Ligand field splittings in core level transitions for transition metal (TM) oxides: Tanabe-Sugano diagrams and (TM) dangling bonds in vacated O-atom defects

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Abstract: Defect states in the forbidden band-gap below the conduction band edge are active as electron traps in nano-grain high-κ TM oxides with thickness >0.3 nm, e.g., ZrO2 and HfO2. These oxides have received considerable attention as gate-dielectrics in complementary metal oxide semiconductor (CMOS) devices, and more recently are emerging as candidates for charge storage and memory devices. To provide a theoretical basis for device functionality, ab-initio many-electron theory is combined with X-ray absorption spectroscopy (XAS) to study O K edge and TM core level transitions. These studies identify ligand field splittings (ΔLF) for defect state features, when compared with those obtained from O-atom and TM-atom core spectroscopic transitions, this provides direct information about defect state bonding arrangements. Comparisons are made for (i) elemental TiO2 and Ti2O3 with different formal ionic charges, Ti4+ and Ti3+, and for (ii) Magneli Phase alloys, Ti2O2n-1, n is an integer 9>3, and (TiO2)x(HfO2)1-x alloys. The alloys display multi-valent behavior from (i) different ionic-charge states, (ii) local bond-strain, and (iii) metallic hopping transport. The intrinsic bonding defects in TM oxides are identified as pairs of singly occupied dangling bonds. For 6-fold coordinated Ti-oxides defect excited states in 2nd derivative O K pre-edge spectra are essentially the same as single Ti-atom d2 transitions in Tanabe-Sugano (T-S) diagrams. O-vacated site defects in 8-fold coordinated ZrO2 and HfO2 are described by d8 T-S diagrams. T-S defect state ordering and splittings are functions of the coordination and symmetry of vacated site bordering TM atoms. ΔLF values from the analysis of T-S diagrams indicate medium range order (MRO) extending to 3rd and 4th nearest-neighbor (NN) TM-atoms. Values are different for 6-fold Ti, and 8-fold ZrO2 and HfO2, and scale inversely with differences in respective formal ionic radii. O-vacated site bonding defects in TM nano-grain oxides are qualitatively similar to vacant-site defects in non-crystalline SiO2 and GeO2 for ultra-thin films, < 0.2 nm thick, and yield similar performance in MOSCAPs on Ge substrates heralding applications in aggressively-scale CMOS devices.

1. Introduction and Chapter-Overview

There is considerable interest in identifying the local bonding of intrinsic chemical defects in ultra-thin nano-grain (ng-) high-κ TM oxides, ng-HfO2 and ng-ZrO2 [1-5]. These have been targeted as gate dielectrics for the ultimate limits of integration of Si devices. One proposal is for Ge channel regions grown in wells on a Si wafer where higher hole mobilities reduce the footprint CMOS unit cells. The Robertson and Shlugger groups have employed DFT methods to study high-κ vacancy defects [1,2]. These results are applicable only to singlet TM-atom defect states with a maximum occupancy of two [6]. In contrast, the Lucovsky group, has proposed a qualitatively different approach initially designated as an effective d2-model [3-5]. The alternative model assigns two-electron wave functions
to TM-atom excited X-ray excited states. This includes singlet and triplet spin excited states including ground-state holes. This approach takes specific account of the hole generated in an X-ray, visible or vacuum ultra-violet excitation process. As such, the $d^2$-model is based on a CTM formalism using symmetry adapted combinations (SALC) of atomic states [7,8,9,10]. This approach has been applied to nc-SiO$_2$ and ng-HfO$_2$, as examples (nc- and ng- not be used from this point forward). This chapter discusses in detail the use X-ray absorption spectroscopy (XAS), applied first for the assignment of pre-existing, process-induced defect for SiO$_2$ and GeO$_2$ and used here as for the TM-atom studies as well [10].

