Density functional calculations on atomic and electronic structures of amorphous HfO$_2$/Si(001) interface

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The interface properties of amorphous hafnium dioxide ($a$-HfO$_2$) in contact with silicon have been investigated by using the projector augmented wave method within the generalized gradient approximation. The $a$-HfO$_2$ model structure of the interface is generated by $ab$ initio molecular dynamics simulations in a melt-and-quench scheme. Calculations indicate that the simulated $a$-HfO$_2$ essentially shows the characteristics of the experimental $a$-HfO$_2$ structure. The results on $a$-HfO$_2$/Si interface suggest that atomic coordination of interface Si atoms would significantly affect the interface electronic properties, e.g., the Hf–Si bond formed at the interface could result in metallic behavior. With band lineup of the core level, the valence band offset of $a$-HfO$_2$/Si interface is determined to be 2.62 ± 0.35 eV, in good agreement with recent experimental data. © 2009 American Institute of Physics. [doi:10.1063/1.3226636]

Hafnium dioxide (HfO$_2$) has many characteristics meeting the requirements to replace the conventional SiO$_2$ or SiON as gate dielectric of the metal oxide semiconductor field-effect transistors (MOSFETs). The higher dielectric constant of HfO$_2$ and its interface quality in contact with Si are two fundamental advantages.

It has been reported that the growth of HfO$_2$ on Si usually leads to amorphous phase, which tends to recrystallize through further thermal processing. Many experimental efforts were devoted to exploring various techniques and experimental conditions to get a stable $a$-HfO$_2$. Amorphous HfO$_2$ has several advantages over its crystalline counterpart: isotropic dielectric constant, no crystalline domain boundary, and compatibility with the conventional MOSFETs fabrication process. Therefore, it is necessary to investigate the properties of $a$-HfO$_2$ and its interface in contact with Si. Actually, $ab$ initio molecular dynamics (MD) has been widely used to investigate $a$-HfO$_2$ (Refs. 4–6), and its structural, electronic, dielectric properties or defects are also studied. Moreover, previous theoretical studies of the HfO$_2$/Si interface mostly focused on the system related to crystalline HfO$_2$ (Ref. 9) or the $a$-HfO$_2$/Si interface with a SiO$_2$ interlayer (i.e., HfO$_2$/SiO$_2$/Si) rather than on the interface of $a$-HfO$_2$ in direct contact with Si.

In present study, $ab$ initio MD based on density functional theory (DFT) is employed to generate reasonable $a$-HfO$_2$ model structure in “melt-and-quench” scheme. The structural properties of obtained $a$-HfO$_2$ are characterized via the atomic coordination number analysis. The interface properties of $a$-HfO$_2$/Si system are well studied, including bonding characteristics of the interface atoms, the electronic structures, and the band offsets.

All simulations are performed by using the projector augmented wave method with a plane-wave basis set, as implemented in the Vienna $ab$ initio simulation package. The exchange and correlation potential is treated by means of the generalized gradient approximation (GGA) with Perdew and Wang functionals (GGA-PW91). The Kohn–Sham wave functions are expanded by plane waves up to an energy cutoff of 500 eV.

The mass density of present optimized $a$-HfO$_2$ is 8.93 g/cm$^3$. The Hf–O bond length is around 2.06 ± 0.10 Å, which compares well to the average 2.15 Å in the crystalline phase and is also close to 1.90 Å reported in a recent experiment. The coordination number for the O and Hf atoms in the monoclinic HfO$_2$ ($m$-HfO$_2$) and the obtained $a$-HfO$_2$ sample are shown in Fig. 1. A cutoff radius of 2.50 Å, derived from the behavior of Hf–O bonds, is used to determine the coordination number. In $m$-HfO$_2$ [Fig. 1(a)], all Hf atoms are sevenfold-coordinated and O atoms are 50% threefold-coordinated and 50% fourfold-coordinated, the same as reported. For $a$-HfO$_2$ [Fig. 1(b)], six-coordinated Hf and three-coordinated O atoms are dominating with some five-coordinated Hf and two-coordinated O atoms appearing. This indicates the lower coordination in amorphous structure, which confirms the rationality of the present $a$-HfO$_2$ model structure obtained in melt-and-quench scheme.

A supercell consisting of the generated $a$-HfO$_2$ (Ref. 11) and the clean Si(001)-c(2×2) surface and one 12 Å thick

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All the Si atoms States (eV)

The Si from bulk Si with calculated lattice constant. To get the initial interface configuration, following considerations are taken: (i) the surface area of a-HfO$_2$ is chosen to match that of the Si(001)-c(2×2) surface and (ii) the cross section of a-HfO$_2$ is chosen to make sure the number of O atoms at the interface is larger than that of Hf atoms. The a-HfO$_2$/Si interface is optimized by a constraint relaxation with the bottom three Si layers fixed. A tolerance force on atoms is set as 0.025 eV/Å with a k-point sampling by $3 \times 3 \times 1$ in Brillouin Zone (BZ).

