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Interfacial bonding and electronic structure of HfO_2/GaSb interfaces: A first principles study

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The interfacial bonding and electronic structure of HfO_2/GaSb interfaces has been investigated through first principles calculations. The calculated electronic structures of these interfaces reveal that some O-rich interfaces are semiconducting interfaces without any gap states. In contrast, for the interfaces with lower interfacial O content, gap states appear in the GaSb band gap, close to the conduction band. The valence band offsets are found to vary from 2.2 eV to 3.6 eV, depending on the interfacial O content. Our results suggest that GaSb is a suitable material to form high quality interface with HfO_2 . © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4775665>]

As the continued scaling of the dimensions of the complementary metal oxide semiconductor (CMOS) field effect transistors (FETs), Si is predicted to reach its fundamental physical limits for being as the channel material.¹ This has led to intensive research for suitable high mobility III–V semiconductor materials to replace Si as alternative channel materials.^{2–6} However, the integration of III–V compounds into CMOS devices is hindered by the poor interface quality between the high dielectric constant (high-k) gate dielectric and the III–V channel, which causes Fermi level pinning. During the past decades, considerable efforts have been dedicated on how to improve the interface quality of III–V/high-k oxide interfaces.^{7–13}

Gallium Antimonide has attracted attention in recent years due to its high hole mobility, which makes it a promising candidate for p-type MOSFETs.^{14–18} It has been reported recently that the Fermi level is unpinned for the $\text{GaSb}/\text{Al}_2\text{O}_3$ MOS capacitors. Unlike GaAs/oxide or $\text{InGaAs}/\text{oxide}$ interfaces where the formation of their native oxides causes the gap states, the unpinning of the Fermi level of the $\text{GaSb}/\text{Al}_2\text{O}_3$ interface is due to the presence of a surface oxide on GaSb.¹⁷ Therefore, it is necessary to understand why the behavior of GaSb is different as compared to the arsenides. To date, there is no theoretical study of $\text{GaSb}/\text{high-k}$ oxide interface. In this work, we investigate at the atomic level the electronic structure of GaSb/HfO_2 interface by first principles calculations. We consider the ideal abrupt GaSb/HfO_2 interface because we aim to investigate the intrinsic properties of the interface. Oxygen concentration at the interface is systematically varied to enable the study of defect formation analogous to interfaces generated from relevant deposition conditions, such as atomic layer deposition.

Our calculations are based on the density functional theory (DFT) with the Perdew-Burke-Ernzerhof (PBE) ver-

sion of the generalized gradient approximation (GGA) for the exchange-correlation potential, as implemented in a plane-wave basis code VASP.¹⁹ The pseudopotential is described by projector-augmented-wave (PAW) method.²⁰ An energy cutoff of 400 eV and a $4 \times 4 \times 1$ k-point with a Gamma centered k mesh are used in our calculations. The forces are converged to 0.01 eV/Å during the atomic structure optimization.

The interfaces are modeled by a superlattice containing one interface with 10 Å vacuum on top. We consider the cubic (c-) $\text{HfO}_2(001)/\text{GaSb}(100)$ interface, as $\text{GaSb}(100)$ is observed experimentally. For HfO_2 , we choose the simplest cubic phase, which is easier to model computationally and structurally as compared to the monoclinic and tetragonal phases. However, the conclusions hold for all three phases because the interface electronic structure depends on the local bonding configurations rather than long range crystalline symmetry. In our supercell, the O-terminated $\text{HfO}_2(001)$ slab is expanded by 6% and rotated counter-clockwise by 28.04° to match the Ga-terminated $\text{GaSb}(100)$ slab, similar as what was shown in our previous work on GaAs/HfO_2 interfaces.²¹ The interfacial Ga-O bonding configuration is supported by experimental data, which the low energy ion scattering spectroscopy (ISS) reveals a Ga-rich GaSb surface. The GaSb slab is 28.65 Å thick with 10 layers of Ga and 9 layers of Sb, while the HfO_2 slab is 13.42 Å thick with 5 layers of Hf and 6 layers of O. Since the ideal cleaved $\text{HfO}_2(001)$ surface has 10 oxygen atoms, we consider various HfO_2/GaSb interface configurations by systematically changing the number of interfacial oxygen atoms. The interface configuration is denoted by the number of interfacial oxygen atoms (e.g., O_{10} and O_0 represent interfaces with 10 interfacial oxygen atoms and zero interfacial oxygen atoms within the interface unit cell, respectively).

