Atomic Scale Effects of Zirconium and Hafnium Incorporation at a Model Silicon/Silicate Interface by First Principles Calculations

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***Abstract*—First principles calculations aimed at quantifying the effects of zirconium and hafnium incorporation at a model silicon/silicate interface have been performed. The tetrahedral bonding character of silicates allows useful comparisons as well as important new distinctions to be drawn with the familiar Si/SiO$_2$ system. The calculated energy cost of forming (Zr, Hf)-Si bonds suggests that SiO$_2$-like bonding is energetically favored over silicide-like bonding at the Si interface. The calculations also suggest that the volume strain associated with Zr or Hf incorporation may lead to increased stress, both in the bulk oxide and in the interfacial transition region.**

***Index Terms*—Computer aided engineering, dielectric materials, semiconductor device modeling, semiconductor materials.**

I. INTRODUCTION

DEVELOPING an alternative high-k gate dielectric to replace silicon dioxide (SiO$_2$) has emerged as a key scaling challenge for sub-100 nm CMOS technology [1]. For any proposed material, achieving a high quality interface with silicon (Si) is essential. Zirconium (Zr) and hafnium (Hf) silicates are high-k dielectrics which are thermally stable in direct contact with Si [2]. Silicates are attractive because they are incremental modifications of SiO$_2$. New understanding can be built upon the existing Si/SiO$_2$ knowledge base. Since silicates contain a mixture of Si, oxygen (O), and Zr or Hf, the interface bonding structure is of interest, including the possibility that silicide-like bonds are formed. Since Zr–O bonds are longer than Si–O bonds, Zr incorporation may lead to stress. Results of a first principles study aimed at quantifying these effects are presented.

II. COMPUTATIONAL EXPERIMENTS

Two studies were performed, one aimed at understanding bulk silicates, the other focusing on the Si/silicate interface. The computations are based on density functional theory within the local density approximation (DFT-LDA), the first principles method-of-choice in condensed matter physics [3]–[5]. DFT-LDA has been widely applied to study the Si/SiO$_2$ interface [6]–[9].

The amount of Zr or Hf incorporation in experimental silicate films is relatively low (<10 atomic %). Experimental results suggest that the bulk film may be thought of as a "doped" form of SiO$_2$ [2]. Consequently, in the first study, the silicate was modeled by replacing a single Si atom in crystalline SiO$_2$ (β-quartz), which led to approximately 11% Zr or Hf concentration in the unit cell in terms of overall atomic composition, or equivalently 50% Zr or Hf in terms of cation ratio. Due to the computational cost of DFT-LDA, it is standard practice to use periodic crystals to model oxides, even though SiO$_2$ is experimentally amorphous. The Zr initially forms Zr–O bonds of length 1.62 Å, corresponding to the Si–O bond length in β-quartz. This should be compared to Zr–O bonds in other materials, such as the silicate zircon, ZrSiO$_4$ (2.15 Å–2.29 Å) [10]. The expected longer lengths of (Zr, Hf)–O bonds generated stress in the model silicate. The atomic positions and lattice vectors were then relaxed toward the total energy minimum under DFT-LDA. The relaxation resulted in Zr–O bond lengths of 1.94 Å and Hf–O bond lengths of 1.96 Å, representing 24.8% and 25.6% volume expansions for the Zr and Hf silicate models, respectively. Such volume expansions may lead to localized strain near regions of Zr or Hf incorporation. While this study only considers SiO$_2$-like tetrahedral bonding arrangements, Zr atoms can have higher oxygen coordinations. For example, in ZrSiO$_4$, Zr atoms are coordinated by four first nearest neighbor oxygens and by four additional second nearest neighbor oxygens. It seems reasonable to expect that the additional volume required to accommodate more oxygen bonds would lead to greater strain.

An interface model was next formed by attaching β-quartz SiO$_2$ to Si(001) so as to minimize lattice mismatch. The resulting model is similar to those of previous studies [6], [8]. The lateral dimensions correspond to the Si lattice constant (5.43 Å), while the vertical dimension contains seven Si layers ($\sim$8 Å) and eight monolayers of oxide ($\sim$8.5 Å). The model cell size corresponds to the computational limits of a high performance workstation. An oxygen bridge was formed to eliminate interface states due to unsaturated bonds. All atoms were relaxed