A combination of XAS O pre-K edge spectra and ab-initio theory, coupled with previously published electron spin resonance (ESR) studies has established that the pre-existing defects of Galeener in SiO$_2$ [10], are vacated O-atom Si-O-Si bonding groups that have never contained an O-atom [10,11]. The defects are a pair of nearest neighbor (NN) Si- or Ge-atom neutral dangling bonds projecting in the vacated site with sufficient radial wave-function overlap to satisfy conditions for Fermion wave functions, and hence Pauli exclusion to apply [7]. The appropriated CTMs are associated with two-electron Fermion wave-functions with 3-vector spatial, and 4-vector spin components [7-9,13-15]. The NN dangling bonds are then functionally equivalent atomic states of TM occupied states. For TM defect excite states the $d^2$ diagram is used for 2-electron ground-states, and the $d^8$ diagram for 2-hole ground states. These are (i) $d^2$ diagrams for Ti oxides with octahedral or distorted octahedral primitive unit cells, and (ii) $d^8$ diagrams for Zr and Hf oxides with 2-hole ground states, $d^8$, in tetrahedral, cubic, tetragonal or monoclinic arrangements in ZrO$_2$ and HfO$_2$.

Tunabe-Sugano (T-S) diagrams are used to characterize the dangling-bond pair excited states singlet and triplet states, in particular their ordering in energy and two-electron state symmetries [14]. This chapter establishes that ligand field splittings of the defects, $\Delta_{LF}$, are determined by the energy separation between $eg$ and $t_{2g}$ excited states are local properties of the dangling bond site, including up to 3rd and 4th NNs. The values of $\Delta_{LF}$ are readily extracted from XAS O pre-K edge defect spectra, are the same to within the uncertainty of these measurements, $\pm 0.2$ V, as the values of $\Delta_{LF}$, respectively obtained TM core level atomic spectra. For Ti-oxides, elemental oxides and composite or complex mixed oxides the $\Delta_{LF}$ values from Ti L$_{2,3}$ spectra that are approximately the same with small differences associated for different formal ionic charges, +4 in TiO$_2$, and +3 in Ti$_2$O$_3$. Local bond-strain induced multi-valency accounts in for most of the multiplicity of Ti L$_{2,3}$ spectral features in Magneli-phase and TiO$_2$-HfO$_2$ composite oxides. There is also additional multi-valency explained by a hopping assisted transport mechanism for metallic conductivity present in Ti$_2$O$_3$, and the Ti-oxide based alloys.

Background studies in Ref. 11 for SiO$_2$ and GeO$_2$ indicate that there is intrinsic medium range order (MRO) at the vacated O-atom defect sites. The MRO extends to 3rd NN Si-O distances, and 4th NN O-O distances as well. One important manifestation of MRO is that the basis set of vectors that apply are comprised of SALC directed along site-determined cartesian-coordinate axes [16]. This representation includes the local site symmetry of the Si or Ge atom, and their respective back-bonded O-atom neighbors. The MRO includes the singly occupied Si or Ge dangling bonds projected into the vacated O-atom site. The vacated O-atom must be counted defining a 1st nearest neighbor to each of the 2-dangling bonds. This means the value of $\Delta_{LF}$ obtained from an analysis of defect state symmetries and degeneracies includes the energy difference between a pair of $eg$ and $t_{2g}$ singlet states localized at the defect site. This is approach is exact for T-S diagrams that apply to a pair of dangling bonds with some degree of radial wave function overlap. A test case for this model is demonstrated in Section 4 where it is shown that defect state symmetries and ordering are the same for TiO$_2$ with a formal valence of +4 for Ti, and in Ti$_2$O$_3$ where the formal valence for Ti is +3. The values of $\Delta_{LF}$ differer by $\sim 12\%$ due differences in formal ionic radii, $\sim 0.40$ nm for the +4 valence and 0.52 nm for the +3 valences, When these are taken into account the results are by the experimentally-determined uncertainty, and the resolution of the X-ray monochromater, at most of order $\pm 0.15$ eV.
2. Experimental methods: deposition and characterization of electronic structure of TM oxide

