1. Introduction

There are significant qualitative and quantitative differences between the electronic structure of i) transition metal/rare earth high-k gate dielectrics, and ii) the SiO2 and silicon oxynitride dielectrics used in current state of the art devices [1]. The lowest conduction band states in the high-k dielectrics are derived from spatially localized d-states of the constituent transition and rare earth atoms, whereas the corresponding conduction band states in SiO2 and Si oxynitride alloy dielectrics are derived from extended, free-electron-like Si s*-states. The * superscript signifies the anti-bonding or, equivalently, the lowest conduction band states. These differences in thin film electronic structure result in significantly different electronic properties at their interfaces in metal-oxide-semiconductor (MOS) devices with crystalline Si, and polysilicon or metal gate electrodes. This talk emphasizes band alignments and properties at Si high-k gate dielectric interfaces as well as intrinsic bonding defects.

The conduction band offset energies of high-k are determined by the energies of the localized d-states, and these energies are generally lower than the SiO2 band offset energies by about 1-2 eV [2]. The same d-states are also responsible for reduced electron tunneling masses, and increased interfacial fixed charge, trapping and carrier injection relative to SiO2. High-k elemental oxides, such as HfO2, Y2O3 and La2O3 are also ionic conductors and this as well [3].

Additionally, the increased bond ionicity of the proposed transition metal and rare earth dielectrics leads to significant issues relative to the operation of the symmetric NMOS and PMOS devices required for the operation of complementary MOS (CMOS) circuits. This issue is related to the integration of polysilicon and metal gate electrodes into advanced devices, and in particular to threshold voltage control and reliability. This last point, which is perhaps the most significant, is not addressed in this paper.

This paper introduces a new class of complex rare earth/transition metal (Ce/Tm) oxides in which the energies of the lowest conduction band states can be controlled through bonding of the constituent Ce and Tm atoms to a common oxygen atom. This d-state coupling is established through spectroscopic studies of the electronic structure of GdScO3, the electronic band edge structure of Sc2O3, and an ab initio theory approach that is validated through in the next section that addresses the interpretation of the spectroscopic results for the group IVB transition metal dielectrics in the context of ab initio quantum chemistry calculations based on small clusters (~18 atoms).

2. Electronic structure of group IVB transition metal oxides, silicates and aluminates: comparisons between spectroscopic studies and ab initio calculations

The electronic structure of ZrO2 and Zr silicate alloys has been studied in detail by advanced spectroscopic techniques including x-ray absorption spectroscopy (XAS), x-ray photoelectron spectroscopy (XPS), ultraviolet photoemission spectroscopy (UPS), vacuum ultraviolet spectroscopic ellipsometry (VUV SE) and Auger electron spectroscopy (AES) [1,2,4]. Similar experimental studies have also been performed on HfO2 and Hf silicate and aluminate alloys, and TiO2. In all instances the films were prepared by remote plasma enhanced chemical vapor deposition, and alloy compositions were determined by Rutherford backscattering (RBS) and on-line AES [2 and references therein].

The lowest conduction band states of ZrO2 as determined from XAS, and VUV SE measurements are associated with Zr 4d*-states. Figure 1(a) displays the XAS Zr M3 spectrum which displays features associated with localized transitions from the Zr 3p3/2 spin-orbit split state at approximately 330 eV below vacuum, to i) a Zr 4d* doublet, and ii) a Zr 5s* state. The 4d* doublet separation is ~2.5 eV, and the energy differences between the lowest 4d* peak and the 5s* feature is ~12.5 eV. Figure 1(b) displays the O K1 spectra associated with transitions from the O 1s
coew state approximately 540 eV below vacuum to two broad overlapping bands; i) the first associated with O 2p° states mixed with Zr 4d° states, and ii) the second with O 2p° states mixed with Zr 5s° states. It also shows transitions to a third multi-component band that has considerable O 2p° character, and additional mixing with Zr 5p° states. The 4d° splitting is reduced to ~1.5 eV (as determined by spectral deconvolution), and the 4d°-5s° energy difference is also reduced with respect to the M₁ spectrum to a value of ~4 eV. Figure 1(c) displays the band edge optical absorption constant, α, as a function of photon energy obtained from analysis of VUV SE data. The 4d° state splitting is ~1.4 eV, approximately the same as in the O K₁ edge, and there is a significant overlap of the second 4d° state by the Zr 5s° band. Finally, Fig. 1(d) displays respectively a Zr K₁ edge spectrum for an alloy with 55% ZrO₂. After a 30 s anneal in Ar at 900°C this alloy phase separates into crystalline ZrO₂ imbedded in non-crystalline SiO₂ [2]. Estimates of the maximum 4d° state splitting, and the energy difference between the 4d° and 5s° states have been made on using the 900°C annealed spectra in Fig 1(d) as well as a differentiated spectrum (not shown). This observation is consistent with similar spectra and differentiated spectra for alloy compositions up to 84% ZrO₂. The maximum 4d° state splitting is ~1.5 eV, and the 4d°-5s° separation is 14±1 eV. The assignments in Figs. 1(a) to (d) are based in large part on comparisons with the results of ab initio calculations which have been discussed in detail elsewhere [5]. Similar XAS spectra have been obtained for HfO₂ and the 5d° splittings, and 5d°-6s° energy separations are included in Table I.

