JOURNAL OF APPLIED PHYSICS VOLUME 90, NUMBER 3 1 AUGUST 2001

First principles investigation of scaling trends of zirconium silicate interface band offsets

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(Received 20 February 2001; accepted for publication 13 April 2001)

First principles density functional theory calculations are carried out to investigate the scaling trends of band offsets at model silicon/zirconium silicate interfaces. Owing to the *d* character of zirconium silicate conduction bands, the band gap and band offset are shown to decrease as the zirconium concentration is increased. Since the valence band character of silicates remains unchanged relative to SiO_2, the conduction band offset alone decreases, leading to increasingly asymmetric band offsets at higher zirconium concentrations. The use of charge transfer dipoles at the interface is investigated as a possible remedy to restore the band offset symmetry by shifting the silicate bands relative to the silicon bands. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1378338]

I. INTRODUCTION

Aggressive scaling of complementary metal–oxide–semiconductor (CMOS) transistors has resulted in silicon dioxide (SiO_2) gate oxide films so thin that direct tunneling of carriers through the insulator contributes substantially to the overall device leakage current. Gate leakage leads to unacceptable levels of standby power dissipation and presents a fundamental limit to continued scaling.[1] Leakage through an ultrathin oxide arises from direct tunneling of carriers through the potential barrier presented by the insulator. Since the transmission through such a potential has a strong dependence on the barrier thickness, much effort has focused on the development of alternative high-*k* gate dielectric materials. The higher dielectric constant in these materials allows for a physically thicker barrier, thus potentially reducing tunneling transmission, while maintaining the gate capacitance needed for scaled device operation.

Many high-*k* dielectrics are composed of oxides or silicates of *d*-electron transition metals, in which the enhanced polarizability and phonon mode softening of the metal–oxygen bond leads to a higher dielectric constant. Silicates of zirconium (Zr) and hafnium (Hf) are promising dielectric materials with demonstrated thermal stability in direct contact with Si.[2] Conceptually, Zr silicates can be modeled as a mixture of zirconium and silicon dioxide $(ZrO_2)_x(SiO_2)_{1-x}$. The conventional wisdom is that the concentration of the transition metal in the silicate can be steadily increased to meet the capacitance requirements of each technology generation, while maintaining a sufficiently thick film to prevent excessive gate leakage. However, increases in the transition metal concentration also tend to reduce the band gap of the material, since the silicate becomes increasingly ZrO_2 like, which has a smaller band gap than SiO_2. The reduction of the insulator band gap consequently degrades the height of the potential barrier presented to tunneling carriers. Since the tunneling transmission depends on both barrier thickness and barrier height, an important design tradeoff arises as the transition metal concentration is increased in future technology generations.

This article presents a computational study of the scaling trends of band offsets at model Si/Zr silicate interfaces. Based on analysis of the electronic structure of silicates, the degradation of the potential barrier is shown to primarily affect the conduction band offset, leading to asymmetric barrier heights as the Zr concentration is increased. By explicitly altering the surface termination, charge transfer dipoles at the interface are investigated as a possible means of restoring symmetry in the band offsets. The article is organized as follows. Section II describes the computational approach. All calculations presented are based on first principles density functional theory (DFT) methods. Section III describes the bulk structural and electronic properties of several high-*k* dielectrics with varying concentrations of Zr, from model and known silicates to pure ZrO_2. Section IV describes the expected scaling trends of Zr silicate band offsets using model interface calculations.

II. COMPUTATIONAL THEORY

All calculations reported in this article used the Vienna *ab initio* simulation package (VASP) program.[3–5] VASP is widely used to perform first principles DFT calculations and has been applied to study diverse materials, including ZrO_2 polymorphs.[6] The exchange-correlation energy was described by the local density approximation (LDA) functional

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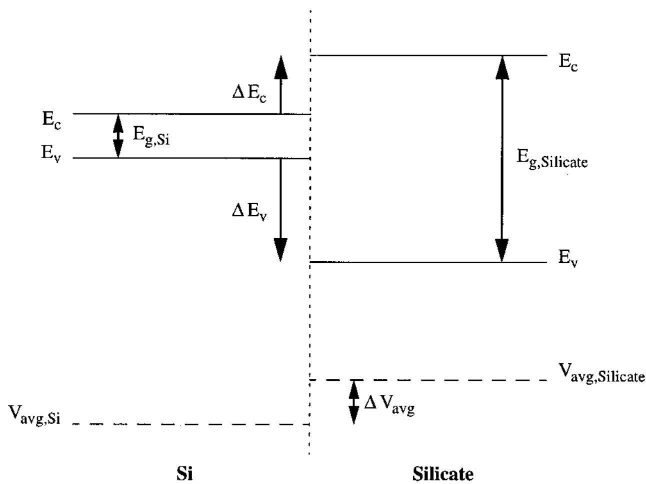

FIG. 1. Diagram showing Van de Walle's band offset calculation procedure. The band structures and average potential energies ($V_{avg,Si}$ and $V_{avg,Silicate}$) are obtained from bulk calculations. The potential shift ΔV between the average levels in Si and Zr silicate is obtained from a superlattice calculation in which the two materials form an interface. The resulting lineup of the bulk band structures gives ΔE_c and ΔE_v, the conduction and valence band offsets.