To determine the stability of these interface configurations, we calculated their formation energies. This is in general a function of chemical potentials and can be expressed as²²

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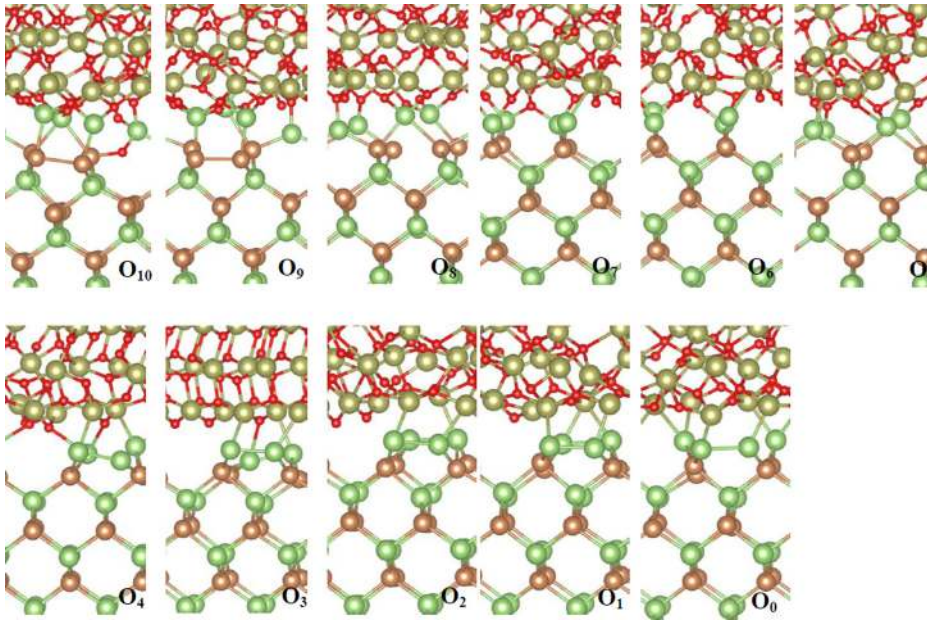


FIG. 1. The relaxed atomic structures of O_{10} - O_0 interfaces. The Ga atoms are in light green; the Sb atoms are in brown; the Hf atoms are in brass; and the O atoms are in red.

$$E_{form} = \frac{E_{total} - n_{Hf}E_{HfO_2} - (n_{Ga} - n_{Sb})E_{Ga} - n_{Sb}E_{GaSb} + (2n_{Hf} - n_O)\mu_O}{A},$$

where E_{total} is the total energy of the given supercell, n_x is the number of atoms of element x ($=O, Hf, Ga$, or Sb); A is the interface area of the supercell; E_{HfO_2} and E_{GaSb} are the total energies per formula unit in HfO_2 and $GaSb$, respectively; E_{Ga} is the total energy per atom in bulk Ga. There is a single independent parameter determined by the growth conditions, the O chemical potential μ_O . Its highest value is $\mu_O^{O_2}$, the energy of the O_2 molecule. Its lowest value is for thermodynamic equilibrium with HfO_2 . Taking the formation enthalpy of bulk HfO_2 as $\Delta H \sim -11$ eV, the limiting values of μ_O are thus $\mu_O = \mu_O^{O_2} + (\Delta H/2)$ (Hf-rich) and $\mu_O = \mu_O^{O_2}$ (O-rich).

The relaxed atomic structures of various interface configurations are given in Figure 1. The relaxed atomic structure of the O_{10} interface shows that the Ga atoms move upwards to form bonds with O atoms. The interfacial Ga atoms are 4- or 5-fold coordinated. This movement causes the relaxation of the beneath Sb layer. As a result, the Sb-Sb dimer is formed and the Sb-Sb bond length is 2.878 Å. Meanwhile, one interfacial O atom moves to the GaSb side and stays at the bridge site between one Ga and one Sb. So for the Sb layer beneath the top interfacial Ga layer, all Sb atoms are 4-fold coordinated. From the Bader charge analysis, the formation of the Sb-Sb dimer compensates the charge loss of the Sb ($Sb^{-0.2}$) as compared to that of the Sb ($Sb^{-0.3}$) in GaSb. The charge state of the interfacial Ga atom is $Ga^{+1.3}$, which is much more positive than that of the Ga ($Ga^{+0.3}$) in bulk GaSb due to the charge transfer from Ga to O, but close to that of the Ga ($Ga^{+1.7}$) in Ga_2O_3 .

