

## Bonding, Energies, and Band Offsets of Si-ZrO<sub>2</sub> and HfO<sub>2</sub> Gate Oxide Interfaces

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New oxides with high dielectric constant are required for gate oxides. ZrO<sub>2</sub> is a typical example with ionic bonding. We give the rules for bonding at interfaces between Si and ionic oxides, to satisfy valence requirements and give an insulating interface. Total energies and band offsets are calculated for various (100)Si:ZrO<sub>2</sub> and HfO<sub>2</sub> interface structures. The oxygen-terminated interface is found to be favored for devices, because it has no gap states and has a band offset which is rather independent of interfacial bonding.

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The decrease of dimensions of complementary metal oxide silicon transistors has led to a need to replace the SiO<sub>2</sub> gate oxide with oxides of higher dielectric constant (K), in order to maintain a small gate leakage current [1]. The oxide must satisfy various conditions such as being stable in contact with Si [2] and having sufficient band offsets to be a barrier for both electrons and holes [3]. This restricts the choice to the oxides of Hf, Zr, La, Y, and Al, with the leading contenders being HfO<sub>2</sub>, Hf silicates, and their nitride alloys [4–8]. The oxides must also form a high quality interface with Si, with no interface states within the Si band gap. The current in the field effect transistor flows in the Si channel next to the interface, so the transistor performance depends fundamentally on the quality of this interface. The interface quality determines both carrier mobility and device stability. However, despite the intensive work on high K oxides, the performance of devices with high K gate oxides is still rather poor compared to those with SiO<sub>2</sub> gate oxides, in terms of their trapped charge and the carrier mobility [7,8], so that a deeper understanding of the interfaces is urgently needed.

The Si:SiO<sub>2</sub> interface is understood in great detail [9]. This is partly because SiO<sub>2</sub> is covalently bonded like Si, so that simple atomic models can be constructed using electron-pair bonds. Broken bonds must be avoided as these give states in the Si band gap. In contrast, high K oxides have ionic bonding without a fixed coordination, so a new set of rules is needed. The bonding must satisfy electron counting requirements and also give no interface states in the Si gap. This Letter describes these rules, finds the stable interface configurations and finds the effects of different interface bonding on band offsets. The rules are illustrated for epitaxial (100)Si:ZrO<sub>2</sub> interfaces, but they hold generally.

We use epitaxial oxides for simplicity. We choose the Si:ZrO<sub>2</sub> system because it forms a stable, epitaxial interface. The lattice constants of Si and cubic ZrO<sub>2</sub> are 5.43 and 5.07 Å, respectively. This would allow ZrO<sub>2</sub> to grow epitaxially on Si(100) [10,11], with ZrO<sub>2</sub>(100) || Si(100) and ZrO<sub>2</sub>[001] || Si[001]. Si:ZrO<sub>2</sub> is representative of HfO<sub>2</sub>, the silicates, and other cubic oxides such as CeO<sub>2</sub>

[12] and the bixbyite series (Y, La)<sub>2</sub>O<sub>3</sub> [5]. Our results complement recent work on the Si:SrTiO<sub>3</sub>(100) interface [13–15], the prototype interface of Si to ferroelectric or magnetic oxides.

Cubic ZrO<sub>2</sub> has the fluorite structure in which each Zr atom is eightfold coordinated and each oxygen is fourfold coordinated. Other fluorite compounds NiSi<sub>2</sub> and CaF<sub>2</sub> also form epitaxial interfaces with Si which were extensively studied [16–19]. At Si:NiSi<sub>2</sub> interfaces, the Si sublattice continues into the silicide. The (100)Si:NiSi<sub>2</sub> interface has only one configuration with a sixfold coordinated Ni. CaF<sub>2</sub> interfaces are more complex because CaF<sub>2</sub> has no common element with Si, so there can be Ca-terminated or F-terminated interfaces [19]. Ideal (100) and (111) faces of CaF<sub>2</sub> are polar, with only Ca<sup>2+</sup> or F<sup>-</sup> ions. Their charge makes these ideal surfaces unstable. However, one can think of a CaF<sub>2</sub> lattice as consisting of F<sup>-</sup>Ca<sup>2+</sup>F<sup>-</sup> trilayers stacked along [100] or [111] (Fig. 1). These faces now contain half the number of F<sup>-</sup> ions and are nonpolar with a closed-shell configuration.