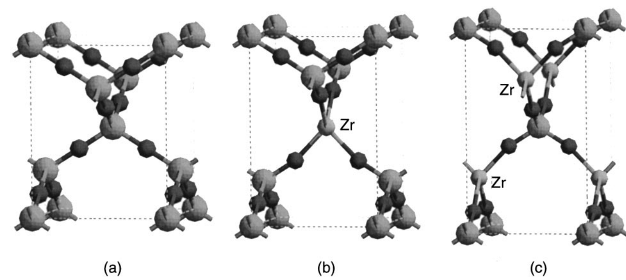

FIG. 2. (a) Crystal structure of β-cristobalite SiO_2. (b) Crystal structure of model silicate, $Zr_1Si_3O_8$, with 8.3 at. % Zr concentration. (c) Crystal structure of model silicate, $Zr_2Si_2O_8$, with 16.7 at. % Zr concentration. Each model is lattice matched along the *a* axis to the Si lattice constant. Large atoms are Si, small atoms are O. Zr atoms are indicated.

of Ceperley and Alder as parametrized by Perdew and Zunger.[7] Ultrasoft pseudopotentials with Zr($4p$,$4d$,$5s$), Si($3s$,$3p$), and O($2s$,$2p$) levels treated as valence states were employed.[8,9] A Monkhorst–Pack *k*-point mesh of $2\times2\times2$ for bulk calculations and $2\times2\times1$ for interface calculations were used. A plane wave basis kinetic energy cutoff of 36 Ryd was used in all calculations.

While experimental silicate films are amorphous, all models studied in this article are crystalline. The computational cost of DFT prevents direct study of large, amorphous materials characterized by long-range disorder. Instead, smaller periodic crystals whose local bonding units are representative of those found in the amorphous phase are typically used. This approach has worked well for studies of SiO_2, since the important material physics is contained in the local SiO_4 tetrahedra.[10] Since silicates are an incremental modification of SiO_2, it is expected that this approach should still be valid.

To determine the band offsets, the bulk energy levels of Si and Zr silicate must be aligned at the interface. However, the lack of a well-defined absolute energy reference in an infinite periodic solid prevents a direct comparison of energy levels from two different bulk materials. To circumvent this difficulty, a method first proposed by Van de Walle and Martin was followed.[11] Separate bulk calculations were carried out to obtain the band gap and average potential energy in each material. A superlattice calculation was then used to extract a potential shift ΔV between the average bulk potential levels on either side of the interface. The ΔV term includes any effects of structural relaxation and charge transfer dipoles at the interface on the resulting band offsets. Figure 1 shows the procedure graphically.

III. BULK CALCULATIONS

Calculations of several bulk oxides and silicates were carried out within DFT–LDA to study the effect of increasing Zr concentration on the underlying electronic structure. Three known crystals served as references for comparison: β-cristobalite SiO_2 with 0 at. % Zr; the silicate zircon, $ZrSiO_4$, with 16.7 at. % Zr; and monoclinic ZrO_2 with 33 at. % Zr.[12–14] Since only the SiO_2 model can be used to form a well-defined, lattice-matched interface with crystalline Si, the $ZrSiO_4$ and ZrO_2 crystals alone cannot be used to study the expected behavior of band offsets at the Si interface. Thus two additional model silicates were formed as described below.

Cubic β-cristobalite was chosen as the reference SiO_2 crystal.[12] The equilibrium lattice constant was found to be 7.34 Å, in good agreement with 7.39–7.41 Å as predicted by previous first principles studies.[15,16] At this lattice constant, the Si–O bond length was 1.59 Å and the Si–O–Si bond angle was 180°. In order to form an SiO_2 model compatible with the Si lattice, a prescription first proposed by Herman and Kasowski was followed. The Herman construction has been used in a number of previous theoretical studies of the Si/SiO_2 interface.[16–20] A tetragonal lattice which is nearly lattice matched with Si(001) was first formed by rotating the β-cristobalite 45° along its *c* axis. This tetragonal cell has a lattice constant of 5.19 Å along the *a* axis, representing a 4.4% lattice mismatch with Si. In practice, all proposed crystalline models of the Si/SiO_2 interface introduce such mismatch, and it is standard practice to simply expand or contract the SiO_2 model to match the Si lattice constant.[21,22] By a Poisson's ratio argument, it is expected that expansion along the *a* axis would cause contraction along the *c* axis. By searching for the total energy minimum, the optimized *c*-axis lattice constant was found to be 6.90 Å. The resulting lattice-matched crystal structure is shown in Fig. 2(a), and the relevant structural parameters of both models are summarized in Table I.

The high degree of symmetry of the lattice-matched β-cristobalite structure allows it to be completely specified by a single Si–O bond length of 1.61 Å and Si–O–Si bond angle of 180°. This facilitates an important goal of the model silicate study, which is to isolate as much as possible the effect of varying the Zr concentration by keeping constant all other factors, such as the Si–O bonding and lattice parameters. Based on the lattice-matched β-cristobalite structure, a model silicate ($Zr_1Si_3O_8$) with 8.3 at. % Zr was formed by replacing a single Si atom in the SiO_2 model with Zr. By

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TABLE I. Structural properties and band gap values of model silicates based on the β-cristobalite SiO_2 crystal. Both the raw LDA and corrected LDA band gap values are given. An empirical correction factor of 1.66 has been used to obtain the latter values. Note that all Si–O–Si bond angles are 180° and all Zr–O–Si bond angles are 166°.

Model	Zr (at. %)	Lattice constant (Å)	O-coord. around Zr	Si–O bond length (Å)	Zr–O bond length (Å)	LDA band gap (eV)	Corrected LDA band gap (eV)
β-cristobalite SiO_2	0	5.19, 5.19, 7.34	4	1.59	—	5.37	8.9
β-cristobalite SiO_2[a]	0	5.43, 5.43, 6.90	4	1.61	—	5.06	8.39
$Zr_1Si_3O_8$[a]	8.3	5.43, 5.43, 8.03	4	1.61	1.97	3.98	6.59
$Zr_2Si_2O_8$[a]	16.7	5.43, 5.43, 9.16	4	1.61	1.97	3.84	6.36

[a]Models lattice matched along the *a* axis to the Si lattice constant and used in the subsequent interface calculations.

varying only the Zr–O bond length to accommodate the larger Zr atom, the lowest energy structure was found at a Zr–O bond length of 1.97 Å. This compares reasonably to a Zr–O bond length of 1.94 Å obtained in a previous study in which a β-quartz SiO_2 model with Zr substitution for Si at 11 at. % Zr was allowed to fully relax towards its total energy minimum.[23] A second model silicate ($Zr_2Si_2O_8$) with 16.7 at. % Zr was formed by replacing a second Si atom with Zr and maintaining the Zr–O bond length at 1.97 Å. Figures 2(b) and 2(c) show the resulting model silicate structures, and structural parameters of both models are summarized in Table I.