For the O_9 interface, similar to that of the O_{10} interface, it also has an interfacial Sb-Sb dimer with the Sb-Sb bond length of 2.919 Å. It also shows that one interfacial Ga-Sb bond is broken, resulting in an unsaturated 3-fold coordinated Sb. For the interfacial Ga atoms, we see that one Ga atom is 3-fold coordinated, with one bonded to O and the

other two bonded to Sb. The remaining Ga atoms are all 5-fold coordinated, bonding to four O and one Sb. The charge state of the 3- and 5-fold coordinated Ga atoms are $Ga^{+0.69}$ and $Ga^{+1.38}$, respectively. It is interesting to compare them with those in Ga_2O and Ga_2O_3 , which are $Ga^{+0.52}$ and $Ga^{+1.7}$, respectively. Among all these interface configurations, only O_{10} and O_9 have Sb-Sb dimer. The O_8 interface is a charge neutral interface because it meets the valence electron saturation requirements.²³ The interfacial bonding of this interface is similar to that of the O_9 interface, except that there is no Sb-Sb dimer formation.

For the O_7 interface, due to further reduction of the interfacial O, the formation of the Ga-Hf bond (bond length:

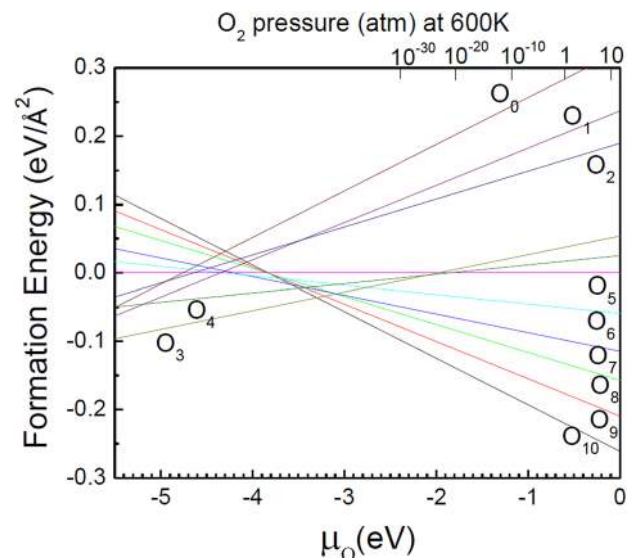


FIG. 2. Formation energies of various interface configurations as a function of O chemical potential.

