Spectroscopic studies of the electrical structure of transition metal and rare earth complex oxides

G. Lucovskya,*, Yu Zhanga, J.L. Whittenb, D.G. Schlomc, J.L. Freeoufd

aDepartment of Physics, North Carolina State University, Raleigh, NC 27695, USA
bDepartment of Chemistry, North Carolina State University, Raleigh, NC, USA
cDepartment of Materials Science, Penn. State University, College Park, USA
dDepartment of Electrical Engineering, Oregon Graduate Institute, Portland, OR, USA

Abstract

Spectroscopic studies of transition metal (Tm) and rare earth (Re) oxides, combined with ab initio theory identify the band edge electronic structure of high-K dielectrics. The lowest conduction band states are derived from anti-bonding Tm (Re) d*-states. A novel method for obtaining independent control of band gap energies and dielectric constants in complex oxides, ReTmO3, results from coupling of Tm and Re atom d-states bonded to the same oxygen atom.

© 2003 Published by Elsevier B.V.
PACS: 71.15.Nc; 71.15.Qe; 78.20.−e; 78.40.−q; 78.70.Dm

Keywords: High-K dielectrics; Transition metal oxides; Rare earth oxides; Complex oxides

1. Introduction

The band edge electronic structure of the group IVB Tm oxides, TiO2, ZrO2, and HfO2, has been studied by X-ray absorption spectroscopy (XAS) and vacuum ultra-violet spectroscopic ellipsometry (VUVSE). Combined with ab initio calculations, these studies provide the basis for a quantitative understanding of an empirically determined scaling of band gap, and band offset energy with respect to Si as function of Tm or Re atomic d-state energies. Based on scaling, and confirmed by experiment, elemental oxides, and silicate and aluminate alloys containing Sc, Ti, Ta and Nb have band offset energies too small (< 1 eV) for achieving the low levels of tunneling required for advanced devices in spite of 5-fold increases in thickness relative to SiO2.

Spectroscopic studies of GdScO3 provide an additional dimension to scaling issues. It is shown that the coupling of Re and Tm d-states through bonding to a common C-atom increases minimum band gaps and conduction band offset energies with respect to Si, identifying a novel approach for atomic engineering of advanced gate dielectrics.

2. Spectroscopic studies of group IVB Tm oxides and GdScO3

The lowest conduction band states of Zr(Hf)O2 as determined from XAS [1], and VUVSE measurements [2] are associated with Zr(Hf) 4(5)d*-states and are...
Table 1
Measured and calculated (italics) \( d^*-d^* \) and \( d^*-s^* \) splittings (±0.2 eV)

<table>
<thead>
<tr>
<th>Oxide</th>
<th>( Zr ) M(<em>{2,3} ) Hf N(</em>{2,3} ) d(^<em>-d^</em> ) (d(^<em>-s^</em> ))</th>
<th>O K(_1 ) Edge d(^<em>-d^</em> ) (d–s)</th>
<th>Band Edge d(^<em>-d^</em> ) (d(^<em>-s^</em> ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ZrO_2 )</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 ) (1.3)</td>
</tr>
<tr>
<td>( HfO_2 )</td>
<td>(&lt; 2 ) (10) ( 1.3 ) (10.4)</td>
<td>1.5 (4.0) ( 1.6 ) (3.0)</td>
<td>1.4 ((&lt; 2)) ( 1.3 ) (1.5)</td>
</tr>
</tbody>
</table>

Fig. 1. GdScO\(_3\) spectra: (a) \( L_{2,3} \) spectrum for Sc, (b) O K\(_1 \) edge spectrum, (c) absorption constant, and (d) intra 4f level transitions.

The spectra for the group IVB oxides have been interpreted through ab initio calculations [5]. The calculations are done initially via a self-consistent field (SCF) Hartree–Fock calculation with a single determinant wave function, not including electron correlation. Following this, there is a configuration
interaction (CI) refinement of the bonding orbitals based on a multi-determinant expansion wave function, and including electron correlation. This method has been applied to small clusters that include bonding of a Tm atom to O neighbors terminated by H. Calculations have been made for the ground state energy, and the Tm K1, the Tm X2,3 (X = L, M and N) the O K1, and the AO2 (A = Ti, Zr and Hf) band edge transitions. Comparisons between the ab initio calculations for d∗–d∗ and d∗–s∗ splittings of the lowest anti-bonding states and experimental data in Table 1 are in excellent agreement. The calculated band edge electronic structure for ZrO\textsubscript{2} and TiO\textsubscript{2} are included in Fig. 2 with the lowest band gap energies determined from experiment.

Fig. 2. Calculated band edge electronic structure of ZrO\textsubscript{2} and TiO\textsubscript{2}. Energies are referenced to the top of the valence band.

Energies in Fig. 2 are referenced to the top of the valence band, which is comprised of O 2p π non-bonding states. In order of increasing binding energy the valence band states are non-bonding O 2p π, and 3d Ti (4d Zr) π and 3d Ti (4d Zr) σ states bonded with O 2p π or σ orbitals. The overlap is larger for Ti 3d-O/2p π-bonding than for Zr 4d/O 2p π-bonding, hence the energy difference of ∼ 2 eV. The separation of conduction band d-states comes from the calculations, and the relative energy of the lowest conduction band states is from experiment. The energies of the lowest Tm conduction band states have a reversed π*/σ* ordering, and their energies relative to the atomic Ti 3d and Zr 4d states are smaller.