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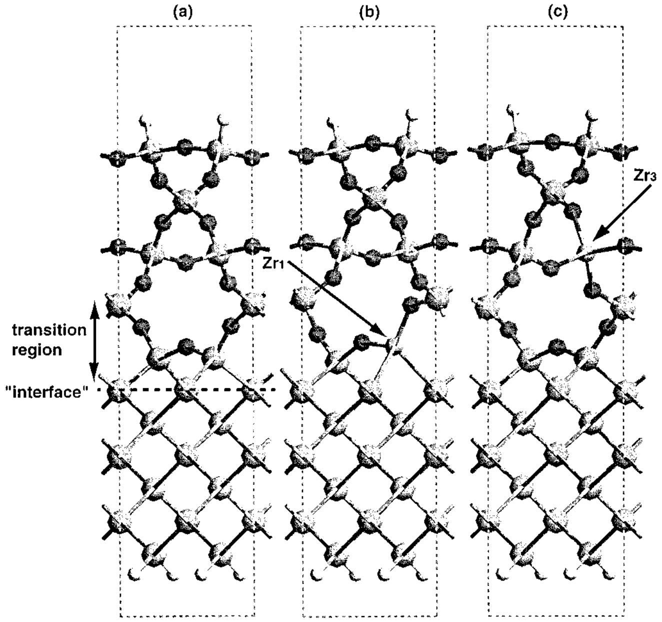

Fig. 1. (a) Reference Si/SiO_2 interface model formed by attaching β-quartz SiO_2 to Si(001). Large atoms are silicon, small atoms are oxygen. The extremities are saturated with hydrogen atoms. (b) and (c) Relaxed structures for model Si/silicate interface with Zr incorporation 1 layer (Zr_1 model) and three layers (Zr_3 model) above the interface. Note that Zr-Si and Zr-O bonds are substantially longer than the corresponding Si-Si and Si-O bonds.

except for the bottom three layers of Si, which were fixed [1]. The lattice vectors were also held fixed. The boundary conditions were intended to model a thin film atop a thick substrate. Fig. 1(a) shows the resulting structure, which serves as the reference for an interface without Zr or Hf incorporation.

Four additional calculations were performed in which Zr or Hf replaced a Si atom one or three layers away from the interface. The atomic positions were again relaxed. The resulting structures for Zr incorporation are shown in Fig. 1(b) and (c), referred to as Zr_1 and Zr_3 models. The corresponding structures for Hf were similar. The small size of the cell prevented replacing the boundary Si atom two layers away, since symmetry would have artificially prevented lateral relaxation.

III. Results and Discussion

The total energy of the Zr_3 model (-9135.93 eV) was 0.61 eV less than that of the Zr_1 model. The total energy of the Hf_3 model (-7937.29 eV) was 0.56 eV less than that of the Hf_1 model. The substantial energy differences suggest that Zr and Hf are more likely to be found in a bulk-like environment, tetrahedrally bonded to four oxygens, rather than at the interface forming two bonds each to O and Si. In other words, SiO_2-like bonding is energetically favored over silicide-like bonding at the interface. This may help to explain recent experimental observations that a thin layer of SiO_2 inevitably forms at Si/silicate interfaces fabricated under various processing conditions [11].

This energy difference is attributed in part to the added cost of forming silicide-like bonds at the interface. Simple bond counting shows that the Zr_1 model contains two Zr–Si and two Si–O bonds more than the Zr_3 model, while the Zr_3 model contains two Si–Si and two Zr–O bonds more than the Zr_1 model. The Zr–Si bonds of the Zr_1 model (2.66 Å) were measured to be 13 to 15% longer than the corresponding Si–Si bonds of the Zr_3 model (2.31–2.36 Å), indicating weaker bond formation. The Zr–O bonds of the Zr_3 model (1.91–1.94 Å) were 17–21% longer than the Si–O bonds of the Zr_1 model (1.60–1.63 Å). Similarly, the Hf–Si bonds of the Hf_1 model (2.61 Å) were 11 to 13% longer than the corresponding Si–Si bonds of the Hf_3 model (2.32–2.36 Å), while the Hf–O bonds of the Hf_3 model (1.95–1.97 Å) were 20 to 23% longer than the Si–O bonds of the Hf_1 model (1.60–1.63 Å). Evidently, the cost of forming Zr–Si and Hf–Si bonds in the Zr_1 and Hf_1 models more than offsets the cost of forming Zr–O and Hf–O bonds in the Zr_3 and Hf_3 models. This may be explained in part by the observation that the Zr–Si and Hf–Si bonds form at the interface, where they are constrained by the rigid Si substrate. The Zr–O and Hf–O bonds form in the bulk oxide, where greater relaxation is possible. Oxygen is known to form flexible bonds between neighboring tetrahedral units, so that local distortions can be accommodated with little energy cost [6].

The calculated energy differences depend on the chosen structural model. In particular, the present Si/SiO_2 interface model contains only the Si^{+2} partial oxidation state ("suboxide") at the oxygen bridge. Previous first principles studies have considered alternative models, which also include the Si^{+1} and Si^{+3} states in the transition region, leading to a different density of Si–Si bonds at the interface [6], [9]. It seems reasonable to expect that interfacial incorporation of Zr or Hf would become even more costly for lower suboxidation states (e.g., Si^{+1}), due to the increased density of Si–Si bonds and of Zr–Si or Hf–Si bonds that would result.