We can make a (111)Si:CaF<sub>2</sub> interface by placing the nonpolar FCaF unit on a Si surface. However, this is not an insulating interface. The Si(111) face has one half-filled dangling bond (DB) per surface Si atom. Joining it to a closed-shell unit leaves the Si DB still half-filled, giving a metallic interface, Fig. 1(a). An insulating interface is created by joining Si to a *polar* face, FFCaF or CaF, forming a F-terminated or Ca-terminated interface, respectively. For FFCaF, the first F forms a strong polar Si-F bond to the Si and sweeps the Si DB state out of the gap, to give a ≡SiFF<sup>-</sup>Ca<sup>2+</sup>F<sup>-</sup> unit (the lines denote covalent bonds). The CaF unit also satisfies interface valences. CaF donates one electron to the Si DB, making it negative, and Ca repels its state into the valence band [19] to give ≡Si<sup>-</sup>Ca<sup>2+</sup>F<sup>-</sup>.

We now transfer these basic ideas to Si:ZrO<sub>2</sub> interfaces, first (111). ZrO<sub>2</sub> is written as O<sup>2-</sup>Zr<sup>4+</sup>O<sup>2-</sup> units. As with CaF<sub>2</sub>, placing a OZrO unit on a Si(111) surface leaves half-filled Si DBs and a metallic interface, Fig. 1(b). We again try polar OZrO or ZrO units. However, this time it does not work. Oxygen needs two more electrons to fill

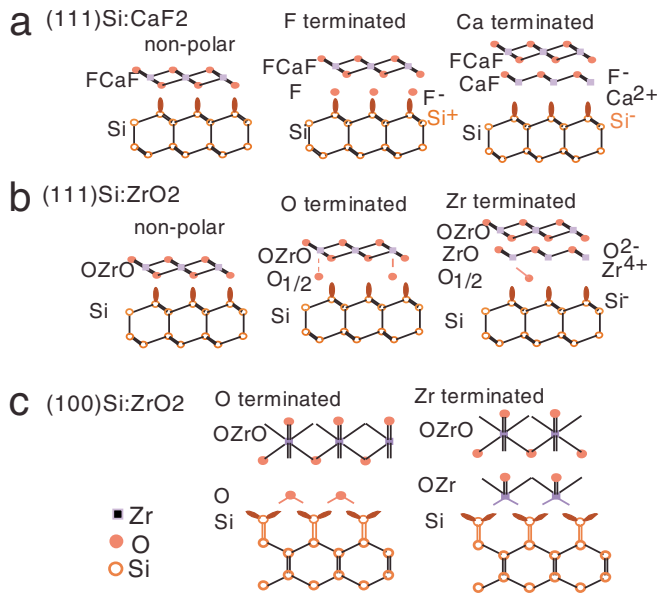


FIG. 1 (color online). Model (111)Si:CaF<sub>2</sub>, (111)Si:ZrO<sub>2</sub>, and (100)Si:ZrO<sub>2</sub> interfaces. FCaF and OZrO units are nonpolar. Lobes are Si dangling bonds. Polar interfaces are insulating for (111)Si:CaF<sub>2</sub> and (100)Si:ZrO<sub>2</sub>. At (111)Si:ZrO<sub>2</sub>, a half monolayer of oxygen is added to make an insulating interface.

its shell, but a Si DB gives only one electron. Thus, this surface is metallic. The 4-2 valences of Zr and O are incompatible with a single DB per Si on Si(111).

Now consider the ideal (100)Si surface, Fig. 1(c). This now has two DBs per surface Si. Putting a nonpolar OZrO unit on (100)Si leaves the Si DBs half-filled and gives a metallic interface. However, if we put a OOZrO unit onto (100)Si, the last O will form two Si-O bonds with the two Si DBs to give =Si=OO<sup>2-</sup>Zr<sup>4+</sup>O<sup>2-</sup>. The interface valence is now satisfied. This is also true for ZrO units. In this case, the Zr forms two polar bonds with the two Si DBs, to give =Si<sup>2-</sup>Zr<sup>4+</sup>O<sup>2-</sup>. Thus, the 4-2 valences of Zr and O are compatible with (100) epitaxy.

Thus, the general bonding rules are as follows: (1) terminate with faces with enough excess oxygen so that the interfacial Si DBs are formally Si<sup>+</sup> and empty, or (2) terminate with excess metal so the Si DBs are formally Si<sup>-</sup> and filled. These rules are general, and also describe the bonding at (111) interfaces, other oxides like Si:SrTiO<sub>3</sub> [15], and interfaces with amorphous oxides.