The most important aspect of Fig. 2 is the energy difference of ∼ 2 eV between the atomic d-states, –11.1 eV for the Ti 3d state and –8.13 for the Zr 4d state, and the respective, lowest anti-bonding states. This explains the approximately linear dependence of the elemental oxide band gaps with the energies of the respective atomic d-states (see Fig. 3) in the energy range between –11 and –8 eV. This range includes in order of increasing (more positive) d-state energy, Ti, Nb, Ta, Sc, Zr and Hf. The bending over at higher energies, e.g., for Y (or La), is a manifestation of

Fig. 3. (a) Empirical scaling of band gaps versus atomic d-state energy (b) Empirical scaling of conduction band offset energies with respect to Si versus atomic d-state energy. Solid line—trend for transition metal oxides, dashed line—predicted scaling for complex oxides with d-state coupling.
increased overlap between higher lying \((n+1)\) s*-states, and the n d- \(s\) band. The flattening out at lower energy occurs for oxides that are not high-\(K\) candidates.

Based on the results presented in Ref. [7], the minimum band gap in GdScO\(_3\) is associated with transitions to Sc 3d*-anti-bonding states and is \(\sim 4.3 \pm 0.1\) eV [6]. Scaling arguments suggest the lowest band gap in GdScO\(_3\) should be at approximately the same energy, \(< 4.5\) eV, rather than at the measured value of \(\sim 5.7\) eV.

4. Interpretation of the spectra for GdScO\(_3\)

The lowest band gap in GdScO\(_3\) is at \(\sim 5.7\) eV and this represents a marked departure from the empirical scaling discussed 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. 4. The upper part of the figure illustrates bonding in elemental Tm (Re) oxides such as Sc\(_2\)O\(_3\) (Gd\(_2\)O\(_3\)) in which Tm or Re atoms are bonded to a common O atom. The lower portion illustrates bonding in complex oxides in which Tm and Re atoms are bonded to the same O atom. For GdScO\(_3\), the overlap between Sc 3d \(\pi\) states and O 2p states is greater than for Gd 5d \(\pi\) states. These overlaps shift the valence band, and anti-bonding states from their values in the respective end member oxides. Based on these overlaps, the valence band \(s\)-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\(_3\).

The basis for the scaling of Re/Tm complex oxide band gaps and band offsets with d-states energies is developed from comparisons between GdScO\(_3\) and ZrO\(_2\), where the onset of strong absorption occur at \(\sim 5.7\) eV, suggesting that GdScO\(_3\) has a band gap characteristic of a 4d Tm oxide. In this context the average atomic d-state energy of Sc and Gd is \(-8.0\) eV, approximately equal to the d-state energy of Zr, \(-8.13\) eV. Additionally, the band gaps of Sc\(_2\)O\(_3\), \(\sim 4.3\) eV, and Gd\(_2\)O\(_3\), \(\sim 6.3\) eV, average to \(\sim 5.3\) eV. This suggests a virtual crystal model for complex Tm/Re oxides in which d-states of the constituent atoms are coupled through bonding to the same O atoms. Bonding in Tm/Re silicates and aluminates is qualitatively different, and this has been addressed in Ref. [1]. The energies of Zr and Si core states track across Zr silicate alloys with a constant separation [7]. This is equivalent to the difference between the band edge transitions between O 2p \(\pi\) non-bonding states and Zr 4d* and Si 3s* states maintaining a constant energy. Tm/Re silicate and aluminate alloys are then 2-band systems, where conduction band energies are maintained at relative end-member oxide levels, but absorption strengths scale with relative concentration. The complex ReTmO\(_3\) display a qualitatively different 1-band behavior. However, oxides of Gd\(_2\)O\(_3\) and Sc\(_2\)O\(_3\), with other than a 1:1 ratio are expected to display spectra characteristic of more than one d-state bonding group; Sc\(_2\)O\(_3\)-rich alloys should display multiple d*-state features characteristic of Sc–O–Sc, and Sc–O–Gd bonding.

5. Discussion

Fig. 4 includes the application of the virtual crystal model to complex oxides. The square point is the experimental value for GdScO\(_3\) and is plotted at the Sc atomic d-state energy of \(-9.35\) eV. The
diamond shape point is calculated for a HfO₂ (5d) –TiO₂ (3d), 1:1 alloy, TiHfO₄, where the predicted band gap is 4.45 eV, the average of HfO₂ (5.8 eV) and TiO₂ (3.1 eV). Conduction band offset energies are estimated on the basis of the same model. GdScO₃ is equivalent to ZrO₂ with an offset of ∼ 1.5 eV, and Hf(Zr)TiO₄ is expected to have an offset energy of approximately ∼ 1 eV, whilst a Ta₂O₅–2HfO₂ alloy may have an offset as high as 1.4 eV.

References