Table I summarizes the relative energies of the conduction band edge electronic states for ZrO₂ and HfO₂ as determined from the experimental data presented above, and also includes the relevant energy differences determined from the ab initio calculations. The agreement between ab initio calculations and experiment is excellent.

<table>
<thead>
<tr>
<th>oxide</th>
<th>Tm K₁ Δd° (Δd°,s°) (±0.2 eV)</th>
<th>Tm X₁₂,₃ Δd° (Δd°,s°) (±0.2 eV)</th>
<th>O K₁ Δd° (Δd°,s°) (±0.2 eV)</th>
<th>band gap Δd° (Δd°,s°) (±0.2 eV)</th>
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<tr>
<td>ZrO₂</td>
<td>&lt;2 (14) 0.9 (13.9)</td>
<td>2.5 (12) 1.9 (12.6)</td>
<td>1.5 (4.0) 1.5 (3.5)</td>
<td>1.4 (&lt;2) 1.3 (1.0)</td>
</tr>
<tr>
<td>HfO₂</td>
<td>not measured</td>
<td>1.2 (10.4) 1.6 (3.0)</td>
<td>1.5 (4.0) 1.3 (1.0)</td>
<td>1.4 (&lt;2) 1.3 (1.0)</td>
</tr>
</tbody>
</table>

* only one broad feature.

Figure 2 summarizes the spectroscopic results for ZrO₂. Since the agreement between the ab initio calculations and the spectroscopic data is excellent, the Fig. 2 includes only the ab initio results. The results presented in Table I and Fig. 2 provide two important insights for the application of XAS spectra to band edge electronic structure of transition metal (and also rare earth) alternative gate dielectric materials. First the Tm K₁ and X₁₂,₃ (M₂,₃ for Zr and N₂,₃ for Hf) spectra are intra-atomic with transitions originating in Zr 1s (Hf 1s), or Zr 3p (Hf 4p) spin orbit split core states, and terminating respectively in Zr 4d° and 5s° states (Hf 5d° and 6s°) states. In contrast the O K₁ and band gap spectra are inter-atomic in the sense that the initial states are respectively an O 1s core state, and the O 2p π non-bonding states that comprise the top of the valence band, and the final states are O 2p° states that are mixed with conduction band edge d° and s° states: 4d° and 5s° for ZrO₂, (5d° and 6s° for HfO₂). This difference is reflected in the d°-s° energy separations, denoted as Δ(d°,s°) in Table I. For example, for the intra-atomic transitions in ZrO₂, Δ(d°,s°) = ~14 eV for the K₁ transitions and ~12.5 eV for the M₂,₃ transitions. These energy differences are to be compared with an energy difference of less than 2.5 eV in the corresponding Zr atomic states in the 5s°-4d° configuration appropriate to oxides (oxide alloys) of Zr. The large Δ(d°,s°) splittings are a final state effect associated with the localized character of the Zr 1s core state hole, and i) the localized character of the Zr 4d° states as contrasted with, ii) the extended character of the Zr 5s° states. The results displayed in Fig. 2 indicate that the large energy separation is derived from a shift of the 4d° states to lower energy, rather than an upward shift of the 5s° states. The d°-state splittings in the O K₁ edge and the band edge transitions reflect mixing of the Zr 4d° states with the O 2p° states, as well as the multiplicity of O neighbors. Zr atoms are eight-fold coordinated in ZrO₂, and O atoms are four-fold coordinated. The decrease in the value of Δ(d°,s°) between the O K₁ edge and band edge spectra reflects the increased delocalization of the hole in the non-bonding valence band states of ZrO₂. These differences in final state effects demonstrate that O K₁ edge spectra provide i) a good indicator d°-state splittings in band edge transitions, and indicate the maximum possible splitting between the d° and s° states for the band edge transitions are well.

