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

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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, $ReTmO_3$, results from coupling of Tm and Re atom d-states bonded to the same oxygen atom.
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1. Introduction

The band edge electronic structure of the group IVB Tm oxides, TiO_2, ZrO_2, and HfO_2, 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 SiO_2.

Spectroscopic studies of $GdScO_3$ 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 $GdScO_3$

The lowest conduction band states of $Zr(Hf)O_2$ as determined from XAS [1], and VUVSE measurements [2] are associated with Zr(Hf) 4(5)d*-states and are

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Table 1
Measured and calculated (italics) d*–d* and d*–s* splittings (± 0.2 eV)

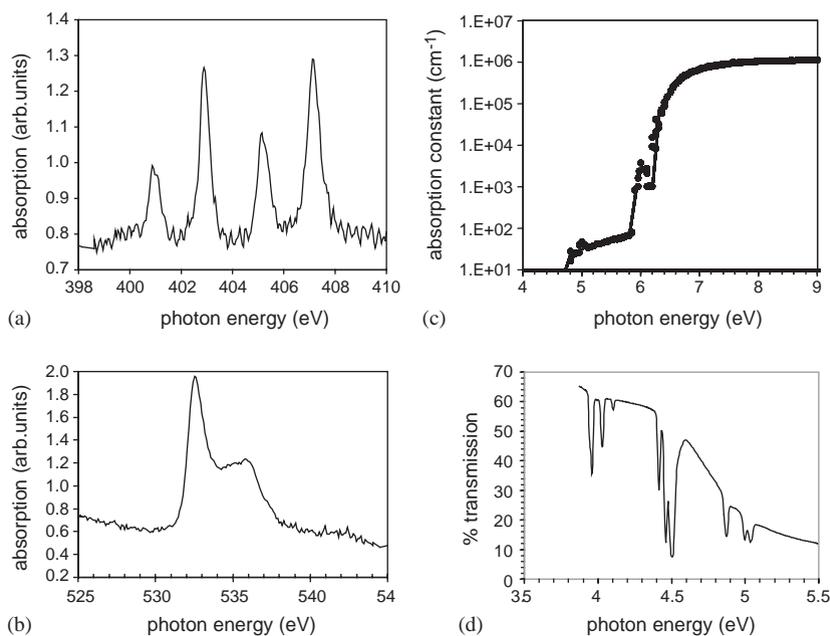| Oxide	Zr M$_{2,3}$ Hf N$_{2,3}$ d*–d* (d*–s*)	O K$_1$ Edge d*–d* (d–s)	Band Edge d*–d* (d*–s*)
ZrO$_2$	2.5 (12) *1.9 (12.6)*	1.5 (4.0) *1.5 (3.5)*	1.4 (< 2) *1.3 (1.3)*
HfO$_2$	< 2 (10) *1.3 (10.4)*	1.5 (4.0) *1.6 (3.0)*	1.4 (< 2) *1.3 (1.5)*

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.

presented in Table 1. Fig. 1 displays the XAS, VUVSE and optical absorption measurements for crystalline GdScO$_3$ [3]. The features in the Sc L$_{2,3}$ spectrum in Fig. 1(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 features at $\sim$ 532.5 and 536 eV in the O K$_1$ edge in Fig. 1(b) are associated, respectively, with transitions to d*- and s*-states. Based on its width the lower energy feature is Sc 3d*-like, but also includes Gd 5d*. The splitting between these states of $\sim$ 3.5 eV is smaller than the splittings of $\sim$ 4.0 eV in ZrO$_2$ (4d*–5s*) and HfO$_2$ (5d*–6s*). Fig. 1(c) displays the band edge optical absorption constant, α, as a function of photon energy obtained from analysis of VUVSE data. The transmission spectrum in Fig. 1(d) establishes that features between about 4.8

and 5.8 eV are due to intra-4f level transitions characteristic of the half-occupied 4f-shell of Gd [4]. The threshold for absorption at $\sim$ 5.7 eV in Fig. 1(c) marks the onset of transitions to the lowest d*-state, and the rapid rise of absorption at $\sim$ 6 eV, the onset of transitions to s*-states.

