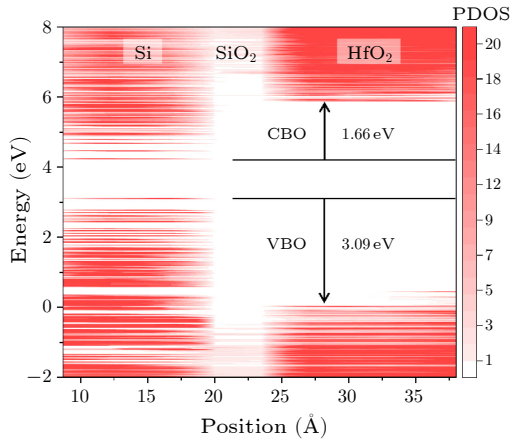

Fig. 2. Clear band alignment of $Si/SiO_2/HfO_2$ manifested by partial density of states (PDOS) of each atom layer along the stack direction.

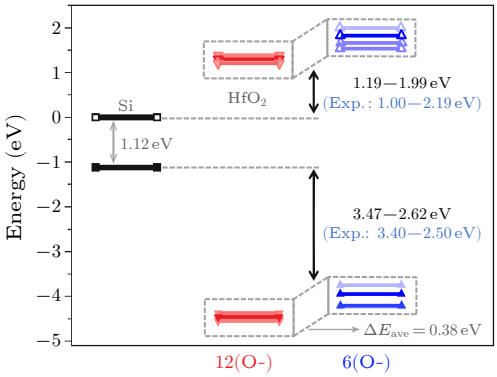

Fig. 3. Fluctuating but regular band offsets between Si and HfO_2. The calculated results are in good agreement with experimental ones, and the models with less interfacial (O-) (blue lines) always have larger CBO and smaller VBO.

A typical band alignment of $Si/SiO_2/HfO_2$, obtained by calculating the partial density of states (PDOS) of each atomic layer along the stack direction, is shown in Fig. 2. It can be clearly shown that the CBO between Si and HfO_2 is 1.66 eV, and the VBO is 3.09 eV. These values locate well at the middle of previously reported range 1.1–2.2 eV and 2.5–3.4 eV. Nevertheless, similar to the experimental reports, the band offsets of the different models fluctuated significantly, as shown collectively in Fig. 3. First, the CBO varies from 1.19 to 1.99 eV while the VBO varies from 2.62 to 3.47 eV. Both values were very close to the experimentally reported range. Second, the models with fewer oxygen dangling bonds (blue lines) before HfO_2 deposition always exhibit larger CBOs and smaller VBOs, which implies that the variation in oxygen density at the SiO_2 surface results in an overall band shift of HfO_2. This implies that the band alignment can be tuned by controlling the oxygen density at the SiO_2 surface before HfO_2 deposition.

Here, we need to emphasize that the conduction bands and valence bands shift upwards consistently, and the overall variation of CBO and VBO is 0.8 eV and 0.85 eV, respectively, which is very close to each other. Another interesting fact is that the energy level of the oxygen vacancy defect inside HfO_2 shifts with the band offsets, as shown in Fig. S1 in Supplementary Material.

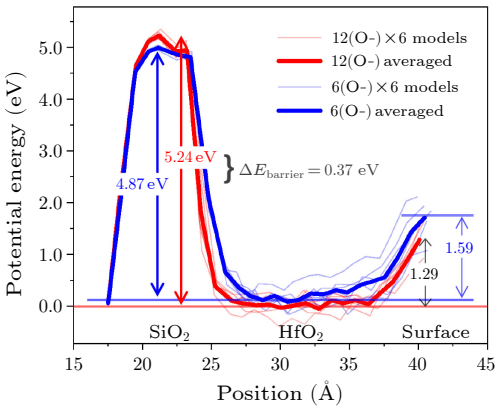

Fig. 4. Average potential energy of oxygen atoms along the stack direction, indicating the existence of interfaces and surface dipoles.

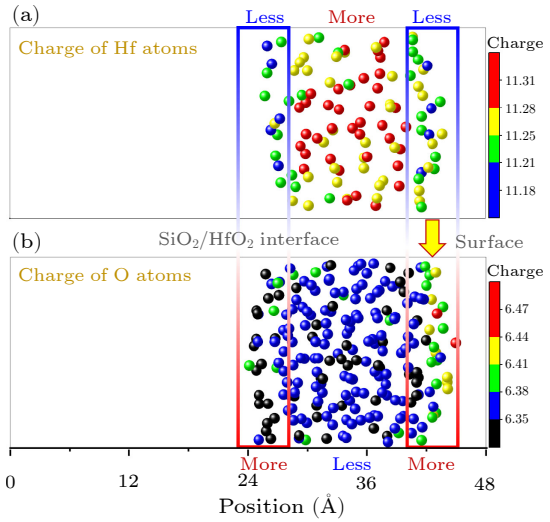

Fig. 5. Atomic charge distribution of Hf and O atoms, indicating charge transfer from Hf to O at the SiO_2/HfO_2 interface and HfO_2 surface.