The assumption that Zr is fourfold coordinated by oxygen (O) at the concentrations considered is an important limitation of the study. While Zr does indeed appear to be tetrahedrally bonded to O at low Zr concentration, recent experiments have shown that the Zr coordination increases at higher concentrations. Based on extended x-ray absorption fine structure spectroscopy measurements of Zr silicate films, Lucovsky has found that the average Zr coordination indeed increased from 4.5 ± 1 for samples with ~3.3 at. % Zr to 7.2 ± 1 for samples with ~8.3 at. % Zr.[24] However, the difficulty in defining a silicate structure with eightfold coordinated Zr that can form a lattice-matched interface with Si prevents direct study of the interface properties of such silicates.

While their interface properties are not explicitly addressed, the bulk structural and electronic properties of two known crystals with higher than fourfold Zr coordination are studied and compared to those of model silicates based on the β-cristobalite structure. Zircon ($ZrSiO_4$) is a known crystalline silicate with 16.7 at. % Zr.[13] The tetragonal unit cell consists of parallel chains of edge-sharing fourfold coordinated SiO_4 units and eightfold coordinated ZrO_8 units. Monoclinic ZrO_2 with 33 at. % Zr is the known ground state of Zr oxide and consists of sevenfold coordinated Zr atoms.[14] Structural parameters of both crystals obtained from full relaxation within DFT–LDA are listed in Table II along with experimental values. DFT typically predicts ground state structural properties very accurately, and the agreement with experiment in this case is quite good. An interesting observation is that the mass density of the tetrahedral model sili-

TABLE II. Structural properties and band gap values of known Zr silicate and oxide crystals. Both the raw LDA and corrected LDA band gap values are given. An empirical correction factor of 1.66 has been used to obtain the latter values. Experimental values for $ZrSiO_4$[a] and ZrO_2[b] are noted in parentheses where available.

Model	Zr (at. %)	Lattice constant (Å)	O-coord. around Zr	Si–O bond length (Å)	Zr–O bond length (Å)	LDA band gap (eV)	Corrected LDA band gap (eV)
$ZrSiO_4$	16.7	6.61, 6.61, 5.95 (6.61, 6.61, 6.00)	8	1.61 (1.62)	2.14, 2.26 (2.13, 2.27)	4.58	7.59
monocl. ZrO_2	33	5.07, 5.23, 5.30 (5.15, 5.21, 5.31)	7	—	2.05–2.24 (2.04–2.26)	3.41	5.64

[a]See Ref. 13.
[b]See Ref. 14.

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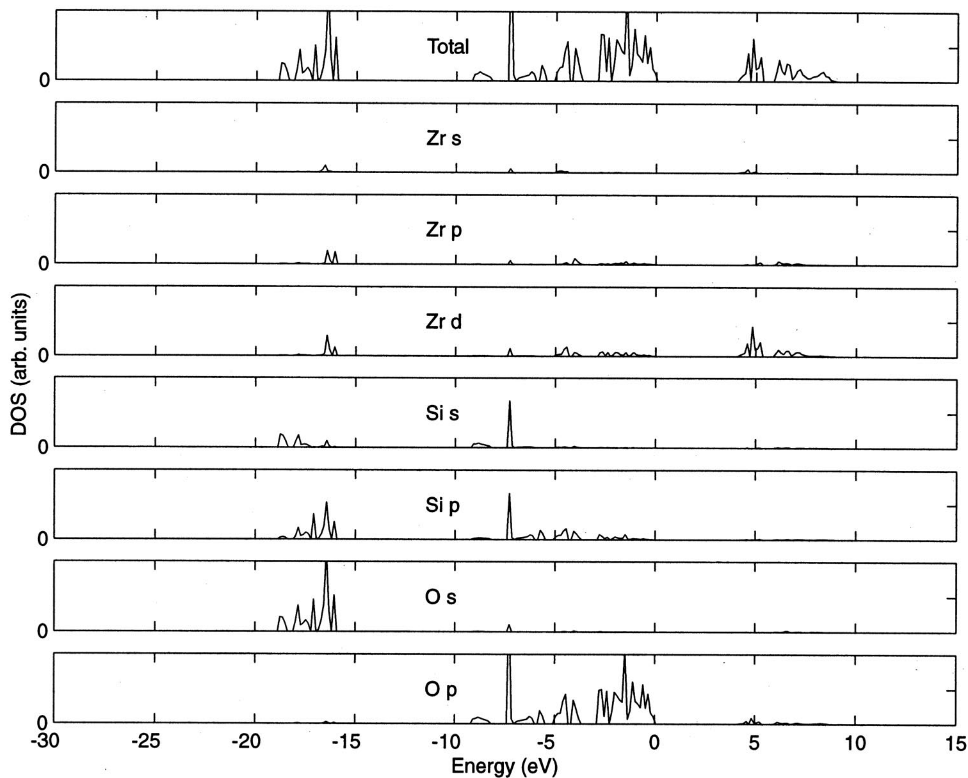

FIG. 3. Partial density of states (PDOS) of the model silicate $Zr_1Si_3O_8$. The zero of energy represents the Fermi level.