3. Ab initio calculations

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
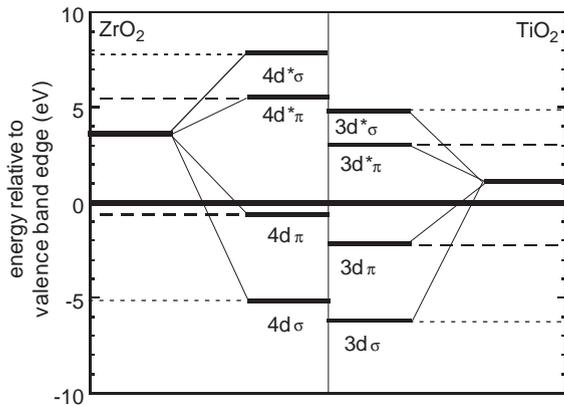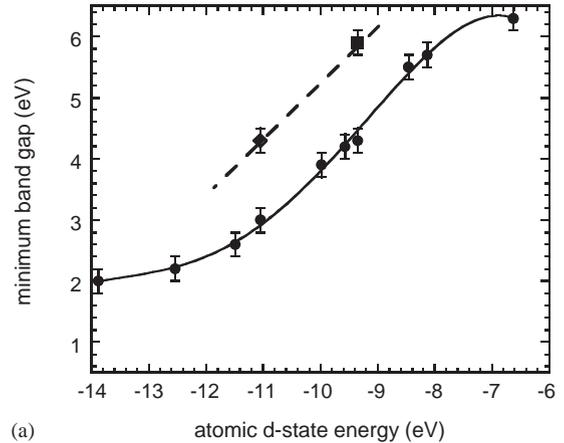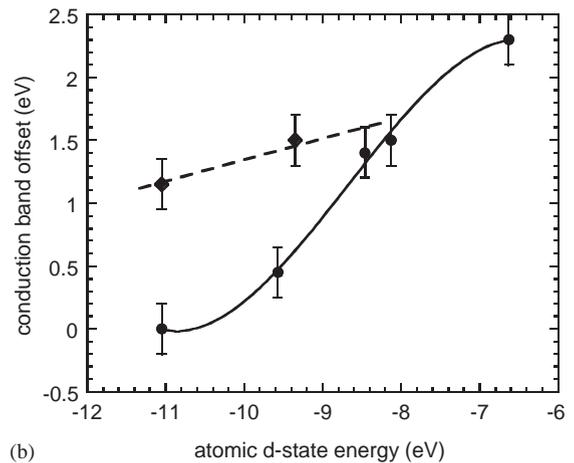
Fig. 2. Calculated band edge electronic structure of ZrO$_2$ and TiO$_2$. Energies are referenced to the top of the valence band.

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.

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 K$_1$, the Tm X$_{2,3}$ (X = L, M and N) the O K$_1$, and the AO$_2$ (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$_2$ and TiO$_2$ are included in Fig. 2 with the lowest band gap energies determined from experiment.

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 $\sim$ 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 $\sim$ 2 eV between the atomic d-states, −11.1 eV for the Ti 3d state and −8.13 for the Zr 4d state. 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
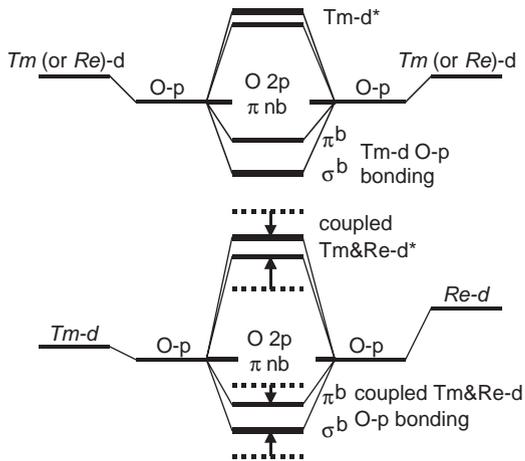
Fig. 4. Schematic representation of molecular orbitals for band edge electronic structure for elemental transition metal and rare earth oxides, and for complex oxides with d-state coupling through O atoms.

increased overlap between higher lying $(n + 1)$ s^*-states, and the n d- σ 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 ~ 5.7 eV.

4. Interpretation of the spectra for GdScO₃

The lowest band gap in $GdScO_3$ is at ~ 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_2O_3 (Gd_2O_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 π states and O 2p states is greater than for Gd 5d π 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 π-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_2O_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 ~ 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 ScO_3, ~ 4.3 eV, and Gd_2O_3, ~ 6.3 eV, average to ~ 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 π 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_2O_3 and Sc_2O_3, with other than a 1:1 ratio are expected to display spectra characteristic of more than one d-state bonding group; Sc_2O_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 HfO_2 (5d) $-TiO_2$ (3d), 1:1 alloy, $TiHfO_4$, where the predicted band gap is 4.45 eV, the average of HfO_2 (5.8 eV) and TiO_2 (3.1 eV). Conduction band offset energies are estimated on the basis of the same model. $GdScO_3$ is *equivalent* to ZrO_2 with an offset of ~ 1.5 eV, and $Hf(Zr)TiO_4$ is expected to have an offset energy of approximately ~ 1 eV, whilst a Ta_2O_5–$2HfO_2$ alloy may have an offset as high as 1.4 eV.

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