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Studies of the coupling of final d*-states in mixed Hf and Ti oxides $(HfO_2)_x(TiO_x)_{1-x}$ and other complex oxides

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Abstract

X-ray absorption spectroscopy and vacuum ultra-violet spectroscopic ellipsometry are used to study the electronic structure of complex oxides comprised of mixed TM/TM and TM/RE oxides. Experimental spectra for $HfTiO_4$ and $Gd(Dy)ScO_3$ indicate multiple d-state features in the O K_1 edge. These are compared with the empirical models for atomic d-state mixing. It is concluded that a mean field, virtual alloy model does not apply, and that the effects associated with the differences in atomic coordination and deviations from ideal octahedral or cubic bonding play a determinant role in d-state atom mixing. The results are applied band edge engineering options for high-*k* dielectric applications.

Keywords: Complex oxides; X-ray absorption spectra; Spectroscopic ellipsometry; d-State coupling; Band gap engineering

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1. Introduction

There has been an increasing interest in stoichiometric complex oxides as high-*k* dielectrics for scaled Si CMOS. In contrast to the TM and RE silicates and aluminates, these oxides are binary alloys between TM and RE oxides, or two different TM or RE oxides in which there are equal numbers of TM and/or RE atom pairs. This ensures that these atoms are connected through bonding to the same O-atom as in $GdScO_3$, $HfTiO_4$ and $LaLuO_3$. O K_1 edge spectra for $HfTiO_4$, and $DyScO_3$ and $GdScO_3$ show multiple d-state features which are addressed in terms of the empirical models for d-state coupling.

2. Experimental results

Fig. 1(a–c) presents O K_1 spectra for $HfTiO_4$, $DyScO_3$ and $GdScO_3$, respectively. The spectrum in Fig. 1(a) displays three features at ∼530, 533 and 536 eV that are attributed to the d-states derived from the Hf and Ti atoms. The broader feature with a spectral peak at approximately 543 eV is assigned to Hf and Ti 6s* and 4s* states. The respective TM d*-state and s*-states are mixed with O-atom 2p* states.

Fig. 1(b and c) are qualitatively similar with regard to the multiplicity of d*-states with each spectrum displaying relative strong features at ∼532, 536 and 542 eV as well as a weaker spectral feature at ∼539 eV. The 539 eV feature has been confirmed by numerical differentiation of the spectra in Fig. 1(b and c). Fig. 1(d) displays the optical absorption constant of $GdScO_3$ as determined from spectroscopic ellipsometry data [1]. The sharp feature at about 6 eV corresponds to the 532 eV feature in the O K_1 edge [1]. The feature marked “iii” is an 4f to 4f* intra-atom transition characteristic of Gd and the threshold marked E'_g is the threshold for the absorption associated with an additional d*-state that is too weak to be detected in the XAS O K_1 edge spectrum.

3. Discussion

A mean field model was initially proposed for the complex oxides [1]. This model of d-state coupling predicts that the band gaps and conduction band offset energies are the averages of the constituent oxides. This model, shown in Fig. 2(a),

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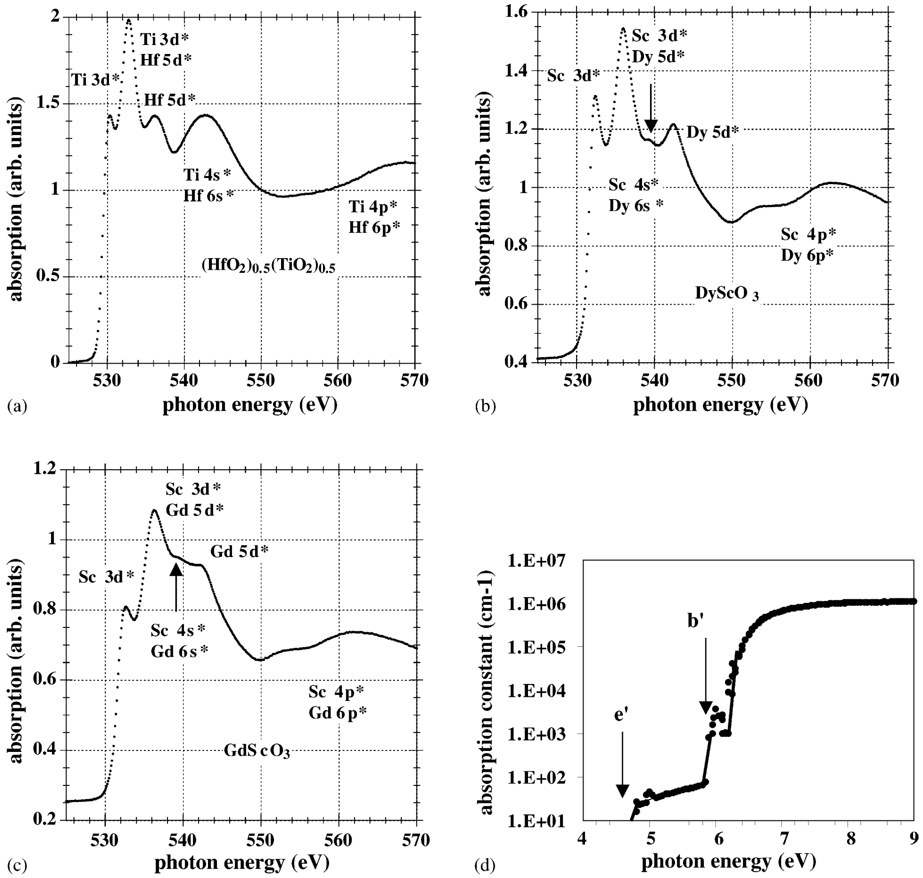