2.1. Thin film deposition. Nano-grain thin films of TiO₂, and TiₙO₂ₙ₋₁ alloys, ZrO₂ and HfO₂ were deposited at 300°C by remote plasma-enhanced chemical vapor deposition (RPECVD or simply RPD) onto (i) SiON passivated crystalline Si and (ii) remote plasma nitrided crystalline Ge [17]. Prior to deposition onto Ge, native oxides were removed by a wet-chemical etching/rinsing process [18]. The films were subsequently annealed at temperatures between 400°C and 950°C in Ar. Thin nano-grain films of TiO₂-HfO₂ alloys and ZrO₂ were also deposited by reactive evaporation on oxidized Si substrates, and annealed at temperatures between 700°C and 900°C in Ar as well [19]. The TM core-level spectra of the HfO₂ and ZrO₂ were qualitatively and quantitatively the same as those obtained from RPECVD (RPD) films.

2.2. XAS spectra at the Stanford synchrotron research lightsource.

The O K edge, and pre-O K edge XAS spectra were obtained on Beam-line 10-1 at the Stanford Synchrotron Research Lightsource (SSRL) in Menlo Park, Ca. Energies of conduction band state, the pre-conduction band edge defect states electronic transitions have been obtained by X-ray absorption spectroscopy (XAS) using the total electron yield (TEY) detection method [20]. This is based on a measurement of current required to neutralize positive charge created by relaxation of XAS final virtual bound excited states by photoemission events. This approach provides an excellent measure of the linear absorption coefficient with a precision of a few percent. The signal to noise ratio (>3000:1) and the spectral resolution (~ 0.1 eV) for these measurements are sufficient for performing a 2nd derivative analysis of the O K edge and O pre-edge regimes, and core level 2p to 3d core level L2,3 transitions for Ti oxides, as well p-to-d transitions applicable to other TM oxides with 3p (ZrO₂ and Y₂O₃) and 5p (HfO₂) core-level states. The Si L2,3 spectra, and Ge M3,4 spectra were also obtained by the same TEY method, but on BL 8-1 at SSRL. BL 10-1 covers a spectral range of X-ray energies between about 200 and 1200 eV, and BL 8-1 covers a spectral range from about 50 eV to 200 eV. Equally important O K edge, and pre-K-edge data were taken on BL 10-1 with continuous scanning, and with sampling intervals ranging from 30 to 40 meV, well inside a resolution limit of ~0.1 eV as determined by the X-ray monochromator aperture and grating. Finally, O-pre-K edge absorption for TiO₂ and c-Ti₂O₃ done at different times with different interval sampling, 30 meV and 50 meV, yield the same number and ordering of pre-edge defect states. This establishes that background noise is not an issue for this experimental X-ray spectroscopy results presented below, particularly the defect related 2nd derivative O K pre-edge spectra.

![Fig. 1. (a). The second derivative Zr M3,4 spectrum for ZrO₂; (b). The O K edge spectrum, and the O K edge 2nd derivative spectrum.](image-url)
3. Ligand Field Determinations from ZrO$_2$: Zr M3,4 and ZrO$_2$ O K-edge spectra

Zr M3.4 and ZrO$_2$ O K-edge spectra are presented for ZrO$_2$ to identify the spectral change resulting from differences between $\Delta$SO in the Zr M3,4 spectrum, and an effective $\Delta$SO’ in the ZrO$_2$ O K-edge replicated spectral features. $\Delta$SO’ is a splitting between 4p$\sigma$ and 4p$\pi$ states in the valence band molecular orbital states of ZrO$_2$.