To test these ideas, we carried out total energy calculations on various interface configurations. The calculations are carried out on periodic supercells containing typically nine layers of Si with two atoms per layer, five layers of ZrO<sub>2</sub> and no vacuum, repeated along [001], giving typically 46–52 atom cells (18 Si, 10 Zr, 24 O) 23–27 Å high and ~5.4 Å wide. The electronic structure and total energies are calculated using the CASTEP code [20], with Vanderbilt [21] ultrasoft pseudopotentials, a plane wave cutoff energy of 350 eV, and forces converged

to 0.05 eV/Å. The exchange-correlation energy is given by the Perdew-Wang (PW91) version of the generalized gradient approximation. All atom positions can relax, and symmetry was unconstrained except for fixed 90° cell angles. The possibility of reconstruction along the interface was tested in larger supercells with ~100 atoms. Convergence was tested to give total energies of under 0.05 eV per interface Si atom. Similar results are found for (100)Si:HfO<sub>2</sub> where cubic HfO<sub>2</sub> is the stable phase.

Figure 2(a) shows the ideal Si:OZrO interface based on Fig. 1(c). This has fourfold coordinated interface O sites. We denote this as O<sub>4V</sub>, V denoting an oxygen vacancy. We find this interface is metallic, as expected from the above discussion.

Figure 2(b) shows the ideal Si:OOZrO (O-terminated) interface. The interface O layer has twice as many oxygens compared to O<sub>4V</sub>. The interface oxygens are fourfold bonded to two Si and two Zr atoms. We denote this as O<sub>4</sub>. The interface Si atoms start as sixfold bonded, to four O's and two Si's. The structure relaxes to that in Fig. 2(c). Half the oxygens form Si-O-Si bridges by relaxing towards the Si layer. The other oxygens, lying above Si's two layers down, relax up towards the ZrO<sub>2</sub>. It has relaxed towards the configuration of a closed-shell Si-O-Si bridge and OZrO unit, with Si's again fourfold bonded. The

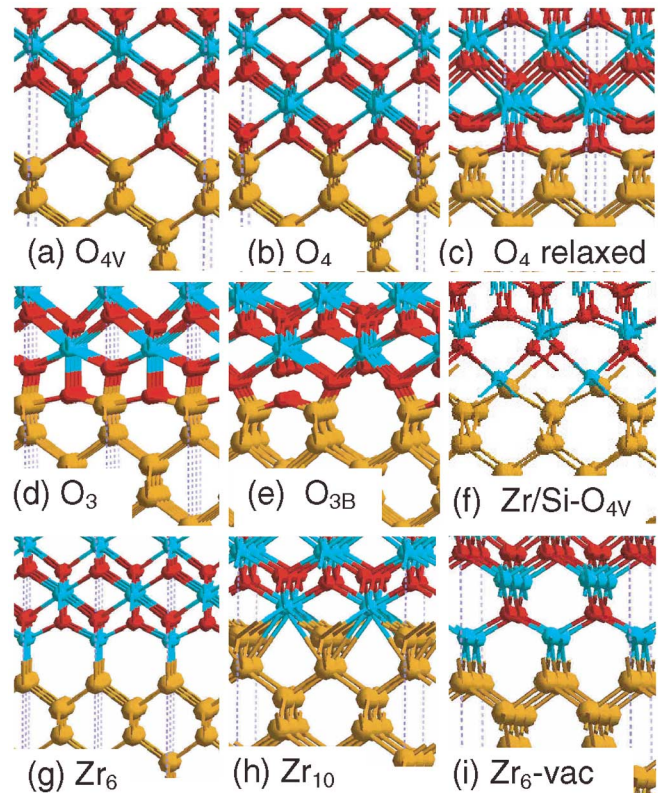


FIG. 2 (color online). Atomic configurations of various unrelaxed [(b) only] and relaxed Si:ZrO<sub>2</sub> interfaces, viewed in the (110) plane.