cate $Zr_2Si_2O_8$ (1.4 amu/Å^3) is approximately half that of $ZrSiO_4$ (2.8 amu/Å^3). The large density difference implies that local stress–strain conditions may influence the stability of various oxygen coordinations within the silicate film. Since the $Zr_2Si_2O_8$ and $ZrSiO_4$ structures contain the same Zr concentration, it is also possible to directly compare their total energies. The $Zr_2Si_2O_8$ model contains two $ZrSiO_4$ bonding units and has an energy of −54.79 eV per Zr bonding unit while zircon contains four $ZrSiO_4$ bonding units and has an energy of −57.32 eV per Zr bonding unit, so that the higher coordinated zircon model is 2.52 eV per Zr bonding unit more stable. This large energy gain helps to explain the higher average Zr coordinations observed in experimental silicate films with higher than a few atomic % Zr.[24]

The electronic structure of each silicate was analyzed by calculating the partial density of states (PDOS) and the band structure. The PDOS is particularly useful for identifying the nature of bonding in a material. It is well known that in SiO_2, the lowest conduction band states are formed from the Si *s* states, while the highest valence band states are formed from the O *p* states.[25] In contrast, the PDOS of the model silicate $Zr_1Si_3O_8$ shown in Fig. 3 indicates that the lowest conduction band states are formed from the Zr *d* states, while the highest valence band states are still formed from the O *p* states. The $Zr_2Si_2O_8$ model has a very similar PDOS and is not shown. The PDOS of the known silicate $ZrSiO_4$ was also computed as shown in Fig. 4. Comparing the two PDOS near the band gap, the bonding character in fourfold coordinated and eightfold coordinated Zr silicates is qualitatively similar. The lowest conduction states consist of Zr *d* states, while the highest valence states consist of O *p* states. Since *d* electron levels are lower in energy than *s* electron levels, the band gap in Zr silicates and oxides is smaller than in SiO_2. This has been identified as an important shortcoming of transition metal silicates and oxides in general.[25,26]

The minimum band gap values were determined by analyzing the calculated band structures and are reported in Tables I and II. An important limitation of the local density approximation (LDA) employed in most first principles calculations is that excited state energies, including the band gap, are typically underestimated. Compared to experimental band gaps of 8.9 eV for SiO_2 and 5.83 eV for monoclinic ZrO_2, the present calculations yield 5.37 and 3.41 eV, respectively.[27] A common first-order correction is to empirically fit the LDA band gap to a known experimental value.[16] The difficulty with this approach is that experimental band gap measurements for Zr silicates are not available, and it is not clear whether a single factor can describe the band gap enhancement across a range of Zr concentrations. It can be observed, however, that a factor of 1.66 which fits the SiO_2 band gap, also brings the ZrO_2 band gap within 3% of experiment. The remainder of this study assumes that the same empirical factor which fits the end members SiO_2 and ZrO_2 can also be applied to silicates across a range of Zr concentrations. While the correction factor is empirical, it is expected that the important trends of silicate band offsets observed in Sec. IV are still meaningful. It is worth noting that the quasiparticle GW method, which represents a higher level of theory beyond DFT–LDA, has been shown to accurately predict excited state energies for a wide range of materials, including transition metal oxides such as ZrO_2.[28,29] While the GW approach is more computationally intensive than DFT–LDA, such a study of silicate band structures may be of significant interest to the high-*k* community.

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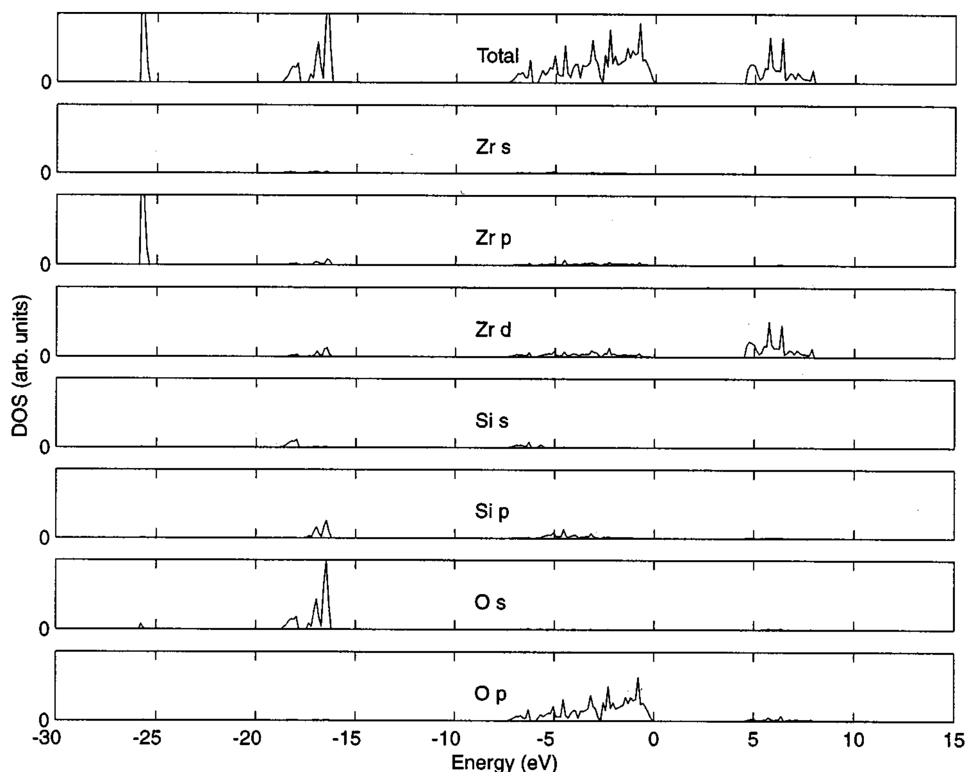

FIG. 4. Partial density of states (PDOS) of the crystal zircon, $ZrSiO_4$. The zero of energy represents the Fermi level.