The optimized structure of a-HfO$_2$/Si interface is shown in Fig. 2. The nearest-neighbor distance and number of the Si–Hf and Si–O bonds related with the marked Si atoms (Fig. 2) are listed in Table I. The Si–O bond lengths range from 1.67 to 1.80 Å, larger than 1.6 Å in α-quartz SiO$_2$ and 1.61 Å in HfSiO$_4$ (Ref. 17). The Si–Hf bond lengths range from 2.72 to 3.38 Å, also larger than 2.10 and 2.24 Å (Ref. 17) in HfSiO$_4$. These indicate that no SiO$_2$ or HfSiO$_4$ appear from 2.72 to 3.38 Å, also larger than 2.10 and 2.24 Å in HfSiO$_4$. These indicate that no SiO$_2$ or HfSiO$_4$ appear from 2.72 to 3.38 Å, also larger than 2.10 and 2.24 Å in HfSiO$_4$. These indicate that no SiO$_2$ or HfSiO$_4$ appear in the optimized a-HfO$_2$/Si interface. From Table I, it can be seen that for interface Si atoms, the number of the Si–Hf bond is larger than that of the Si–O bond. The total density of states (DOS) of the a-HfO$_2$/Si interface and the partial DOS of the interface atoms are shown in Fig. 3. It can be seen that the interface system exhibits metallic behavior. The states at the Fermi level are mainly contributed by the interface Si atoms with a small contribution from the interface Hf atoms. This could be understood because more Hf–Si metallic bonds than Si–O bonds have formed at the interface (see Table I). Besides, a peak dominated by interface Si atoms appears at $-0.2$ eV below Fermi level. Therefore, present results indicate that the electronic properties of a-HfO$_2$/Si interface would be greatly affected by the bonding characteristics of interface Si atoms.

For high-$\kappa$ materials to be integrated in the gate dielectric stack, their conduction band offset (CBO) and valence band offset (VBO) with respect to Si should be large enough to achieve an acceptable low leakage current. It is well known that the sum of CBO and VBO is equal to the experimental band gap difference $\Delta E_g$ between gate oxide and Si, i.e.,

$$\text{CBO} + \text{VBO} = \Delta E_g.$$  

(1)

The experimental values of the band gap of HfO$_2$ and Si are 5.70 (Ref. 16) and 1.12 eV, respectively; thus $\Delta E_g$ is 4.58 eV. Since the band gap of semiconductor or insulator is usually underestimated in GGA calculation, the DFT is used to calculate the VBO and then the corresponding CBO can be obtained from Eq. (1). For the VBO of a-HfO$_2$/Si interface, it is evaluated by means of the band lineup of the core levels (CLs) (Ref. 19) (see Fig. 4).

$$\text{VBO} = (E_{\text{VBM}} - E_{\text{CL}})_{\text{Si}} - (E_{\text{VBM}} - E_{\text{CL}})_{\text{HfO$_2$}} + \Delta E_{\text{CL}},$$  

(2)

where $(E_{\text{VBM}} - E_{\text{CL}})_{\text{Si}}$ and $(E_{\text{VBM}} - E_{\text{CL}})_{\text{HfO$_2$}}$ are the energy separations between VBM and CL for pure Si and a-HfO$_2$, respectively. They can be obtained from calculations on bulk Si and bulk a-HfO$_2$. The last term in Eq. (2) is the difference of the CL binding energy between a-HfO$_2$ and Si of the a-HfO$_2$/Si interface. In determination of CL, only those atoms that have the same coordination number and similar

![FIG. 2. (Color online) Optimized structure of a-HfO$_2$/Si interface. Eight interface Si atoms are marked with numbers.](image-url)

![FIG. 3. (Color online) DOS of a-HfO$_2$/Si interface. (a) Total DOS, [(b)–(d)] Partial DOS of all Si, Hf, and O (black line) and the interface Si, Hf, and O atoms (red line).](image-url)

<table>
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<th>Table I. Bonding characteristics of the eight interface Si atoms. The number in Si(##) indicates marked Si atom in Fig. 2. $n_{\text{Si-Hf}}$ and $n_{\text{Si-O}}$ represent the number of the interface Si–Hf bonds and Si–O bonds. $d_{\text{Si-Hf}}$ and $d_{\text{Si-O}}$ (in Å) stand for the interface Si–Hf and Si–O bond lengths, respectively.</th>
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The melt-and-quench scheme is proposed with the interface electronic properties. The VBO of characteristics of the interface Si atoms would affect significantly states at the Fermi level and suggest that the bonding character that the interface Si–Hf bond could induce metallic-like behavior in a-HfO2. The results of MD. The assumption used in this bulk-plus-lineup procedure is that amorphous HfO2 provides sufficient tunneling barriers for electrons and holes, making them suitable for application as alternative gate dielectric.

In summary, a reasonable atomic structure of a-HfO2 in melt-and-quench scheme is proposed with \textit{ab initio} MD. The analysis of atomic coordination number indicates that the atoms in a-HfO2 have lower coordination than those in the crystalline HfO2. The results of a-HfO2/Si interface show that the interface Si–Hf bond could induce metallic-like states at the Fermi level and suggest that the bonding characteristics of the interface Si atoms would affect significantly the interface electronic properties. The VBO of a-HfO2 with respect to Si is found to be 2.62 ± 0.35 eV, in good agreement with reported experimental values.

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