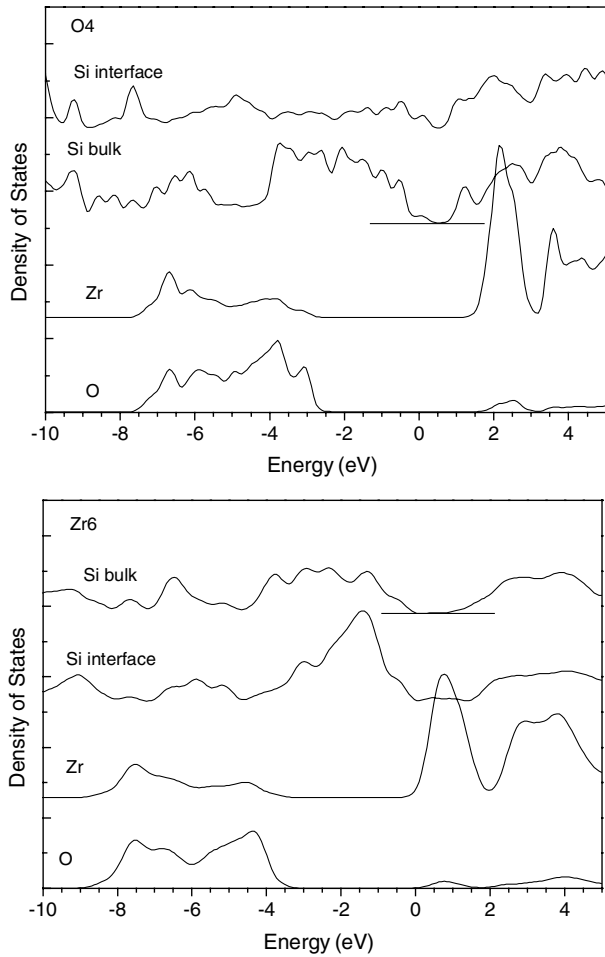


FIG. 3. Partial density of states at (a)  $O_4$  and (b)  $Zr_6$  interfaces.

partial density states in Fig. 3(a) show that this interface is insulating with no states in the gap, following our simple picture above.

Another possible interface has the interface oxygens in a row along  $[110]$  and initially threefold coordinated as in  $ZrSiO_4$ . This interface relaxes to that shown in Fig. 2(d). Here half the oxygens bond to two Si's and one Zr, and the other half bond to two Zr's and one Si. The interfacial Si's are fivefold bonded.

A final O-terminated interface is Fig. 2(e). Here, one of the two Si DBs pairs off in a Si-O-Si bridge. The second DB bonds to an O of a  $OZrO$  unit. But the Si DB needs to give away an electron, which it cannot to the closed-shell  $OZrO$  unit. It needs an extra half monolayer of O for this. This gives a  $Si^+(O^{2-})_{0.5}OZrO$  configuration overall. We denote this interface as  $O_{3B}$ , with B for bridge.

The last three interfaces have the same number of oxygens. Their total energies per surface Si are compared in Table I. The  $O_3$  interface is found to be the most stable structure. The  $O_4$  interface is marginally less stable.

Figure 2(g) shows a Zr-terminated interface with six-fold coordinated Zr, denoted  $Zr_6$ . There are two Zr-Si

TABLE I. Interface energy with respect to the most stable O- or Zr-terminated interface, valence band offset, and insulating quality of various interfaces.

Interface	Energy (eV/Si)	VB offset (eV)	Metal?
$O_4$	0.27	2.9	No
$O_3$	0	2.9	No
$O_{3B}$	0.39	2.7	No
$Zr_6$	1.2	3.3	No
$Zr_{10}$	0	2.6	Yes
$Zr_6-O_{VAC}$		3.3	Yes
Bulk CNL (LDA)		3.1	

bonds per interfacial Si atom. These are polar electron-pair bonds, with Si negatively charged, as in a Zintl compound. The interfacial Zr-Si bonds relax to 2.7 Å in length. As Zr is tetravalent, its bonding requirements are satisfied. This interface has a gap; see Fig. 3(b). However, it has gap states so this interface is not ideal for devices. The gap states occur partly because Zr is less electro-positive than Ca in  $CaF_2$  so it does not repel the Si DB state fully into the valence band.

Other Zr-terminated interfaces are possible. The Zr coordination in  $ZrSi_2$  is tenfold, so we can construct a  $Zr_{10}$  terminated interface, Fig. 2(h). Here, the Zr atoms are bonded to four Si's in layer 1, two more Si's in layer 2, and four oxygens in the  $ZrO_2$ . This interface is found to be more stable than  $Zr_6$ . This is partly because of its higher Zr coordination. The  $Zr_6$  is also destabilized by a  $Si^{2-}$  site which is too repulsive. The  $Zr_{10}$  interface should be insulating on electron counting rules, but is metallic as the high Zr coordination causes band overlap.

