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Impact of Native Defects in the High Dielectric Constant Oxide $HfSiO_4$ on MOS Device Performance *

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Native defects in $HfSiO_4$ are investigated by first principles calculations. Transition levels of native defects can be accurately described by employing the nonlocal HSE06 hybrid functional. This methodology overcomes the band gap problem in traditional functionals. By band alignments among the Si, GaAs and $HfSiO_4$, we are able to determine the position of defect levels in Si and GaAs relative to the $HfSiO_4$ band gap. We evaluate the possibility of these defects acting as fixed charge. Native defects lead to the change of valence and conduction band offsets. Gate leakage current is evaluated by the band offset. In addition, we also investigate diffusions of native defects, and discuss how they affect the MOS device performance.

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High permittivity gate dielectrics have been attracting much attention since silicon dioxide is reaching its fundamental physical limit in metal oxide semiconductor field effect transistors (MOSFETs).[1,2] Oxides with higher dielectric constants have to be explored to integrate into the devices to maintain the leakage current across a very thin gate oxide at a relatively low level. The oxides must satisfy various conditions such as being thermodynamically stabile in contact with the semiconductors and having sufficient valence and conduction band offsets. Thus HfO_2 becomes one of the promising candidates.[3,4] Due to the fact that HfO_2 crystallizes at quite low temperatures, it needs to be alloyed with SiO_2 to raise its crystallization temperature. Thus $HfSiO_4$ is a preferred dielectric.[5,6] The native defects in the oxides have much impact on MOS device performance.[7−9] They can be usually be identified by photoemission during the oxide growth process.[10] However, there has been no direct chemical probing for defect states in the band gap. Thus the first principles simulation is useful in helping to investigate defect ionization and migration.[11−15] Unfortunately, information about ionization and migration of native defects in $HfSiO_4$ is currently limited.

In this Letter, we use the first principles calculations to determine the formation energies and transition levels of native defects in $HfSiO_4$. Our calculations are based on the HSE06 hybrid functional, which overcomes the traditional problem of underestimation of the band gap in DFT by using LDA or GGA exchange functional. The method can obtain the accurate position of defect levels relative to the semiconductor band gap. This allows us to assess which defects have impact on MOS device performance.

The HSE06 is a hybrid density functional which employs a screened, short-range Hartree–Fock exchange instead of the full exact exchange to avoid the band gap underestimate of semiconductors and insulators.[16] The calculations are performed by using the CASTEP code. The cores are represented by the norm-conserving pseudopotential, while the valence states are expanded in a plane-wave basis set with 600 eV. Crystalline $HfSiO_4$ has $I4/amd$ body centered tetragonal space group. The cell of $HfSiO_4$ contains 4 formula units. Here $1 \times 1 \times 2$ $HfSiO_4$ periodic cells containing 48 atoms are chosen to calculate formation energies and transition levels of native defects. In most defect formation energy calculations, the defect wave functional will determine the supercell size. It is found that the defect wave functional in $HfSiO_4$ is very localized. Therefore, the $1 \times 1 \times 2$ supercell is chosen to be large enough to allow the considerable atomic relaxations around the defects, which have been carefully checked in Ref. [17]. The Monkhorst–Pack scheme is used for k point sampling with a $4 \times 4 \times 2$ mesh for the density-of-state (DOS) calculations. A larger $2 \times 2 \times 2$ $HfSiO_4$ supercell is used to calculate diffusions of native defects, which contains 192 atoms. The exchange-correlation functional of the CA-PZ of LDA[18] is given in performing the diffusion calculations. The native defects are fully relaxed in various charge states. The optimization will finish if the convergence criterion is satisfied (the maximum force between atoms is 0.01 eV/Å, the maximum stress is 0.05 GPa, the maximum displacement is 10^{-3} Å, and the maximum energy change is 10^{-5} eV/atom).