The band gaps of the lattice-matched model silicates were also calculated and are shown in Table I. It should be noted that the Zr–O bond length of 1.97 Å chosen for these models is shorter than the Zr–O nearest neighbor distances of 2.1 and 2.3 Å reported for experimental silicate films by Lucovsky.[26] To explore the effect of the bond length, additional silicate models were studied with different Zr–O distances. The band gap was found to decrease more than 30% as the Zr–O bond length was increased from 1.9 to 2.1 Å. By comparing the fully relaxed and lattice-matched SiO_2 structures, it was also observed that accommodating the 4.4% lattice mismatch between SiO_2 and Si led to a 6% decrease in the band gap. Again the decrease in band gap was accompanied by an increase in the Si–O bond length, from 1.59 to 1.61 Å. Figure 5 summarizes the corrected LDA band gaps of all structures studied as a function of at. % Zr. The sensitivity of the band gap to the Zr–O bond length and lattice mismatch suggest that local stress–strain conditions in the bulk and at the interface will impact band offsets.

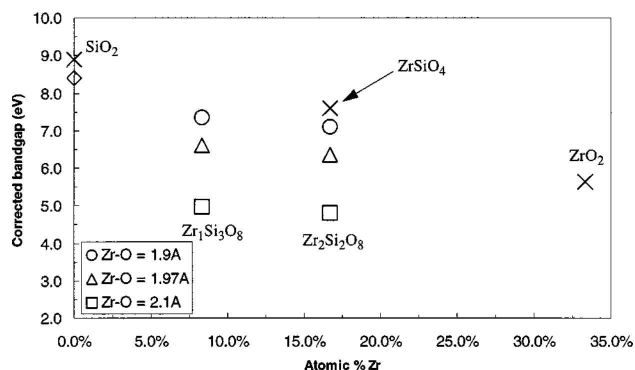

FIG. 5. Corrected LDA band gaps as a function of at. % Zr. An empirical correction factor of 1.66 has been used. Models that were fully allowed to relax are indicated by ×. All other models were lattice matched along the *a* axis to the Si lattice constant.

IV. INTERFACE CALCULATIONS

When two different semiconductors are brought together, there is generally some transfer of charge to equalize the chemical potential across the interface. The resulting interface dipole, along with the electron affinity of the two semiconductors, determines the band lineups.[26,30,31] In the case of Zr silicates, the band offsets are expected to depend on the role of Zr in altering the electronic structure of the reference Si/SiO_2 interface. An interesting observation to this end can be made based on the bonding character of silicates as revealed by the PDOS analysis in the previous section. Recall that the Zr d states form the conduction bands in silicates while Si s states form the conduction bands in SiO_2. O p states form the valence bands in both materials. In the absence of differences in interface dipoles, the valence band offset in silicates is expected to remain similar to that in SiO_2. On the other hand, it is expected that the conduction band offset in silicates will be lower than in SiO_2, since d electron levels are lower in energy than s electron levels. It can then be projected that the conduction band offset alone would decrease with increasing Zr concentration, while the valence band offset will remain unaltered, leading to increasingly asymmetric offsets. Similar conclusions have been drawn based on a Harrison tight-binding model of Zr silicates.[32–34] Robertson has also predicted asymmetric offsets for a wide range of high-k materials consisting of d-electron transition metals.[26] The inherent asymmetry of

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barrier heights in silicates would imply increased susceptibility to electron tunneling relative to hole tunneling.

Several authors have studied the effect of interface dipoles on band lineups at the Si/SiO_2 interface through theoretical methods.[19,20,35,36] Massoud and Lucovsky *et al.* estimated the change in conduction band offset due to dipoles at pure, nitrided, and suboxidized Si/SiO_2 interfaces based on empirical and first principles cluster calculations.[35,36] Kageshima *et al.* correlated the strength of dipoles arising from different surface terminations at model Si/SiO_2 interfaces to changes in the valence band offset using first principles supercell calculations.[19,20] These results suggest that it may be possible to explicitly introduce dipoles at Si/silicate interfaces to restore the symmetry of barrier heights implied by the PDOS analysis. Robertson has suggested such a solution for the case of the Ta_2O_5/Si interface, which has a very asymmetric alignment due to a small conduction band offset.[26] These ideas are explored for the Zr silicate system to gain insight into the design of optimal interface properties.

Following the method of Van de Walle and Martin outlined earlier, Si/silicate interface band offset calculations were carried out using the lattice-matched models developed in Sec. III. Previous studies have followed a similar approach to study band offsets at the Si/SiO_2 interface.[16,20] It is customary to fully relax the atomic positions in order to obtain the lowest energy interface structure. However, in this study, atomic relaxations were limited to the first Si and O layers at the Si/SiO_2 and $Si/Si_1Zr_3O_8$ interfaces. The relaxation led to structural changes at the interface, as the Si–O bond length was observed to change from 1.61 to 1.61–1.64 Å and the Si–O–Si bond angle was observed to change from 180° to 165°–168°. No relaxation was allowed at the $Si/Si_2Zr_2O_8$ interface, so that the Si–O bond length remained 1.61 Å and the Zr–O–Si bond angle remained 166°. These limitations were imposed in order to maintain a constant ZrO_4 bonding unit to facilitate comparison of band offsets at different Zr concentrations.

The Herman construction of the Si/SiO_2 interface is known to leave a single Si dangling bond at the interface.[17,18] In the first set of calculations, the dangling bond in each interface model was hydrogen terminated. The resulting H-terminated models for the $Si/Si_1Zr_3O_8$ and $Si/Si_2Zr_2O_8$ interfaces are shown in Figs. 6(a) and 7(a), respectively. It should be noted that a superlattice structure is required by the Van de Walle method, so that there are two identical interfaces in each supercell. The Si/SiO_2 interface model is not shown. The potential shift ΔV across the interface was calculated for each model to extract the band offsets listed in Table III. As shown in Fig. 8, the valence band offsets remain nearly constant around 4.5 eV, while the conduction band offsets degrade substantially from 2.8 eV with increasing Zr concentration, consistent with the behavior expected based on the PDOS analysis. The increasingly asymmetric ratio of conduction to valence band offset is shown in Table III.