Fig. 1. XAS and VUV spectroscopic ellipsometry spectra: O K_1 edges for (a) $HfTiO_4$, (b) $DyScO_3$, (c) $GdScO_3$, and (d) band edge optical absorption constant for $GdScO_3$.

requires that the triad of atoms be collinear and that the coupled pairs of d-states are relatively close in energy. This model is not supported by high-resolution studies of the O K_1 edges of $HfTiO_4$, $DyScO_3$ and $GdScO_3$ in Fig. 1(a–c). Mean field theory predicts two pairs of d-states, one with doubly degenerate e-symmetry and one triply degenerate with t-symmetry whereas the spectra of the three complex oxides display three strong d*-state features. The mean field model does not take into account the differences in local coordination and symmetry at the two metal atom sites. The multiplicity of final d-states in the O K_1 edge is the same as at the conduction band edge, establishing that O K_1 edge spectra and the theory/model that explains its scaling with atomic d-state energies is also applicable to band edge properties including conduction band offset energies [2].

Deficiencies in mean field theory are remedied in the energy level diagrams of Fig. 2(b and c). This approach includes differences in the atomic coordination of the two atoms of the complex oxide, e.g., 8-fold for Hf and 6-fold for Ti, 12-fold for Dy or Gd and 6-fold for Sc in Fig. 2(b) with distortions from octahedral symmetry as at Sc atom sites as added in Fig. 2(c) [2]. Relative energies of initial e and t d*-states for are approximated from XAS O K_1 spectra of elemental oxides. The model in Fig. 2(b) predicts four states: two "t" states separated by >10 eV, and two closely spaced "e" states that are expected to contribute to only the features in the XAS spectra. A splitting of the triply degenerate "t-" states into a doubly degenerate "e" state and a non-degenerate "a" state introduces two additional states can result from a ferroelectric distortion at the 6-fold coordinated sites is shown in Fig. 2(c).

The XAS O K_1 edge for $HfTiO_4$ displays three features. As applied to this $HfTiO_4$ spectrum, the model in Fig. 2(b) predicts four features, two of which are closely spaced and not observable in the XAS spectrum. Reduced local symmetry at the Ti-atom site can lead to the splitting of the "t" states and lead to band edge tails, however, these have not been reported. When applied to O K_1 spectra for $GdScO_3$ and $DyScO_3$, the model in Fig. 2(c) accounts for the three strong features, at approximately 531, 537 and 541 eV as well as the substantially weaker feature at ∼539.5 eV. The lowest energy e′-state of this model is not detected in the O K_1 spectrum but is detected for $GdScO_3$ by optical transmission and by spectroscopic ellipsometry in Fig. 1(d). This state is also responsible for band-tail effects in internal photoemission (IPE) and photoconductivity (PC) studies [3].

O K_1 edges for non-crystalline and crystalline $LaAlO_3$ in which only the La atom as valence bonding d-states are qualitatively different. In general, non-crystalline complex