The defect formation energies in compound systems can be obtained from the total energy calculation of the supercell,[19,20]

$$\Delta H_{\rm f}(\alpha, q) = \Delta E(\alpha, q) + \sum_{\alpha} n_{\alpha} \Delta\mu_{\alpha} + qE_{\rm F}, \quad (1)$$

$$\Delta E(\alpha, q) = E(\alpha, q) - E({\rm HfSiO_4}) + \sum_{\alpha} n_{\alpha}\mu_{\alpha} + q(E_{\rm v} + \Delta V), \quad (2)$$

where $E(\alpha, q)$ is the total energy of $HfSiO_4$ supercell containing the relaxed defect α in the charge state q,

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$E(HfSiO_4)$ is the total energy for the same $HfSiO_4$ supercell in the absence of defects, n_α is the number of atoms for each defect, E_v represents the valence band maximum (VBM) of the defect-free system, ΔV represents the shift of VBM in a defect supercell, $\Delta\mu_\alpha + \mu_\alpha$ is the absolute value of the chemical potential of the atom, μ_α is the chemical potential of the element, and $\Delta\mu_\alpha$ is the relative chemical potential. The chemical potential depends on the experimental growth condition. In the thermodynamic equilibrium, the Hf, Si and O chemical potentials must satisfy the stability condition $\Delta\mu_{Hf} + \Delta\mu_{Si} + 4\Delta\mu_O = \Delta H_f(HfSiO_4)$. The enthalpy of formation of $\Delta H_f(HfSiO_4)$ is determined from $HfSiO_4$ compound formation free energy relative to bulk Si, bulk Hf and molecular oxygen O_2. The value of $\Delta H_f(HfSiO_4)$ eV is -22.8 eV, which is approximately equal to $\Delta H_f(ZrSiO_4) = -22.3$ eV reported in Ref. [21]. To avoid formation of binary compounds of HfO_2 and SiO_2, chemical potential should also hold: $\Delta\mu_{Hf} + 2\Delta\mu_O \leq \Delta H_f(HfO_2)$ and $\Delta\mu_{Si} + 2\Delta\mu_O \leq \Delta H_f(SiO_2)$. The calculated values are $\Delta H_f(HfO_2) = -12.6$ eV and $\Delta H_f(SiO_2) = -10.2$ eV. They can be compared with the experimental value of $\Delta H_f(HfO_2) = -11.9$ eV[22] and $\Delta H_f(SiO_2) = -9.8$ eV.[21] In this study, we set $\Delta\mu_O = 0.65$ eV,[23] which corresponds to typical growth conditions for ALD, i.e., a temperature of 270℃ and partial oxygen pressures of 1 Torr. To satisfy the stability, we also take $\Delta\mu_{Hf} = -11.3$ eV and $\Delta\mu_{Si} = -8.9$ eV.

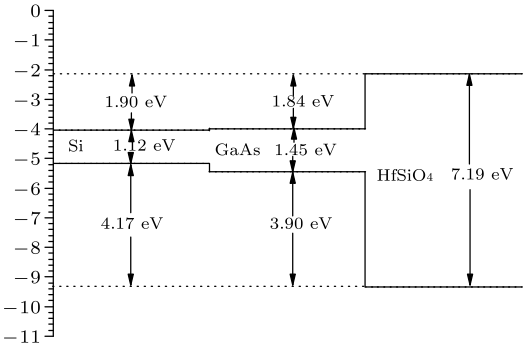

Fig. 1. Band offset diagrams of Si, GaAs and $HfSiO_4$.

Table 1. The calculated and experimental band gaps and enthalpy of formation for Si, Ge and $HfSiO_4$.

	LDA	GGA	B3LAY	HSE06	Experimental
Si	0.55	0.62	1.89	1.12	1.12
GaAs	0.66	0.90	1.74	1.45	1.43
$HfSiO_4$	5.29	5.38	7.78	7.19	6–9

The band gaps of Si, GaAs and $HfSiO_4$ are calculated in the LDA, GGA, B3LYP and HSE06 methods, which are listed in Table 1. It is observed that the band gaps of Si and GaAs calculated by LDA and GGA are much smaller than experimental data. However, the band gap calculated by the hybrid B3LYP functional is slightly larger than the experimental data. At present, we cannot obtain any experimental band gap of crystalline $HfSiO_4$. Previously, Kato *et al.*[24] measured the optical band gap of amorphous $(HfO_2)_x(SiO_2)_{1x}$ with the value in the range of 6–9 eV. Hence we suppose that the experimental data of $HfSiO_4$ band gap is 6–9 eV. The band gap calculated by HSE06 is closer to the experimental data compared with LDA, GGA and B3LYP methods.