The second and most important aspect of the spectral comparisons between theory and experiment for applying band edge electronic structure in the transition metal (rare earth) silicates and aluminates to gate stack applications is based on the similarity between the anti-bonding d°-state splittings revealed in the O K₁ edge, and the band gap VUV SE spectra of the transition metal oxides. Figure 3 displays the O K₁ edge for a series of Zr silicate alloys (x=0.35 to ~0.60) prepared by remote plasma processing. These spectra should be compared with the O K₁ edge spectrum ZrO₂ in Fig. 1(b). The Si 3s° conduction band states overlap the Zr 5s° states completely, and the Zr 4d° state remains the lowest anti-bonding stat as unresolved spectral doublet. This interpretation for th features in the Zr silicate O K₁ edge spectra establishes that the Zr 4d° states are final states in the lowest band gap optical transitions and are also the states that define the band edge coupling to tunneling electrons, i.e., the tunnel effective mass the electrons. The spectra in Fig. 3 further demonstrate that the relative energy separation of the Zr 4d° and Si 3s° features
is not changed with alloying, but that their relative intensities as anticipated scale with alloy composition. The same alloy behavior of is also revealed in XPS studies of the Si 2p, and the Zr 3d states of ZrO2, consistent with model predictions [9,10], and demonstrates a monotonic correlation between i) optical band gaps, and ii) conduction band offset energies with respect to Si, and the atomic d-state energies in s^2d^6 configuration appropriate to bonding in ionic insulators. γ = 3 for group III B transition metals, Sc, Y and La(Lu), and the trivalent lanthanide rare earth elements, and γ = 4 and 5, respectively, for the group IV B (Ti, Zr and Hf), and VB (V, Nb and Ta) transition metals. The linear dependence of band gap versus d-state energy between Ti and Hf has also been obtained directly from electronic structure calculations that provide a theoretical basis for the scaling relationship. Based on the spectroscopic results for Tm silicate and aluminate alloys, the same scaling applies for band offset energies.

The linear behavior between Ti and Hf, and the extension to small d-state energies to Y and La defines the materials that have received the most interest as potential candidates for replacing SiO2 and Si oxynitrides in advanced Si devices. Based on the scaling of conduction band offset energies, Sc, Ti, V, Nb and Ta oxides, and their silicate and aluminate alloys have been eliminated from this list. This derives from the values of conduction band offset energies being less than about 1 eV. Dielectrics with conduction band offsets less than 1 eV generally have direct tunneling or leakage at 1 volt oxide bias for an equivalent oxide (SiO2) thickness (EOT) of ~1.5 nm, that exceed 1-10 A-cm^-2 and do not meet aggressive scaling targets for gate leakage.

Recently our group, in collaboration with Professor Darrell Schlom at Pennsylvania State University, has developed a novel way of overcoming some the conduction band offset energy limitations in for transition metal (and lanthanide rare earth) oxides, and those of their silicate, and aluminate alloys. This approach evolved from spectroscopic studies that demonstrated a coupling between transition metal and rare earth atom d-states through bonding to a common oxygen atom (see Fig. 6). This bonding interaction can increase the optical band gaps, and band offset energies of the alloys these so-called complex oxides.
4. Electronic structure of complex Re/Tm oxides

Figure 7 displays XAS, and VUV SE spectra for crystalline GdScO$_3$. [11]. The features in the Sc L$_{2,3}$ spectrum in Fig. 7(a) are due to localized transitions between spin-orbit split Sc 2p$_{1/2}$ and 2p$_{3/2}$ states, and symmetry split Sc 3d$^*$ states. The transition probability for transitions between the Sc 2p and Sc 4s$^*$ states is about 150 times smaller than for transitions to the 3d$^*$ states, and this feature is not observed in the L$_{2,3}$ spectrum. The features at ~532.5 and 536 eV in the O K$_1$ edge in Fig. 7(b) are associated respectively with transitions to d$^*$-states and s$^*$-states. Based on its spectral shape, the lower energy feature is Sc 3d$^*$-like, but also includes some Gd 5d$^*$ character. This observation is supported by an argument to be presented below. The splitting between the two dominant features in Fig. 7(b) of ~3.5 eV is smaller than the splittings of ~4.0 eV in ZrO$_2$ (4d$^*$ to 5s$^*$) and HfO$_2$ (5d$^*$-6s$^*$). Figure 7(c) displays the edge band optical absorption constant, $\alpha$, as a function of photon energy obtained from analysis of VUV SE data. An optical transmission spectrum (now shown) establishes weak absorption features up to about 5.5 eV are due to intra-4f level transitions characteristic of the half occupied 4f-shell of Gd [12]. The threshold for strong absorption at ~5.7 eV in Fig. 7(c) marks the onset of transitions to the lowest d$^*$-state, and the rapid rise of absorption at ~6 eV, the onset of transitions to s$^*$-states.