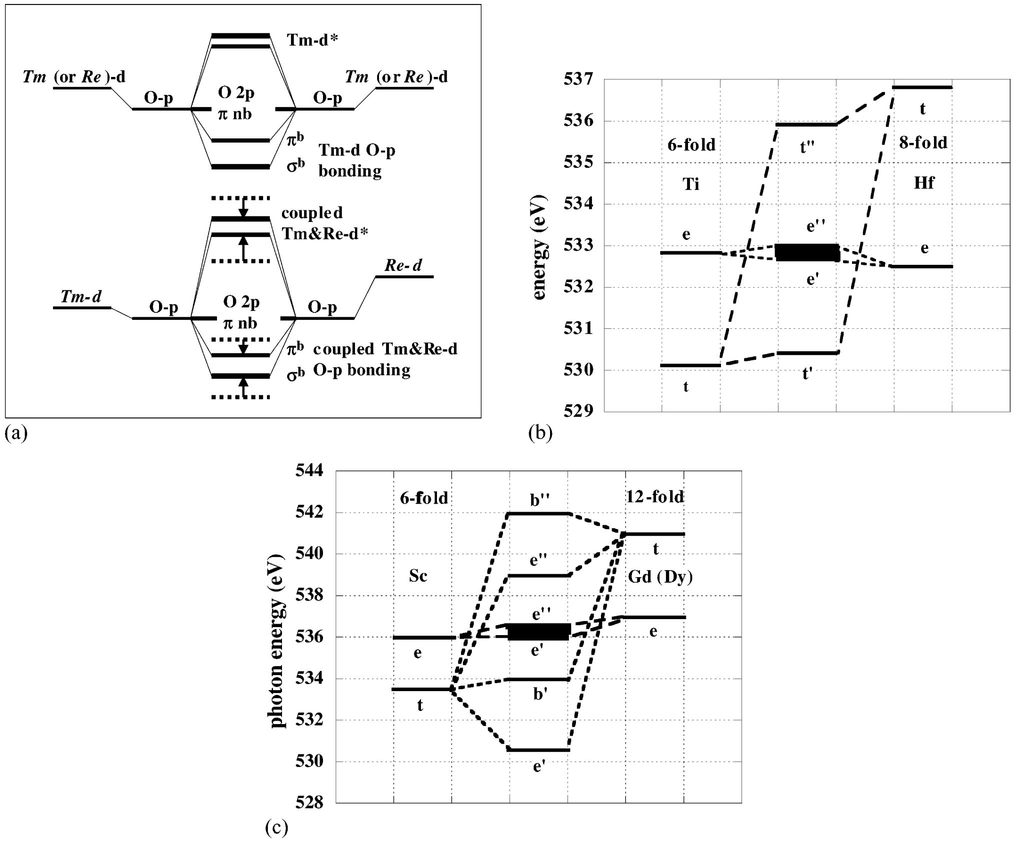

Fig. 2. Empirical energy level schemes for d-state coupling in complex oxides: (a) mean field, virtual crystal model; (b) model that includes different atomic coordinations only, and applies to $HfTiO_4$; and (c) model that includes different atomic coordinations and a strong distortion at one atomic site and applies to $DyScO_3$ and $GdScO_3$.

oxides with stoichiometric compositions in which both the atoms have valence band d-states display qualitatively different O K_1 edge spectra without the strong d-state coupling of their crystalline counterparts. Off stoichiometry non-crystalline compositions are dominated by the oxide with the smaller bandgap, leading to markedly different properties for TiO_2-rich and HfO_2-rich alloys of the HfO_2-TiO_2 alloy system. Finally, the bottom line is that non-crystalline complex oxides yield only marginal small improvements with respect to their constituent elemental oxides, and crystalline complex oxides are expected to show increased trapping due to symmetry reductions and the formation of deep trapping states.

Note added in proof

We have refined our interpretation of the results presented in this paper, and at the VUV conference in Cairns.

A d-state coupling mechanism has been proposed to account for the multiplicity of features the XAS spectra for Gd and Dy scandates in Fig. 1. Subsequent studies, summarized in Ref. [4], have identified the correct mechanism that accounts for the multiplicity of scandate spectral features, as well as the multiplicity of XAS features in the spectra of TiO_2, ZrO_2 and HfO_2, and Zr and Hf titanate alloys.

The following points summarize the research results of Ref. [4]. Thin films of (i) TiO_2, ZrO_2 and HfO_2; (ii) complex scandate oxides; including $LaScO_3$, $DyScO_3$ and $GdScO_3$; and (iii) Zr and Hf titanate alloys are nano-crystalline, on deposition when chemically pure. The lowest conduction band states in these oxides are Jahn-Teller *term split* d-states associated with *intrinsic bonding distortions*. These term-split states have also been detected in band edge spectroscopy measurements, including spectroscopic ellipsometry and photoconductivity, confirming larger differences in matrix elements for optical absorption between octahedrally coordinated Ti and Sc atoms, and eight-fold coordinated Zr and Hf atoms. Localized *band edge traps* resulting from *additional bonding distortions* at grain boundaries are observable in band edge absorption and photoconductivity and contribute to trap assisted tunneling and Frenkel Poole electrical transport for *substrate injection* from *n*-Si.

Acknowledgements

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