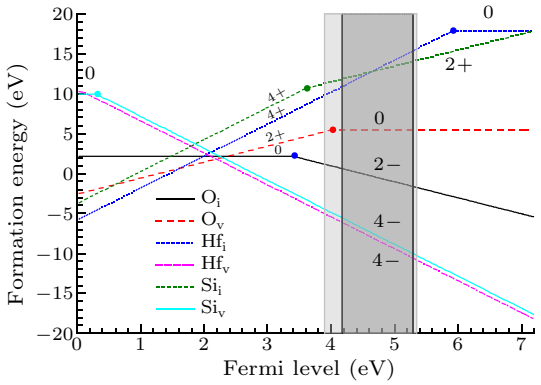

Fig. 2. Formation energy versus Fermi level for native defects in $HfSiO_4$. Light and dark gray regions denote GaAs and Si band gaps, respectively.

The band alignments between the oxides and semiconductors are calculated by the electronic transition level of hydrogen, which has been reported in Ref. [25]. Figure 1 represents a simple band offset diagram of Si, GaAs and $HfSiO_4$. The valence band offset between Si and $HfSiO_4$ is 4.17 eV, which is slightly larger than 3.80 eV calculated by Xiong *et al.*[17] In their studies, the band gap of $HfSiO_4$ calculated by the sX functional is 6.80 eV, which is slightly smaller than 7.19 eV calculated by the HSE06 functional. Therefore, the errors come from divergence of the $HfSiO_4$ band gap calculated by different exchange correlation potentials. The band offset between Si and GaAs is in agreement with the previous investigation.[23] We investigate the formation energies of native defects in $HfSiO_4$, including oxygen vacancy (O_v), hafnium vacancy (Hf_v), silicon vacancy (Si_v), oxygen interstitial (O_i), hafnium interstitial (Hf_i) and silicon interstitial (Si_i). The range of Fermi level corresponding to the GaAs and Si band gaps is shown by the light and dark gray regions in Fig. 2. Here Hf_v is only formed on eightfold coordinated hafnium sites. Hf_v is only stable in Hf_v^0, Hf_v^{2-} and Hf_v^{4-} charged states. Hf_v^0 is higher in energy than Hf_v^{2-} and Hf_v^{4-}. The $(2-/4-)$ transition level occurs at 0.12 eV above the VBM. Si_v is formed on fourfold coordinated silicon sites. It is noted that Si_v^{2-} is higher in energy than Si_v^0 and Si_v^{4-}. The $(0/4-)$ transition level occurs at 0.29 eV. The V_O can be formed on threefold coordinated oxygen sites with connecting one Si and two Hfs. The V_O in $HfSiO_4$ exhibits negative U behavior, i.e., V_O^+ is unstable against V_O^0 and V_O^{2+}. The $(2+/+)$ transition level occurs at 5.27 eV, which is higher than the transition level of $\varepsilon(+/0)$=2.75 eV. We predict that two V_O^+ defects can decay into V_O^0 and V_O^{2+}, which is consistent with the report.[26] The $(2+/0)$ transition level occurs at 4.01 eV above the VBM. The neutral O_i forms a dimer with a lattice oxygen atom with bond length of

1.48 Å. It is found that the structure cannot achieve convergence when an extra electron is added into the system. However, it can form saturation structure of O_i^{2-} as two electrons are added to the system. The bond length is increased to 2.14 Å by Coulomb repulsion interaction between interstitial and lattice oxygen atoms. The (0/2−) transition level occurs at 3.39 eV. Hf_i and Si_i are the most stable at octahedral sites surrounded by six oxygen atoms. For Hf_i defect, transition level of (4+/0) occurs at 5.99 eV. For Si_i defect, transition level of (4+/2+) occurs at 3.60 eV. It is noted from Fig. 2 that Hf_v, Si_v and O_i are lower in formation energy than Hf_i, Si_i and O_v within Si and GaAs band gaps. The results suggest that Hf_v, Si_v and O_i are more likely to form in $HfSiO_4$.