To understand the underlying mechanism, we consider the potential energy along the stack direction. As shown in Fig. 4, an energy barrier exists between SiO_2 and HfO_2; however, this barrier is higher for the 12(O-) (red lines) models. This implies that a higher density of interfacial O atoms increases the interface dipole. Furthermore, the barrier difference is approximately 0.37 eV, which is nearly the same to the average VBO difference (0.38 eV) of two groups of models, as indicated in the bottom right of Fig. 3. This confirms that the shift in the band offset is indeed caused by the change in the interface dipole and that the change in the dipole is caused by the variation in the oxygen density at the SiO_2 surface before HfO_2 deposition. From this perspective, the areal density model is supported. It is worth noting that the potential inside HfO_2 is flat, which implies that there is rarely any dipole left inside HfO_2 after the molecular dynamics simulation and structural relaxation.

We further explored the origin of the interface dipole by examining the charge transfer at SiO_2/HfO_2 interface. Figure 5 shows the atomic charges of Hf and O atoms. Atomic charges were calculated using the Hirshfeld algorithm:

$$Q_i = \int \rho(r) \frac{\rho_{\text{atomtype}(i)}(r - R_i)}{\sum_j \rho_{\text{atomtype}(j)}(r - R_j)} d^3r,$$

where $\rho_{\text{atomtype}(i)}(r)$ denotes the neutral charge density of the atom type described in the pseudopotential file and $\rho(r)$ denotes the charge density in the actual interface model.

The electron configuration of Hf atom is $4s^2p^6d^{10}f^{14}5s^2p^6d^26s^2$, in which the two outermost shells contain 12 electrons. Furthermore, this corresponds to the number of valence electrons used in the Hf pseudopotential file. When an Hf atom loses some of its electrons to nearby oxygen atoms, its charge becomes less than 12.

As shown in Fig. 5, the Hf atoms at the SiO_2/HfO_2 interface and at the HfO_2 surface lost some of their charges. Conversely, O atoms gain some charge. This clearly demonstrates the charge transfer from Hf to O atoms at the interface and surface. The direct result of charge transfer is a potential change, as shown in Fig. 4, where the interface and surface have higher potential energies owing to charge accumulation. These results explain the origins of the interface and surface dipoles. Interestingly, the two types of dipoles are correlated, as shown in Fig. 4, where a larger interface dipole is accompanied by a smaller surface dipole.

Notably, the formation of oxygen vacancies caused by oxygen movement was not observed. This deviates from the areal density model, which tells that the interface dipole originates from positively charged vacancies and negatively charged oxygen centers.[31] Conversely, the observed dipoles were mainly induced by charge transfer from Hf to O, thus supporting the electronegativity model because the electronegativities of O and Si are larger than that of Hf. It is more likely that the areal density is affected by the magnitude of the charge transfer, i.e., the more interfacial or surface O atoms there are, the more charge will be transferred from Hf to O and Si. To be prudent, we need to clarify that the proposed interpretation is based on $Si/SiO_2/HfO_2$ system examined in this study but is not universal to all oxide interfaces. The migration of ions and cations contributes to dipole formation, as discussed by Watanabe.[38] Finally, we examined the impact of the HfO_2 thickness on the band offsets and found that the impact is very small, as shown in Fig. S2, in the Supplementary Material.

In conclusion, through *ab initio* calculations on a series of realistic $Si/SiO_2/HfO_2$ stacks, we showed that the fluctuation of band offsets is directly caused by the potential variation along the stack direction and is physically induced by charge transfer from Hf atoms to O atoms at the SiO_2/HfO_2 interface and at the HfO_2 surface. Charge transfer results in significant interface and surface dipole formations. Interestingly, the band offsets can be tuned by controlling the oxygen density at the SiO_2 surface before HfO_2 deposition. This strategy suggests that a lower oxygen density at the SiO_2/HfO_2 interface would increase the CBO and thus benefit the reliability of the n-MOS; a uniform oxygen density would reduce the band offset variation, and a more precise control of the oxygen density

would aid in tuning the threshold voltage. One open question involves implementing precise control of the oxygen density in the industry, which requires further investigation in the near future. This study mainly focuses on the underlying physics of band alignment fluctuation and tunability strategy, which would be promising in applications once the process is mature because the strategy does not require the insertion of other materials between SiO_2 and HfO_2. Hence, it would be free from many interfacial defects.

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