Changing the surface termination of the Si dangling bond is a direct and controlled way of altering the interface dipole. A number of such terminations for the Si/SiO_2 interface have been considered by Kageshima and Shiraishi and the formation of a Si=O double bond has been shown to saturate the Si dangling bond.[19,20] Since the Si=O bond is much more polar than the Si–H bond, a large change in the interface charge transfer is expected. The resulting O-terminated models for the $Si/Si_1Zr_3O_8$ and $Si/Si_2Zr_2O_8$ interfaces are shown in Figs. 6(b) and 7(b). The calculated band offsets are listed in Table III. As shown in Fig. 9, the general trend that valence band offsets remain nearly constant while the conduction band offsets degrade considerably with increasing Zr concentration holds as in the

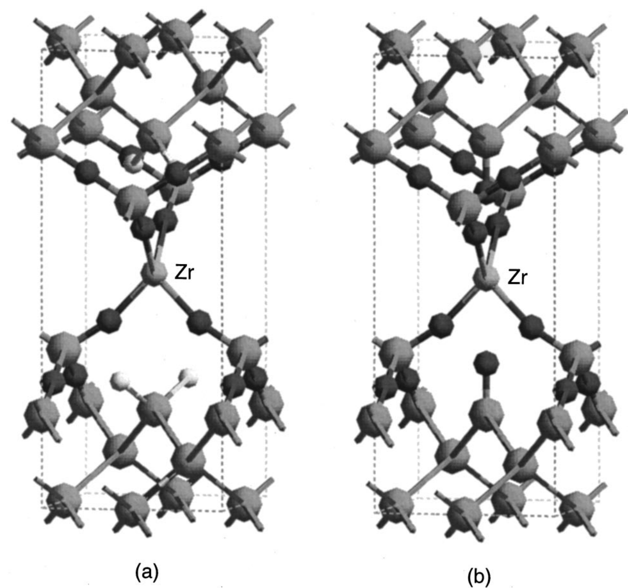

FIG. 6. Interface structure between Si and model silicate, $Zr_1Si_3O_8$. In (a), the Si dangling bond at the interface is H terminated. In (b) the Si dangling bond at the interface is O terminated. Large atoms are Si, small atoms are O. Zr atoms are indicated.

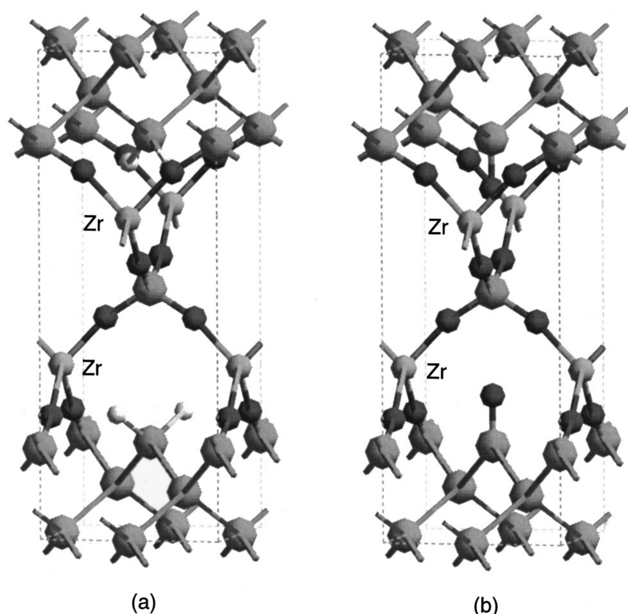

FIG. 7. Interface structure between Si and model silicate, $Zr_2Si_2O_8$. In (a), the Si dangling bond at the interface is H terminated. In (b), the Si dangling bond at the interface is O terminated. Large atoms are Si, small atoms are O. Zr atoms are indicated.

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TABLE III. Conduction and valence band offsets of model Si/silicate interfaces with H and O termination of the Si dangling bond at the interface. The ratio of conduction to valence band offset is also indicated.

Interface model	Termination of Si dangling bond	Conduction band offset ΔE_c (eV)	Valence band offset ΔE_v (eV)	Ratio of conduction to valence band offset
Si/SiO_2	H	2.77	4.49	0.62
	O	4.48	2.78	1.61
Si/$Zr_1Si_3O_8$	H	1.05	4.43	0.24
	O	2.74	2.74	1.00
Si/$Zr_2Si_2O_8$	H	0.61	4.63	0.13
	O	1.80	3.44	0.52

H-terminated case. However, the conduction band offsets are shifted up while the valence band offsets are shifted down relative to the H-terminated model by 1.2–1.7 eV. This is consistent with an upward shift of the silicate bands relative to the Si bands, as depicted in Fig. 10. The potential shift ΔV_{dipole} arises from the electric field due to the charge transfer dipole, as can be shown by successive integrations of Poisson's equation across the interface. The key insight is that the dipole must point from the silicate into the Si substrate. As a consequence of the shift in potential, a more symmetric band alignment has been restored as shown in Table III. Restoring the symmetry is considered important since degraded barrier heights on the order of 1 eV can lead to additional conduction mechanisms, such as Schottky emission.[26] Since the predicted valence band offsets are substantially in excess of 1 eV, it may be desirable to deliberately trade off valence for conduction band offset through the introduction of interface dipoles.

In addition to the explicit dipole introduced by Si dangling bond termination, a more subtle dipole effect exists at the model silicate interface. From Fig. 8, it can be observed that the valence band offsets for H termination change by less than 4% with increasing Zr concentration relative to the Si/SiO_2 interface. For O termination, the valence band offset is seen to decrease by 2% at the Si/$Si_1Zr_3O_8$ and to increase by 24% at the Si/$Si_2Zr_2O_8$ relative to the Si/SiO_2 interface. The large increase at the O-terminated Si/$Si_2Zr_2O_8$ interface implies that the effect of the charge dipole due to O termination has been reduced. To confirm this, the charge transfer at the Si interface in each O-terminated model was estimated by summing one half of the total charge density in the bulk Si region and comparing it to the H-terminated Si/SiO_2 case. Following a previous study of the interface charge transfer, the bulk Si region was defined by the plane midway between the two different Si surface atoms.[20] The estimated charge transfer is observed to scale nearly linearly with the valence band offset, as shown in Fig. 11. As suspected, substantially less charge transfer occurs at the O-terminated Si/$Si_2Zr_2O_8$ interface, consistent with the observed shift in the valence band offset.