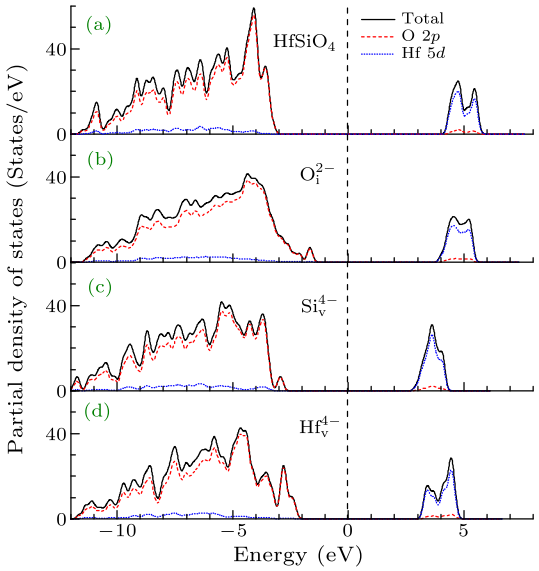

Fig. 3. The density of states: (a) pure $HfSiO_4$, (b) containing O_i^{2-}, (c) containing Si_v^{4-}, and (d) containing Hf_v^{4-}.

Let us consider $HfSiO_4$ based on an n-channel MOS system on a Si substrate. The charged states of Hf_v, Si_v and O_i are 4, 4 and 2, when negative voltage is applied since the p-type substrate is in its accumulation region and holes are majority carriers. In this case, defects exchange an electron with the Si valence band. The electronic chemical potential is determined by the position of Si VBM, which is about 4.17 eV above the $HfSiO_4$ VBM. When a positive voltage is applied to the gate of the MOS system, the channel is in the reversion or depletion region and the Si valence band is full of electrons. The defect exchanges an electron with Si conduction band minimum (CBM) which is about 5.29 eV above $HfSiO_4$ VBM, and charged states of Hf_v, Si_v and O_i still remain as 4, 4 and 2. This means that the total charge states of Hf_v, Si_v and O_i stay negative when the gate voltage sweeps from negative to positive. The above discussion can also be applied to the p channel MOS system. A similar result is found on MOS based on GaAs substrates. The result means that Hf_v, Si_v and O_i will serve as negative fixed charge. As a result, the defects will lead to flat band voltage shifting toward a positive direction.

Figure 3 presents the DOS in $HfSiO_4$ with and without defects. For pure $HfSiO_4$, it is found from Fig. 3(a) that VBM and CBM are determined by O $2p$ and Hf $5d$, respectively. Figure 3(b) presents the DOS of $HfSiO_4$ with O_i^{2-} defects. It is observed that VBM shifts 1.69 eV toward higher energy region by comparing with DOS of pure $HfSiO_4$. The CBM shifts 0.19 eV toward the lower energy region. The tunneling barrier of a hole is decreased from 4.17 eV to 2.48 eV for the Si substrate, and from 3.90 eV to 2.21 eV for the GaAs substrate. Fortunately, the valence band and conduction band offsets in $Si/HfSiO_4$ and $GaAs/HfSiO_4$ are still large enough, therefore O_i^{2-} will not influence leakage current much. Figure 3(c) presents the DOS of $HfSiO_4$ with Si_v^{4-}. As seen in Fig. 3(c), the CBM shifts 1.35 eV toward the lower energy region. The tunneling barriers of electrons are reduced to 0.55 eV in $Si/HfSiO_4$ and 0.49 eV in $GaAs/HfSiO_4$. Thus Si_v^{4-} results in the increase of the leakage current. Figure 3(d) presents the DOS of $HfSiO_4$ with Hf_v^{4-}. It is found that VBM shifts 0.96 eV toward a higher energy region, and CBM shifts 1.00 eV toward the lower energy region. The valence band offsets still stay as 3.21 eV in $Si/HfSiO_4$ and 2.94 eV in $GaAs/HfSiO_4$, respectively. Hence, VBM shifting does not increase the leakage current. However, the conduction band offset will reduce to 0.90 eV in $Si/HfSiO_4$ and 0.84 eV in $GaAs/HfSiO_4$, which will increase the leakage current.[27,28]