The three-electron process that is relevant also increases the spectral width of features in the M3 and M4 features in the O K-edge spectrum relative to the Zr M3,4 spectrum. Figure 1(a) is the second derivative Zr M3,4 spectrum for ZrO$_2$. Respective values of $\Delta$LF and $\Delta$SO’ are 3.2±0.2 eV, and 13.7±0.2 eV. $\Delta$LF is the energy difference between the eg and t$_2g$ features in the M3 and M4 energy regimes, and $\Delta$SO’ is the energy difference between the corresponding eg features in the M3 and M4 regimes. $\Delta$SO is the spin-orbit splitting of the Zr 3p core level. A comparison between the 3p$^6$4d$^0$ to 3p$^5$4d$^1$ transitions, and the 3p$^5$d$^0$ to 3p$^5$s$^1$ transitions gives an energy difference of ~8 eV between the lower lying Zr 3d states and the higher lying 5s states.

Fig. 1(b) includes the O K edge spectrum, and the 2nd derivative of that spectrum as well. Of particular importance are the photon energies for the d-state derived features, and the s-state derived features. The respective values of $\Delta$LF and $\Delta$SO’ are 3.3±0.2 eV, and 10±0.2 eV. As anticipated the extracted $\Delta$LF values are the same to within the experimental uncertainties. On the other hand, the values of $\Delta$SO and $\Delta$SO’ are significantly different. This difference in $\Delta$SO’ is related to the nature of the excitation process the results in M3 and M4 features in O K edge conduction band regime. This difference is the same as the difference in energy between 3p$^5$d$^0$ to 3p$^5$4d$^1$ transitions, and the 3p$^5$d$^0$ to 3p$^5$s$^1$ transitions. This is reduced by 1.5 eV from 8.0 eV in the Zr M3,4 spectrum to 6.5 eV in the ZrO$_2$, at the same time the ligand field splitting remains effectively the same in each spectrum.

The O K-edge spectrum plot extends from 530 eV to 549 eV, with an extrapolated X-ray photon energy of 531.5 eV. Each of the d-state derived features in the Zr M3,4 spectrum has the same relative energy of 531.5 eV. Each of the d-state derived features in the Zr M3,4 spectrum has the same relative energy in each spectrum, but with markedly different matrix elements. Equally important and as noted above, the effective spin-orbit splitting, defined above as $\Delta$SO’ is significantly smaller. This is explained in the context of three-step coherent process that gives rise to M3 and M4 features. The O K-edge spectral features are the result of three-concurrent and coherent CTM transitions [25]. The CTM transitions are initiated by excitations from occupied 1s$^2$ O-core level to two virtual-bound states above the level that defines the Ionization Potential (IP) of an O 1s$^2$ core level that takes into account a partial covalent charcter, and is shifted up in energy by more than 10 eV. This initiating excitation is concurrent and coherent with two other transitions. The first of these is: (i) the filling of the O 1s empty core levels by a transition in which electrons from occupied Zr 4p-derived molecular orbital states in the Zr valence band fill the O 1s core holes, and (ii) a shake-up energy conserving transition to two virtual bound resonance states in the conduction band continuum [25]. The filling of the two 1s$^2$ core-level holes is accompanied by emission of X-rays. The shake-up process is effectively a p-d transition with a large transition energy matrix element. This process explains: (i) the difference between $\Delta$SO and $\Delta$SO’, (ii) the effective shift of the relative final d-state and s-state transitions, and (iii) the different spectral line shapes between the Zr M3,4 and ZrO$_2$ O K-edge spectra. Similar differences occur for the HfO$_2$ O K-edge spectrum, and these are displayed in Fig. 2.

Figure 2 compares OK edge spectra of two HfO$_2$ films marked to indicate features in Hf core level O5,6 spectral features. Two nm thick films annealed at 700°C have a tetragonal (T) HfO$_2$ structure, whereas thicker 5 nm HfO$_2$ films, also annealed at 700°C, display a mixture of tetragonal (T) and monoclinic (M) nano-grains [11]. These films are prepared on nitrified Ge substrates. When annealed at a lower temperature of 500°C after remote plasma deposition at 300°C, the features in both 2 nm and 5 nm thick films are significantly broader as indicated in Fig. 2(b). These differences result from an in-plane Ge surface templating effect at the higher temperature that is absent at the lower temperature. Based on N K-edge spectra, the Ge-N disordered interface remains largely unchanged from its initial spectral character after 500°C annealing, but is removed completely except for on narrow feature after the 700°C anneal. Templating dominates in the thinner 2 nm film, and is
Fig. 2 OK edge spectra of 2 nm and 5 nm HfO2 films annealed (a) at 700°C; (b) at 500°C.

