

# Electronic structure of non-crystalline high-k transition metal and rare earth oxides and their silicate and aluminate alloys

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This paper identifies significant differences between the fundamental amorphous bonding morphology and electronic structure of TM/RE dielectrics and SiO<sub>2</sub> and Si oxynitrides. The scaling variable for tracking these systematic changes is the average Pauling bond ionicity. For example, the bonding in SiO<sub>2</sub> is predominantly covalent and the amorphous morphology is a continuous random network in which the bonding coordinations of Si and O obey the so-called 8-N rule. As transition metal atoms are added to SiO<sub>2</sub> to form silicates average bond ionicity increases, average coordination of O increases, and metal atoms disrupt the covalent network continuity by forming ionic bonding arrangements. The bonding in the TM/RE oxides is completely ionic, and the 8-N rule is no longer applicable or relevant.

The electronic structure of TM/RE atoms has been calculated by ab initio methods applied to small clusters that include the coordination and bonding geometry of TM/RE atoms. The electronic structure of the TM/RE oxides is qualitatively different than SiO<sub>2</sub> (see Fig. 1). The valence band structure is essentially the same, but the lowest conduction band states are derived from TE/RE d-states and are considerably more localized than the s,p-state derived conduction bands in SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, or higher lying conduction bands in the TM/RE dielectrics.

The results of these calculations have been used to interpret UV photoemission spectroscopy (UPS) studies that reveal the valence band structure (see Fig. 2), and X-ray absorption spectroscopy (XAS) studies that reveal the unoccupied conduction band states (see Figs 3 and 4). The agreement between theory and experiment is excellent, and additionally provides significant insights into between the spectroscopic characterizations of TM/RE oxides and silicate and aluminate alloys and the transport states important in device properties.

Comparisons between UPS/XAS studies and bandgaps and band offset energies by X-ray photoemission spectroscopy, bandgaps by photo-conductivity (PC), and band offset energies by internal photoemission (IPE) spectroscopy provide a basis for the determination of the effective conduction band offset energies between crystalline Si and TM/RE dielectrics that are important in developing a quantitative understanding of direct and Fowler-Nordheim tunneling in device structures. This will be discussed in the paper, including effects of the localized d-states and systematic shifts in their energies with increasing principal quantum number, n = 3, 4 or 5.

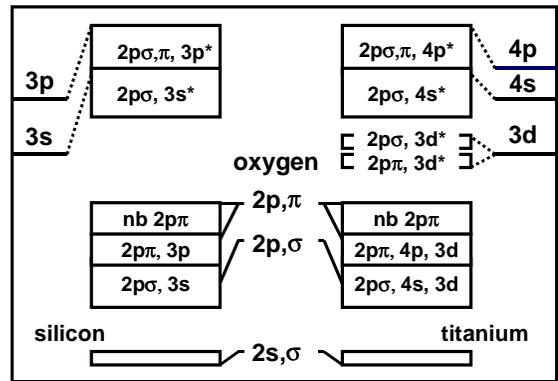


Fig. 1 Schematic presentation of band edge electronic structure of SiO<sub>2</sub> and TiO<sub>2</sub>.

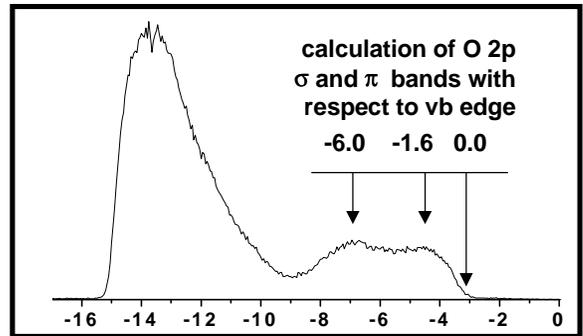


Fig. 2 Comparison between valence band of TiO<sub>2</sub> determined by UPS with ab initio calculation.

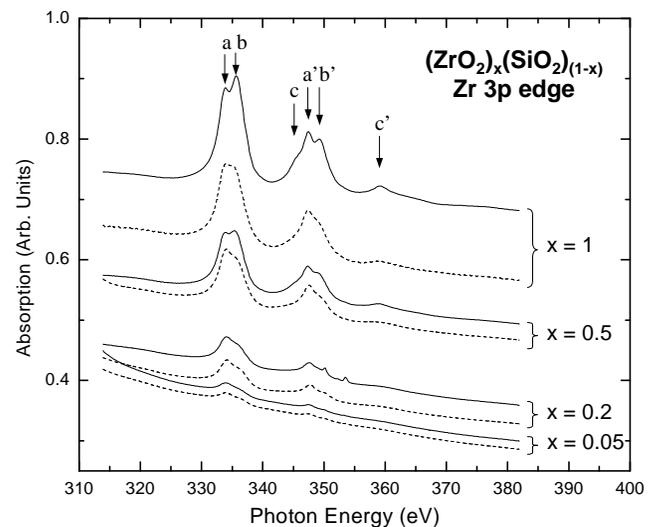


Fig.3 XAS spectra for Zr silicate alloys indicating that features are independent of second neighbor alloy atoms, Si or Zr. a,b and c and a',b' and c' designate energy differences between the M<sub>2</sub> and M<sub>3</sub> p-states, respectively, and the anti-bonding Zr states. Dotted are as-deposited, and dashed are after a 900°C rapid thermal anneal.

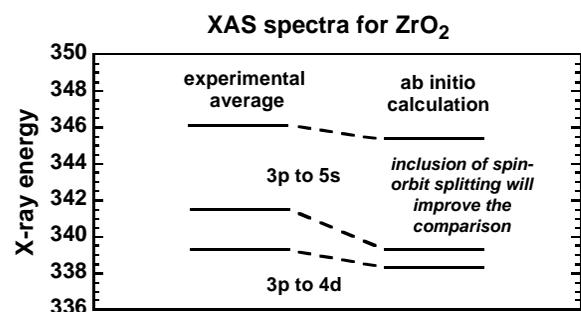


Fig. 4. Comparison between experimentally-averaged XAS features for ZrO<sub>2</sub> and ab initio calculation.