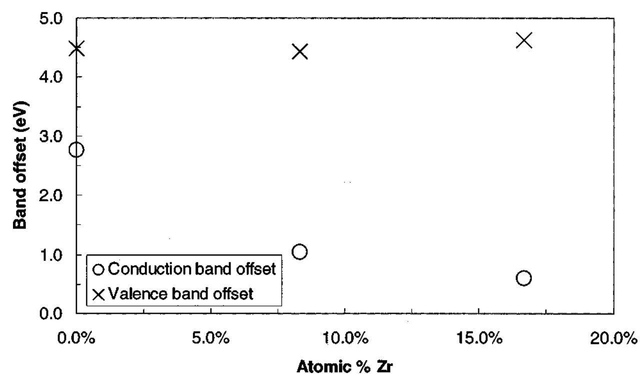

FIG. 8. Conduction and valence band offsets of model Si/silicate interfaces as a function of at. % Zr. The Si dangling bond at the interface is H terminated.

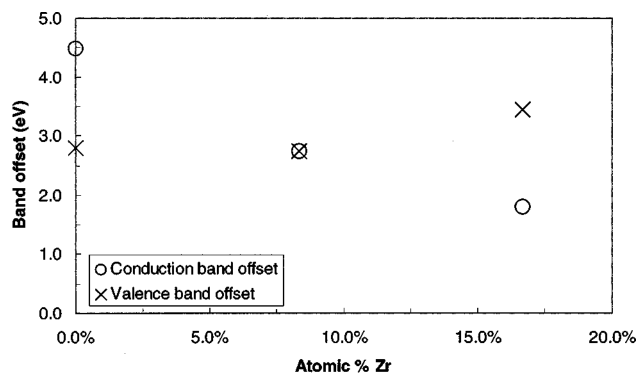

FIG. 9. Conduction and valence band offsets of model Si/silicate interfaces as a function of at. % Zr. The Si dangling bond at the interface is O terminated.

To account for the difference in charge transfer, it can be observed that an obvious feature of the Si/$Si_2Zr_2O_8$ interface model is the presence of Si–O–Zr bonding at the interface, whereas the other models consist of Si–O–Si bonding at the interface. It might be expected that the enhanced polarizability of the Zr–O bond would somehow affect the Si–O interface dipole by transferring additional charge to the O atom. However, any such effect at the model interface is expected to cancel since the Zr atom is tetrahedrally bonded to O atoms in a symmetric manner. The absence of a large change in the band offset at the H-terminated Si/$Si_2Zr_2O_8$ interface also supports this view. However, it is worth noting that an experimental interface is likely to break the perfect symmetry of the tetrahedral bonding units assumed in this study, in which case the presence of Zr–O–Si bonding at the interface may well affect the band lineup. As an alternative explana-

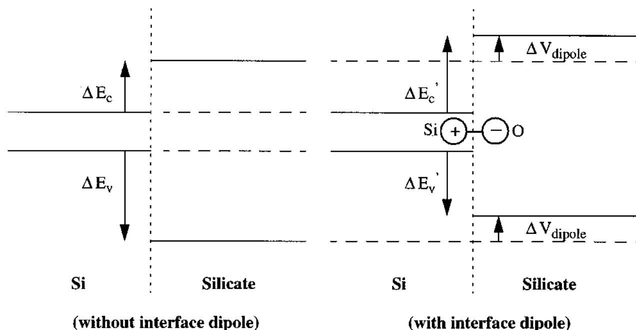

FIG. 10. Band diagram showing role of interface dipoles in altering the conduction and valence band offsets.

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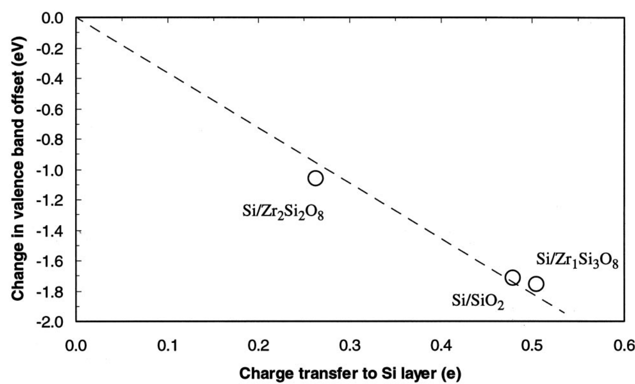

FIG. 11. Change in valence band offset as a function of charge transfer to Si layer for O-terminated interface models.

tion for the decreased charge transfer, it is suggested that the observed change may be due to the electrostatic attraction between the surface O atom, which has a net negative charge, and the Zr atom, which has a net positive charge. Since the $Si/Si_2Zr_2O_8$ interface model places the Zr atom closer to the surface O atom, the effect is expected to be stronger. The Si═O bond has indeed been measured to be 5% longer at the $Si/Si_2Zr_2O_8$ interface, and in general less charge transfer is expected at longer bond lengths. The observed difference in charge transfer may also be due in part to substrate-induced charge redistribution caused by changes in the surface bonding arrangement. Direct calculation of the effective charge of interface atoms by means of response functions may help to clarify the mechanism further.[37]