diminished in the thicker 5 nm yielding changes from T to a combined T-M films texture after the 700°C anneal. The features in thee 500°C films have often been mistaken as being an indicator of the film being amorphous. This is not the case. These films like the higher temperature 700°C annealed films display the same values of ΔLF and ΔSO'. Equally important for technology applications, e.g., CMOS gate dielectrics, the low temperature films do not show strong bias-dependent increases in current for increases in temperature from 25°C to 125°C substrate heating. The resulting J-V characteristics are similar to SiO2, where electron injection is reduced significantly by band-edge excitons situated between the photo-conducting band edge and defect states with the SiO2 layer. Additionally and consistent with XRD results for these films which indicate a significant grain-size dependent broadening, the grain-size is limited by film thickness, and defect sites resent in individual grains requiring inter-grain hopping. This is in contrast with the thicker films where defects reside within grains and on grain-boundaries as well, resulting in hopping-conductivity that is strongly temperature dependent.

Returning to the HfO2 results in Figure 2, the values of ΔLF and ΔSO', respectively in the O K-edge spectra are 3.4±0.15 eV and 8.0±0.15 eV. The 3.4 eV value is the same as in the O5,6 core level transition, but the ΔSO' value is smaller than 8.6 eV the O5,6 core level spin-orbit splitting. Fig. 2(a) that compares OK edge spectra of these films is marked to high-light the features in Hf O5,6 spectral features. The relative 5p66s0 to 5p56s1 position is therefore changed because of the 0.6 eV reduction in the O5 and O6 average energy difference. The changes and relative energy differences parallel the similar changes in ZrO2 films, and also results from the three step coherent process for soft X-ray electron excitations out of the occupied O 1s2 state to the virtual bound regime.

4. Experimental Results: Ti elemental-oxides and alloys

4.1 Ti elemental oxides.

There is a corelation between ΔLF extracted from the analysis of Ti L2,3 spectra, and the spectral widths (ΔSW)of vacated O-atom site singlet and triplet defect spectral features in the O pre K-edge regime [8,9,14]. An approximate empirical relationship is obtained from the T-S diagrams: ΔSW
Fig. 3. XAS spectra and Second derivative XAS spectra: for TiO$_2$: (a) Ti L2,3 edge; and (b) O K pre-edge vacated O- site excited defect spectrum.

$\approx 1.8 \pm 0.15 \times \Delta LF$. This relationship holds for ZrO$_2$ and HfO$_2$ and applies to Ti-oxides as well. This scaling relationship indicates the importance of $\Delta LF$ for both (i) intrinsic final TM d-state derived features, as well as (ii) final states of strongly correlated pairs of TM-atom dangling bond defect transitions. The determination of $\Delta LF$ is based on the splitting of $e_g$ and $t_{2g}$ features in the T-S diagrams that apply; e.g. $d^2$ for TiO$_2$, and $d^8$ for tetragonal HfO$_2$ [15,16]. These are then compared with values of $\Delta LF$ extracted directly from the TEY 2nd derivative core-level absorption spectra transitions, O K edge and Ti L2,3 spectra as well. These transistions are interpreted using symmetry adapted combinations of atomic states (SALC) [17] appropriate to the local symmetry of Ti in the nano-grains of different Ti oxides. X-ray photoemission studies identify the ground state energies of the occupied Ti dangling bond sites that project in the vacancy. This theory based approximation for $\Delta SW$ provides a determination the vacated O-site singlet and triplet state energies relative to the conduction and valence edges that define the forbidden energy gap, $\Delta E_g$. This is the first time this approach has been applied to the Ti$_6$Ti$_{2n-1}$ and TiO$_2$-HfO$_2$ alloys.