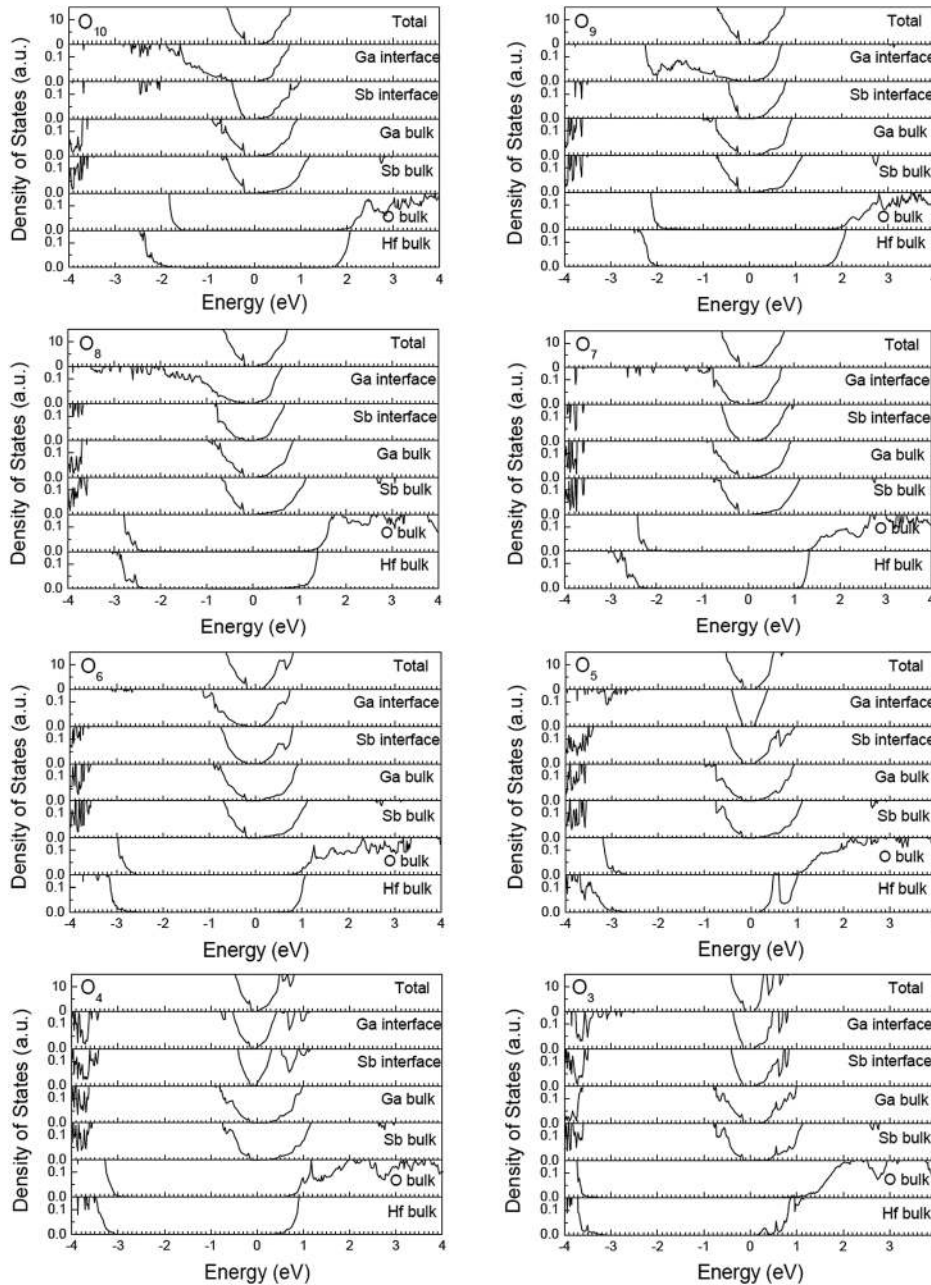


FIG. 3. Calculated total and partial density of states of various interface configurations (O_{10} - O_3). The Fermi level is located at 0 eV.

2.933 Å) has been observed. The Ga atom that bonded to the Hf is 3-fold coordinated. Compared to the Bader charge of other interfacial Ga atoms ($Ga^{+0.89}$, $Ga^{+0.93}$, and Ga^{+1}), this Ga atom has less positive charge ($Ga^{+0.22}$). Clearly, the oxidation state of interfacial Ga atom has been reduced because of the reduction of the interfacial O atoms. From O_6 to O_0 , the number of Ga-Hf bonds increases with the gradual decreasing of the interface O atoms. In addition, the Ga-Ga dimer starts to appear at the O_4 interface and its number increases as the interfacial O atoms decreases (see O_4 - O_0).

Figure 2 shows the calculated formation energies of various interface configurations, plotting as a function of oxygen chemical potential. It shows that above $\mu_O = -3.3$ eV O_{10} is the most stable interfaces. Below $\mu_O = -3.3$ eV, O_3 is the most stable interface. At the O-rich limit, O_{10} is the most stable interface while O_0 is the least stable interface. At the Hf-rich limit, O_3 is the most stable interface. O_2 , O_1 , and O_0 would never be the stable interface. Since in reality the

Hf-rich condition is not an optimal oxide growth condition, the preferred interfaces should be O-rich interfaces. The realistic achievable O chemical potential is determined by the surrounding O_2 atmosphere, which can be expressed as²⁴

$$\mu_O(T, P) = \mu_O(T, P^O) + \frac{1}{2} kT \ln \left(\frac{P}{P^O} \right),$$

where T is the temperature, P and P^O are the pressure at temperature T and at 1 atm, respectively. For the typical atomic layer deposition (ALD) at 600 K, we find that O_2 pressure reaches to 1 atm when $\mu_O = -0.6$ eV. Thus, any O_2 pressure larger than 1 atm causes the highly O-terminated interface O_{10} .

