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Intrinsic limitations for gate stack applications of complex high-k oxides in advanced Si devices: band edge states[1]

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Valence and conduction band edge electronic states in high-k oxide dielectrics have been studied by X-ray absorption spectroscopy (XAS), ultra-violet photoemission spectroscopy (UPS), and vacuum ultra- violet spectroscopic ellipsometry (VUVSE) and photoconductivity (PC). These studies confirm results of *numerous* theoretical studies which have demonstrated that valence and conduction band electronic states are comprised of transition metal/rare earth (TM/RE) atom d-states mixed with O-atom 2p states. Electronic states at the top of the valence band and bottom of the conduction band have a π-bonding symmetry, while those deeper in the valence band and higher in the conduction band have a σ-bonding symmetry. XAS studies of *empty* TM/RE d-states by transitions from deep TM/RE p-states are combined with studies of conduction band edge states by transitions from the O-atom 1s state to provide qualitative and quantitative insights into electronic structure at the conduction band edge. This approach was first applied to HfO_2 and TiO_2, and then to the *complex/binary oxides*: i) $Zr_xTi_{1-x}O_4$, with x = 0.67 and 0.33, $LaAlO_3$, and $LaScO_3$. Thin films of these oxides are nano-crystalline as-deposited and/or after an anneal in an inert ambient at 500 to 1000 $^\circ$C. Analysis of the XAS spectra indicate that d- state degeneracies are completely removed for Hf in HfO_2, Ti in TiO_2 and the Zr titanates, La in $LaAlO_3$, and Sc in $LaScO_3$. This removal indicates a distorted local bonding arrangement for these TM/RE atoms, or equivalently *Jahn-Teller term splittings* that increase the total binding energy. More importantly, the term split states identified in XAS spectra are directly correlated with d-state features at the conduction band edge by VUVSE and PC. These localized π-bonded states limit performance and reliability in scaled Si devices, and are associated with *asymmetric* bias voltage dependent electron transport and trapping.

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