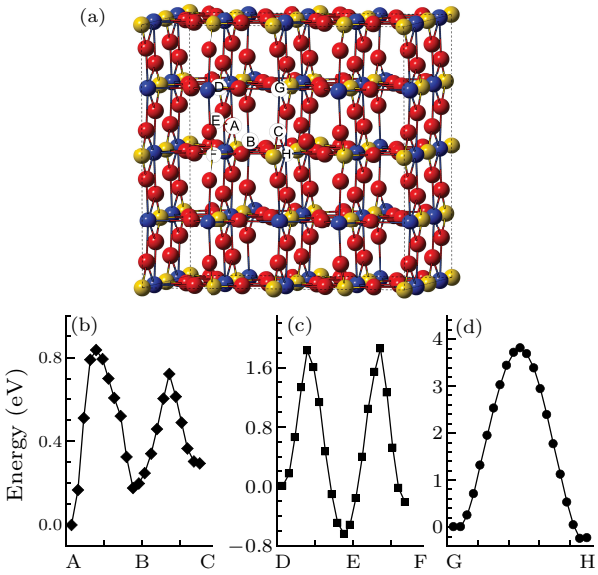

Fig. 4. The model of $HfSiO_4$ and energy profiles for O_i^{2-}, Si_v^{4-} and Hf_v^{4-} diffusion. (a) The model of $HfSiO_4$. O: red balls; Hf: blue balls; and Si: yellow balls. The diffusion path for O interstitial by the circles $A \to B \to C$, the path for Si vacancy is represented by the circles $D \to E \to F$, the path for Hf vacancy is represented by the circles $G \to H$. (b), (c) and (d) are energy profiles for O_i^{2-}, Si_v^{4-} and Hf_v^{4-} diffusion in $HfSiO_4$.

The O_i usually forms a dimer with lattice O atoms. The mechanism of diffusion of O_i in $HfSiO_4$ can be classified as occurring via either an interstitial or an

exchange process. In the interstitial mechanism, the defect diffuses through empty space between the lattice sites. The exchange mechanism involves the continuous replacement of a lattice site by the diffusing defect, and the lattice site then becomes the diffusing species. We investigate diffusion of O_i along path $A \rightarrow B \rightarrow C$ shown in Fig. 4(a). The interstitial mechanism corresponds to path $A \rightarrow B$ and the exchange mechanism corresponds to path $B \rightarrow C$. In the interstitial mechanism, the diffused oxygen atom begins with the strong bond with a lattice oxygen atom. Then the oxygen atom will obtain enough energy and break the bond. Finally, the oxygen atom will migrate and form a new bond with the other lattice oxygen atom. The energy profiles of O_i^{2-} diffusions are shown in Fig. 4(b). The diffusion barrier in the interstitial mechanism is 0.83 eV for O_i^{2-}. In the exchange mechanism, the diffusion barrier of O_i^{2-} is 0.72 eV. The result is in agreement with the value of 0.80 eV in HfO_2.[26] Diffusion of Si_v occurs as a nearest neighbor Si atom in the lattice sites jumps into the vacant sites, leaving a Si_v behind. The energy profiles of Si_v^{4-} diffusions are shown in Fig. 4(c). The diffusion barrier can be obtained by calculating the total energy at various intermediate configurations. The Si_v^{4-} diffuses along path $D \rightarrow E \rightarrow F$. The minimum of the profiles represents local stable equilibrium and the maximum being diffusion barriers for each elementary step. The total diffusion barrier along this path is 1.83 eV for Si_v^{4-}. It is found that Si_v^{4-} achieves a potential well at E point. At E point, Si locates in the oxygen octahedral crystal field. Si interacts with these O atoms with an average bond length of 1.79 Å. Hf_v^{4-} diffuses along path $G \rightarrow H$. The energy profiles of Hf_v^{4-} diffusion are shown in Fig. 4(d). The total diffusion barrier is 3.81 eV for Hf_v^{4-}, which suggests that Hf_v^{4-} in $HfSiO_4$ is hard to diffuse compared with O_i^{2-} and Si_v^{4-}. The diffusion barrier, when combined with the formation energy, leads to the conclusion that O_i^{2-} is the most mobile in $HfSiO_4$. The diffusion of O_i^{2-} will bring the change of charge density distribution in $HfSiO_4$, which results in the drift of C–V curve. The formation and diffusion of charged defect O_i^{2-} will play a significant role in degrading the electrical properties of the device, which is in agreement with the report in Refs. [22,29].

In conclusion, we have studied the formation and diffusion of native defects in $HfSiO_4$. It is found that Hf_v^{4-}, Si_v^{4-} and O_i^{2-} are the most stable defects in Si and GaAs band gaps, which means that they will serve as a negative fixed charge. As a result, they will lead to flat band voltage shifting toward the positive direction. Hf_v^{4-} and Si_v^{4-} defects produce conduction band offset reduction, which will increase the gate leakage current. The diffusion barriers are only 0.83 eV in the interstitial mechanism and 0.72 eV in the exchange mechanism for O_i^{2-}, which indicates that O_i^{2-} more easily diffuses and degrades the electrical properties of the device.

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