The lowest band gap in GdScO$_3$ from Fig. 7(c) is ~5.7 eV; this is larger than the optical band gap of ~4.5 eV for Sc$_2$O$_3$ [13], but smaller than the optical band gap of Gd$_2$O$_3$, estimated to be ~6.3 eV. Based on the scaling arguments presented in Section 3, the lowest band gap of GdScO$_3$ is expected to be ~4.5 eV. As already noted above, the local bonding in GdScO$_3$ includes arrangements in which Gd and Sc atoms are bonded to the same O atom. This promotes a mixing of Sc 3d-states and Gd 5d-states, which changes the band edge electronic structure as shown schematically in Fig. 6. Figure 6 illustrates bonding in elemental transition metal (rare earth) oxides such as Sc$_2$O$_3$ (Gd$_2$O$_3$) in which transition metal (rare earth) atoms are bonded to a common O atom, represented symbolically by Tm-O-Tm and Re-O-Re. Figures 6 illustrates changes that occur in complex oxides in which Tm and Re atoms are second neighbors through bonding to the same O atom in groups represented symbolically by Tm-O-Re. For GdScO$_3$, the overlap between Sc 3d $\pi$ states and O 2p states is greater than for Gd 5d $\pi$ states. This shifts the valence band, and anti-bonding states from their respective end member oxides, Sc$_2$O$_3$ and Gd$_2$O$_3$. Based on overlap integral differences, valence band $\pi$-states are at intermediate energies with respect to the corresponding elemental oxide states, increasing the energy of the lowest conduction band states with respect to Sc$_2$O$_3$, and thereby changing conduction band offset energies with respect to Si as well.

The scaling of Re/Tm complex oxide band gaps and band offset energies with respect to their respective d-states energies to be presented in the final section of the paper is based on these comparisons between GdScO$_3$ and ZrO$_2$, where the onset of strong optical absorption occurs at the same energy of ~5.7 eV. This suggests that GdScO$_3$ has a band gap characteristic of a 4d Tm oxide. In this regard, it is significant to note that the \textit{algebraic average} of the atomic d-state energies of Sc and Gd is ~8.0 eV, and this energy is approximately equal to 4 d-state energy of Zr, ~8.1 eV. Similarly, the band gap of GdScO$_3$ at 5.7 eV is close to the average of the band gaps of Gd$_2$O$_3$ and Sc$_2$O$_3$.

5. Conclusions

The spectroscopic studies presented above for Zr and Hf oxide, and their silicate and aluminate alloys, and for GdScO$_3$ provide important insights to limitations on band gaps and band offset energies for alternative high-k gate dielectrics. The offset energy scaling in Fig. 5 \textit{applies only} to Tm and Re oxides and their respective silicate and aluminate alloys. Based on this scaling Zr, Hf, Y, La and lathanide oxides and silicate and aluminate alloys have conduction band offset energies large enough for integration of these dielectrics into aggressively scaled devices. However, there are many other intrinsic and processing issues to be overcome before any of these dielectrics will find its way into manufacturing.

Figures 5(b) and 5(c), present scaling relationships that apply for complex oxides. These are based on the bonding of two different transition metal atoms, or one transition metal and one rare earth atom bonded to a common oxygen atom. These scaling relationships are based on chemically-ordered oxides, which do not include a statistical distribution of bonding groups similar to those of the constituent oxides. These arrangements would produce excitations at the band edge that correlate with either/or both of the end member oxides, and the limitations would be then be same as in Fig. 5(a).

If the chemical ordering is achieved, then complex oxides would provide a pathway to control the lowest conduction band excitation, and hence the conduction band offset energy with respect to Si, and also benefit from the increased dielectric constants of transition metal species such as Ti, Nb and Ta.

Acknowledgements

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References

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[12] McClure DS, "Electronic Spectra of Molecules and
1069.
Fig. 1 ZrO₂ spectra: (a) Zr M₃ spectrum, (b) O K₁ edge, (c) absorption constant, a, and (d) Zr K₁ edge.

Fig. 2. Calculated energies of anti-bonding states for ZrO₂ reference. Energies are referenced to vacuum, and large dashed line indicates top of valence band in ground state.

Fig. 3 O K₃ edge spectra for Zr silicate alloys.

Fig. 4. Compositional dependence of offset energies for Zr silicate alloys.
Fig. 5. Scaling of band gaps and conduction band offset energies with atomic d-state energies: (a) Tm and Re oxides, silicates and aluminates, (b) and (c) complex oxides. The arrows indicate the changes in conduction band states due to d-state coupling. For (b) and (b) points are for TiHFO₄ and GdScO₃.

Fig. 6. Schematic of molecular orbitals

Fig. 7. GdScO₃ spectra: (a) Sc L₂,₃, (b) O K₂, and (c) absorption constant, α.