# Separate and Independent Control of Interfacial Band Alignments and Dielectric Constants in Transition Metal-Rare Earth Ternary Oxides

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## 1. Introduction

The driving force for the introduction of alternative high-k dielectrics into aggressively scaled Si CMOS devices is to reduce direct tunneling while achieving significant reductions in EOT below 1 nm. It is therefore important to develop new approaches to semiconductor-dielectric hetero-structure formation that can provide separate and independent control of interfacial band alignments and bulk dielectric polarizability, and in which lateral dimensions of can be scaled into the deep nano-scale regime. This paper demonstrates *independent control* of these hetero-structure properties through second nearest-neighbor bonding of transition metal, Tm, and rare earth, Re, atoms to a common oxygen atom in trivalent oxides of the general form ReTmO<sub>3</sub>.

The approach is based the coupling between Re and Tm d- $\pi$  states through bonding to the *same* oxygen atom. This coupling lowers the energy of the  $\pi$ -bonding states in the valence band, and thereby raises the energies of the anti-bonding d- $\pi$ \* states the define the optical band gap and the conduction band offset energy relative to Si. This bonding interaction does not shift the valence band offset energy of the O atom 2p  $\pi$  non-bonding states, nor does it reduce far IR Tm-O vibration contributions to the static dielectric constant.

# 2. Comparisons between Ab Initio Calculations and X-ray Absorption and Optical Band Edge Spectra

The electronic structures of Tm and Re binary elemental oxides, and ternary Tm and Re mixed oxides are qualitatively different from those of SiO<sub>2</sub> and Si oxynitrides. The lowest conduction band states are formed from localized anti-bonding Tm/Re d- $\pi$ \*-states, rather than free-electron-like extended Si 3s- $\sigma$ \*-states. The properties of these localized d- $\pi$ \*-states for Tm/Re elemental and ternary oxides have been studied by complementary photon and electron spectroscopies: X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), X-ray absorption spectroscopy (XAS), and spectroscopic ellipsometry (SE) [1,2]. Based on quantitative agreement between a) the Zr silicate anti-binding state electronic state energies obtained from Zr M<sub>2,3</sub> and O K<sub>1</sub> XAS spectra, and b) *ab initio* calculations on small clusters, the ordering and overlap of

anti-bonding Zr localized 4d\*-states, and extended Zr 5s\*and Si 3s\*-states in the O K<sub>1</sub> spectra has been shown to be the same as the relative ordering and overlap of conduction band electronic states. For example, the ab initio calculations predict splitting between the two 4d\*-anti-bonding bands of ZrO<sub>2</sub> to be i) 1.4 eV for optical transitions from valence band oxygen 2p  $\pi$  non-bonding states, ii) 2.5 eV for intra-atom transitions from either of the Zr 2p spin orbit J = 1/2 or 3/2states; i.e., the M<sub>2,3</sub> spectra, and iii) 4.5 eV for transitions from the oxygen atom 1s core state, the O  $K_1$  edge spectra. The experimental values of 1.4±0.1 eV, 2.5±0.15 eV, and  $4.5\pm0.2$  eV are in excellent agreement with the calculations, and demonstrate that the energies of the anti-bonding states are strongly dependent on the final state configurations; i.e., the core hole energy and localization. Similar results apply to HfO<sub>2</sub> as well, where the experimental splittings are approximately equal to those for ZrO<sub>2</sub>.

Since the lowest conduction bands have a d- $\pi^*$  character, ab initio theory confirms that band gaps and band offset energies of Tm and Re oxides are expected to scale monotonically with the atomic d-state energies of the constituent Tm and Re atoms. This is the case as displayed in Fig. 1. In addition, even though the band gaps of Tm and Re elemental and silicate and aluminate alloys scale respectively with SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> content, the offset energies are constant across a given alloy system, and equal to the same value as in the respective end-member Tm or Re oxide [1,2]. However, the situation is qualitatively different for ReTmO<sub>3</sub> oxides, due to coupling of Tm and Re d- $\pi$  states bonded to the same oxygen atom.

## 3. Experimental Studies of Complex Oxides

These scaling relationships have been extended to Re ternary oxides, including LaAlO<sub>3</sub> and GdScO<sub>3</sub>, through direct comparisons between O K<sub>1</sub> XAS spectra, and band edge optical absorption constants from analysis of SE measurements extending to ~9 eV. These comparisons yield qualitatively different behaviors for i) mixed Re-Tm, ternary oxides such as ReTmO<sub>3</sub>, and ii) Tm or Re silicate and aluminate alloys. As a direct result of near-neighbor interactions between Tm and Re d-states through bonding to a common O atom, the lowest conduction band states are

mixtures of Tm and Re atomic d- $\pi$ -states altering orbital energies of the  $\pi$ -bonding valence band states, and thereby increasing ternary oxide minimum band gaps, and conduction band offset energies. For example the minimum band gap in  $Sc_2O_3$  4.5 eV, and this is increased to 5.0 eV in GdScO<sub>3</sub>. The O K<sub>1</sub> XAS and absorption constant spectra in Figs. 2 and 3 are qualitatively similar to corresponding spectra of ZrO<sub>2</sub> indicating that the coupling atomic of Sc 3d (-9.6 eV) and Gd 5d (-6.6eV) quantum states through bonding to the same O atom in Fig. 4 vields 4d-like electronic states (Zr 4d = -8.4eV). The d\*-state splittings in the O  $K_1$  and band edge spectra of GdScO<sub>3</sub> are respectively  $5\pm0.3$  eV and  $1\pm0.2$  eV, compared to the  $4.5\pm0.2$  eV and  $1.4\pm0.1$  eV splittings in ZrO<sub>2</sub>. The d- $\pi^*$  state coupling interaction identifies new and technologically important opportunities for band gap engineering at the atomic scale. For example, the relative energy shifts of coupled Re and Tm d\*-states reported here are important for the ultimate scaling of CMOS devices. Since the valence band offset energies are determined by O  $2p \pi$  non-bonding states, and therefore not changed by the d-state coupling, the increases in band gap energies result in increases in conduction band offset energies. The offset energies of ternary oxides containing highly polarizible Sc, Ti, Nb or Ta atoms are therefore larger than what was previously identified as a fundamental limitation based the band offset energies of their respective elemental oxides, and/or silicate or aluminate alloys.

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#### References

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Fig. 1. Band gap and band offset energy scaling with atomic d-state energies.



Fig. 2. O K1 XAS spectrum of GdScO3. d\*-spacing indicated.



Fig. 3 Optical absorption versus photon energy for GdScO<sub>3</sub>. d\* spacing is indicated



Fig. 4. Coupling of d-states in elemental oxides (top) and complex ternary oxides such as ReTmO<sub>3</sub> (bottom)