The density of states (DOS) of O_{10} - O_3 interfaces are shown in Figure 3. For the O_{10} interface, the total DOS shows that there is a 0.3 eV band gap. Meanwhile, from the DOS of the Ga and Sb atoms away from the interface, we

TABLE I. Calculated valence band offsets (in eV) of various interface configurations.

Interfaces	VBO
O ₁₀	2.2
O ₉	2.4
O ₈	2.6
O ₇	2.9
O ₆	3.0
O ₅	3.1
O ₄	3.4
O ₃	3.6
CNL (Ref. 26)	3.6

see that the “bulk” GaSb in our model also has a band gap of 0.3 eV. This value is close to what was calculated from bulk GaSb, but less than the experimental value (~ 0.7 eV) due to the well-known LDA error. Thus, O₁₀ is a semiconducting interface without any gap states. Surprisingly, for interfaces O₉-O₆, similar to the case of O₁₀, these interfaces have clean band gaps. In contrast, for DOS of O₅-O₃, there are some states in the band gap, close to the GaSb conduction band (CB). As a result, the band gap reduces by 0.1 eV–0.2 eV, as shown in the total DOS. Since GaSb has a rather narrow band gap and it is well known that LDA underestimates the band gaps of semiconductors and insulators by 30%–50%, to validate the finding mentioned above, we perform calculations using Heyd-Scuseria-Ernzerhof (HSE) hybrid functional, which can give improved band gaps. We find that the trend shown from the HSE results is consistent with the trend observed from the LDA results.²⁵

We also estimate the valence band offset (VBO) of these interface configurations from the calculated DOS, which is listed in Table I. Since GGA cannot predict accurately the VB edge, GW correction is applied to correct the error. We performed GW calculations for individual bulk HfO₂ and GaSb. We find that the GW method corrects the VB edge of HfO₂ by 0.41 eV but it does not have significant impact on that for GaSb. We can see that the VBO increases as the number of interfacial O decreases. By reducing the interfacial O gradually from 10 to 3, the VBO increases from 2.2 eV up to 3.6 eV. Since in HfO₂ the VB is mainly comprised by O 2*p* states, the amount of interfacial O has great impact on the HfO₂ VB but not on that of GaSb. This is clearly shown in the DOS plot, where the bulk GaSb VB edge does not change with respect to the Fermi level but the bulk HfO₂ CB moves downwards gradually as the interfacial O decreases. Rather than reporting on the HfO₂/GaSb interface, several groups have studied the Al₂O₃/GaSb interface and they have found that the VBO is 3.0 eV–3.1 eV.^{18,26–28} Robertson *et al.* has used a semiempirical “charge neutrality level” (CNL) method to estimate a VBO of 3.6 eV for HfO₂/GaSb, which is comparable to our O₃ model.²⁹

The passivation of III–V surfaces and interfaces has been studied for decades. There are a number of theoretical studies on the electronic structures of III–V (in particular GaAs)/high-k oxide interfaces.^{21,30–38} The interface states are identified as interfacial defects such as Ga dangling bonds and As-As dimers. Our calculations show that the electronic structure of

GaSb/HfO₂ interfaces differs from that of HfO₂/GaAs interfaces. The O₁₀-O₆ interface models show that there is no gap states, indicating that the Ga dangling bonds and Sb-Sb antibonding states are located inside the GaSb CB. This may be due to the smaller band gap of GaSb (0.75 eV) as compared to that of GaAs (1.42 eV). For interfaces O₅-O₃, as mentioned above, the large VBO results in a strong interaction between the HfO₂ CB and the GaSb CB, pushing some states into the band gap.

In summary, we have investigated the interfacial bonding and electronic structure of HfO₂/GaSb interfaces. It is found that the O₁₀ interface is energetically favorable for a wide range of O chemical potential. The calculated valence band offset varies from 2.2 eV to 3.6 eV as the interfacial O content decreases from 10 to 3. More importantly, we find that for interfaces with high interfacial O content (O₁₀-O₆) there is no gap state, indicating that these interfaces are semiconducting. In contrast, for interfaces with low interfacial O content (O₅-O₃), there are some states in the band gap, close to the GaSb conduction band. Our results suggest that GaSb is a suitable material to form high quality interface with the O-rich interface of HfO₂.

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