It is necessary to mention that the controlled assumptions made throughout this study introduce some uncertainty into the quantitative predictions presented. For example, the present calculations predict conduction and valence band offsets for the H-terminated Si/SiO_2 model of 2.8 and 4.5 eV, compared to experimental values of 3.5 and 4.4 eV, respectively.[38] It is difficult to know whether the conduction band error arises from the empirical correction factor introduced to fit the LDA band gap to experiment, the assumed interface bonding structure, or the observed decrease in band gap due to lattice mismatch strain. For the $Si/Zr_2Si_2O_8$ interface, the present results predict conduction and valence band offsets of 0.61 and 4.63 eV, respectively, for H termination and 1.80 and 3.44 eV, respectively, for O termination. Robertson's study based on tight-binding calculations predicts conduction and valence band offsets of 1.5 and 3.4 eV, respectively.[26] The agreement of the O-terminated model with Robertson's results is most likely accidental, however. The present study assumes a tetrahedrally bonded silicate structure whose corrected band gap is 6.36 eV. Robertson used the higher coordinated silicate $ZrSiO_4$, whose band gap he estimated to be 6 eV, whereas the present calculations predict 7.59 eV for the same structure. Experimental studies of Zr silicate electronic structure will be needed to further clarify the discrepancies. However, the observed qualitative scaling trends of silicate band offsets are expected to be valid, and the controlled manner in which the present calculations were performed provides insight into the dependence of band offsets on such properties as the Zr–O bond length, the lattice mismatch strain, and the charge transfer dipole at the interface.

The high concentration of Si═O surface termination dipoles used in this study is likely unachievable in practice. The assumed interface bonding is also ideal and abrupt, whereas alternative models have considered the presence of suboxide bonding at the interface which leads to a different density of Si–Si bonds.[10,22,39] Nonetheless, the insight that dipoles pointing into the Si substrate can help to restore symmetry in silicate band offsets can be applied to anticipate the expected effect of various departures from assumptions made in this study. For example, it is expected that an interface which minimizes suboxide bonding at the surface is preferred, since a fully oxidized Si atom with two Si–O bonds should lead to increased charge transfer compared to a suboxidized Si atom with one or more Si–Si bonds instead. The expected effects of higher than fourfold Zr coordination largely depend on the resulting changes in the interface structure. If the interface bonding remains similar to the case of tetrahedral bonding, then any change in the band gap is expected to directly affect the conduction band offset alone, since the interface dipole properties remain unchanged. This is analogous to the observed 1.8 eV decrease in band gap and conduction band offset which occurs in going from the Si/SiO_2 to $Si/Zr_1Si_3O_8$ interface models, since the interface bonding there remains nearly identical. If the interface bonding were to change significantly due to higher Zr coordination, it is expected that the effects of interface dipoles would be greater, since a higher density of O atoms would accompany the Zr atoms. However, whether the additional dipole effects would improve or degrade the band offset asymmetry would depend on the detailed interface structure.

In summary, steadily increasing the Zr concentration is expected to lead to a number of observable changes in the material properties of silicates. The dielectric constant should increase, leading to a physically thicker film and a thicker barrier to tunneling. At the same time, the band gap should decrease, so that carriers see a lower potential barrier to tunneling. In addition to this tradeoff caused by increasing Zr concentration, the actual position of Zr incorporation relative to the Si interface will also play an important role, since any effect on the interface dipole will lead to changes in the band offset. These effects need to be well understood, since an existing design goal requires Zr incorporation close to the Si interface. It is desirable to form a uniform Si/silicate interface rather than an intermediate SiO_2-like transition layer, since this maximizes the effective capacitance of the high-*k* dielectric stack. It is expected that the closer the Zr lies to the interface, the stronger will be any resulting dipole effect, although it may raise or lower the band offsets depending on the resulting structure. These considerations may or may not be achievable in practice, however, since a previous study has found that volume strains generated by the larger size and longer equilibrium bond lengths of Zr atoms relative to Si atoms make Zr incorporation close to the interface energetically unfavorable.[23]

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V. CONCLUSION

First principles calculations were performed to study the scaling trends of band offsets at model Si/Zr silicate interfaces. Based on bulk calculations, the silicate band gap was shown to decrease with increasing Zr concentration. Interface calculations showed that in the absence of changes in interface dipoles, the decrease in the band gap causes a lowering of the conduction band offsets relative to Si/SiO_2, while the valence band offsets remain unchanged. This was projected to lead to increasingly asymmetric barrier heights for electrons and holes. Thus, as the Zr concentration is increased, a tradeoff develops between barrier thickness, which depends on dielectric constant, and the barrier height, which depends on the band offsets. Interface dipoles were then explicitly introduced by varying the surface termination at the interface. Dipoles pointing toward the Si substrate were shown to raise the silicate bands relative to the Si bands, thus increasing the conduction band offset and decreasing the valence band offset, leading to more symmetric band offsets. While the study explicitly focused on Zr silicates, the insight provided by the study is expected to be generally applicable to a wide range of alternative dielectrics, since silicates are representative of a broader class of high-k materials composed of d-electron transition metals. The net effect of the tradeoff between barrier thickness and barrier height on the resulting tunneling transmission needs further investigation in order to evaluate the feasibility of transition metal oxides and silicates as possible replacement gate dielectric materials for SiO_2. The extent to which the inherent asymmetry of barrier heights may affect scaled CMOS device performance also needs to be studied. Though it remains to be seen how strong an effect can be practically realized, the introduction of interface dipoles appears to be one promising way to overcome the limitations of barrier asymmetry exhibited by transition metal oxides and silicates. The extent to which such interface dipoles may degrade carrier mobility in the channel by creating a nonuniform scattering potential will also need to be investigated.

ACKNOWLEDGMENTS

One of the authors (A.K.) thanks John Jameson of Stanford University for insightful discussions on tight-binding analysis of Zr silicates and the influence of interface dipoles on band offsets. He also thanks researchers at Texas Instruments Dallas and IBM T. J. Watson Research Center for useful discussions during research visits. The authors gratefully acknowledge financial support by the National Science Foundation and the Semiconductor Research Corporation.

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