The limited size of the model cell may have artificially constrained relaxation near the Zr atom. To test this, two additional models $\sqrt{2}$ times larger in the lateral directions than the Zr_1 and Zr_3 models were formed (Zr_1' and Zr_3' models). Because these were considerably more expensive to relax, only the Zr models were studied. The increased flexibility for relaxation led to a smaller energy difference of 0.43 eV between the Zr_1' and Zr_3' models. The additional relaxation was concentrated near the Zr atom. However, the substantial change in the energy difference raises the possibility that even the value obtained with the larger cells is still not well converged with respect to the cell size. Hence, the 0.43 eV can only be considered as an upper bound, and it is possible that a larger model cell would lead to an even smaller energy difference.

Electronic structure analysis also revealed that silicide-like bonding in the Zr_1 and Hf_1 models produced interface states with deep energy levels within the Si bandgap. Zr introduces a state 0.24 eV below the conduction band of Si, while Hf introduces a state 0.11 eV below. These estimates are only approximate since the LDA approximation underestimates the bandgap [3]. As commonly done, this work assumes that the underestimation is constant for all models considered, so that deep level energies can be referenced to the conduction band edge. There

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[1] All calculations employed ultrasoft pseudopotentials, a plane wave basis cutoff energy of 25 Ryd, and a 2 × 2 × 1 Monkhorst-Pack grid for k-point sampling. Atoms were relaxed until the RMS force on free atoms was less than 0.05 eV/A

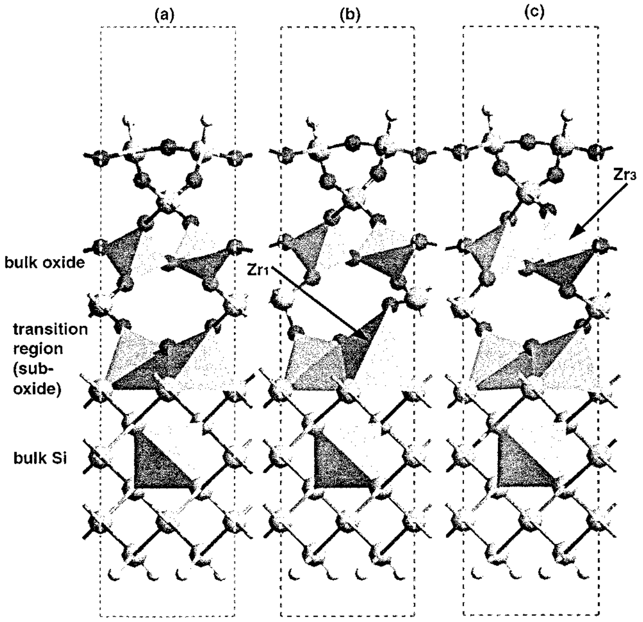

Fig. 2. Tetrahedral volumes of local bonding units for the interface models in Fig. 1. Tetrahedra associated with bulk Si (bottom), the Si^{+2} partial oxidation states at the oxygen bridge (middle), and bulk oxide (top) are indicated.

are well-known corrections that achieve greater accuracy at the cost of increased computation [12]. For the Zr_3 and Hf_3 models, the Zr and Hf states were swept out of the Si bandgap. These calculations were only performed for the smaller models (lateral dimensions of 5.43 Å), as limited workstation resources prevented sampling the band structure for the larger models.

While there is some uncertainty in excited state energies, DFT-LDA is known to be very accurate for ground state structural properties. To characterize the local strain induced by Zr, the volumes of tetrahedral bonding units were measured. Fig. 2(a) shows that for the reference Si/SiO_2 model, the Si^{+2} suboxide state accommodates the structural transition from bulk Si to bulk oxide. Oxide reliability models have considered this region to be especially vulnerable to electrical stress, since oxidation-induced strain is largely localized at the interface [13]. The tetrahedron associated with Zr near the interface in Fig. 2(b) (Zr_1 model) is 45% larger than the corresponding volume in the reference model, suggesting that the transition region may become increasingly strained when Zr is incorporated. For the Hf_1 model the difference is 48%. Similarly, the tetrahedron associated with Zr in the bulk oxide in Fig. 2(c) (Zr_3 model) is 70% larger than the corresponding volume in the reference model. For the Hf_3 model the difference is 78%. It is expected that in an amorphous silicate film, the large volume strains predicted by the present crystalline models would be more easily accommodated, particularly in the bulk oxide. The long-range disorder characterizing amorphous films could provide greater freedom for relaxation near regions of Zr or Hf incorporation via the flexible oxygen bonds.

IV. CONCLUSION

First principles calculations have been performed to quantify the atomic scale effects of Zr and Hf incorporation at a model Si/silicate interface. The calculated energy cost of forming (Zr, Hf)–Si bonds suggests that an abrupt SiO_2-like layer is likely to form between the bulk silicate and the Si substrate. Controlling the extent of such interfacial oxide formation is critical to avoid degrading the achievable capacitance of the dielectric stack. More detailed energetics of the oxide layer formation and possible ways to engineer the interface to avoid such growth deserve further study.

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