Finally, we consider a  $O_{4V}$  structure with 1/2 monolayer of Zr substituted for Si in the top layer, Fig. 2(f), as in Fiorentini and Gulleri [22]. This interface " $Zr/Si-O_{4V}$ " has a half layer of oxygen vacancies like  $O_{4V}$ . We find the symmetric interface to be metallic like  $O_{4V}$ , as expected from our discussion, but unlike these authors [22]. It can become semiconducting by reconstruction by breaking interface Si bonds.

Experimentally, Wang and Ong [11] have grown epitaxial Y-stabilized  $ZrO_2$  on Si(100) with  $Si[001]//ZrO_2[001]$  as here. They took high-resolution electron microscope lattice images of the interface, and their simulations agree with the  $O_4$  interface of Figs. 2(b) and 2(c). This is the most symmetric of O-terminated interfaces, and may occur experimentally over the marginally more stable  $O_3$  interface due to kinetic effects. Thus, the experimental images support the formation of our more stable, insulating interface. However, this is not a full experimental verification, as light elements like oxygen have low visibility in TEM.

The different interface bonding can affect the band offsets. Table I gives the calculated valence band (VB) offsets of each interface. These offsets are found from the

difference of the Si and oxide VB edges in the center of their layers. The conduction band (CB) offset is then found by adding the experimental band gaps (1.1 eV for Si, 5.8 eV for ZrO<sub>2</sub>) [3,23]. CB offsets are not calculated directly, to avoid the band gap error in the local density approximation (LDA).

The calculated VB offsets are compared to those found from the virtual gap state (VGS) model. This model finds the band offset by aligning the charge neutrality levels (CNL) of the bulk solids. In that model, offsets are independent of the actual interface atomic structure, which in reality could introduce an additional dipole.

Our calculations find that the VB offsets of O-terminated interfaces of 2.9–2.7 eV are within 0.2 eV of each other, and are slightly below the calculated VB offset of 3.1 eV in the VGS model in LDA [23]. In contrast, offsets of the two Zr-terminated interfaces are quite different. Experimentally, the CB offsets of ZrO<sub>2</sub> and HfO<sub>2</sub> on Si are about 1.4 eV [24,25], equivalent to a VB offset of 3.3 eV, close to calculated values. This means that the various O-terminated interfaces do not introduce significant extra interface dipoles due to their different bonding configurations.

This is very important technologically. A sufficiently large CB offset of over 1 eV is a key constraint of possible gate oxides. The VGS CB offset by LDA is  $\sim$ 1.6 eV, but this could easily vary if there were an additional dipole layer. The calculations show that the band offset varies little with interface bonding. We also find similar offsets at the O-terminated (111) interface [26]. Thus, the offset should be relatively constant for nanocrystalline or amorphous Si:ZrO<sub>2</sub> interfaces used in reality. Technologically, this means there is a sizable process window for oxygen bonding and oxygen partial pressure to give an acceptable band offset. This is like the desirable case of Si:SiO<sub>2</sub>, where the offsets are within 0.2 eV between (100) and (111) interfaces [27]. On the other hand, Zr-terminated interfaces are less desirable technically. The Zr<sub>10</sub> interface is metallic, while the Zr<sub>6</sub> interface has a CB offset of only 0.8 eV, which is too low. This arises from its long Zr-Si bond. Thus, these conditions should be avoided. Note that the 0.2 eV constancy of offsets for O-terminated Si:ZrO<sub>2</sub> is a nontrivial result. The offsets at Si:CaF<sub>2</sub>(111) interfaces vary by 3 eV for possible structures, and by 1.5 eV for more stable structures [19]. The offsets can be understood in terms of dipole layers. The three O-terminated interfaces have similar net dipoles, which explains their similar offsets. This suggests that we should aim for O-terminated interfaces, as they have the better properties.

We have developed rules for bonding at interfaces between Si and ionic oxides to satisfy valence requirements and give insulating interfaces. The O-terminated interface with initially fourfold coordinated oxygen is found to be the most likely interface with insulating

properties, and its band offsets indicate an absence of additional interfacial dipoles. The rules extend to other interfaces of Si:ZrO<sub>2</sub>, such as (111), to amorphous oxides, and to related oxides like SrTiO<sub>3</sub>.

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