Figure 3 includes XAS spectra and Second derivative XAS spectra for TiO$_2$ films in which rutile edge-connected octahedral bonding dominates after a 500°C anneal, and anatase bonding dominates after a 700°C anneal. Fig. 3(a) presents the Ti L2,3 plots for the 2 annealing conditions. The removal of the $e_g$ into 1 eV split into $A_{1g}$ and $B_{1g}$ components is indicated. The $A_{1g}$ terms are different for anatase (A) and rutile (R) interconnections of the primitive octahedral unit cell. The $B_{1g}$ terms are not evident in the Ti L2,3 spectra. Edge sharing dominates in the (R) structure. This increases the c-axis length and reduces the energy of the $A_{1g}$ term.

Spectra for anatase (A) dominant grains are present in TiO$_2$ films annealed at higher temperatures (not shown), and these indicate a decrease the energy of the $A_{1g}$ split component with a shift to higher X-ray photon energies. The following energy differences have been obtained for this film: (i) $\Delta LF = 2.7$ eV and (ii) $\Delta A-R$, the energy separation between the A and R features is $\sim 1$eV. Finally, $\Delta SO = 6.2$ eV and has been estimated from the energy difference between the $t_{2g}$ features in the L3 and L2 spectral regimes. The inter-connection of octahedra in the anatase (A) structure is via corners, and this leads to contractions in the c-axis and a shift of the $A_{1g}$ feature to a higher energy than in the rutile (R) structured nano-regions.

The Ti L2,3 spectra are dipole allowed X-ray transitions from occupied, spin-orbit split Ti 2p$_{3/2}$ and 2p$_{1/2}$ states at $\sim 460$ eV and $454$ eV, respectively to empty Ti 3d states. There also dipole allowed transitions from Ti 2p$_{3/2}$ and 2p$_{1/2}$ states to empty 4s states [24,25]. Holes in the Ti 2p core level states
play a significant role in the symmetries of the final states for these excitations. The initial and final state symmetries are described in the context charge transfer multiplet (CTM) theory [24,25]. These transitions are represented symbolically in Eqns. 1(a) and 1(b):

\[
2p^63d^0 \rightarrow 2p^53d^1 \quad \text{(a)} \quad \text{and} \quad 2p^64s^0 \rightarrow 2p^54s^1 \quad \text{(b)}.
\]

The final states of the 1(b) transitions are higher in photon energy than those of the 1(a) transitions, and in a different and separated spectral regime centered about 8 eV higher in photon energy. A complete analysis of the final state properties for the transitions in Eqn. 1(b) is beyond the scope of this article, and detailed discussions are included in Ref. 25.

More important, for the L2,3 transitions in the Ti-elemental and complex oxides of this chapter, the ΔLF values are essentially the same as the value found for these Ti oxides. The value of ΔSO is also approximately the same in all of the oxides studied, 6.3±0.2 eV. The spread of values includes the nominal value of the 2p core state spin-orbit splitting: ΔSO = 6.4±0.1 eV. More important, the relative values of ΔLF and ΔSO are sufficiently different and give rise to separate and distinct L2 and L3 energy regimes in the L2,3 spectrum. Stated in more quantitative way, as long as ΔSO > 2xΔLF, the L2 and L3 regions are separate and distinct. This is also the case for the other group IV oxides, ZrO2 and HfO2, addressed above. Moving on the O-K pre-edge spectrum in Fig. 3(c), and has 16 features. This number is the same as number features in the Ti L2,3 spectra in Fig. 3(a). However in this case the number is determined by the symmetry and coordination of the Ti-atom dangling bonds projected into the vacated O-atom site. It is a property of the excited states, and consistent with the number of detectable features in the d^2 T-S diagram that applies. The sixteen (16) triplet and singlet features as a function of increasing energy corresponds to the T-S d^2 plot for cubic octahedral local symmetry. This includes the 3-fold degeneracy of 3T2g and 3T1g states removed by final state effects associated with the spin-orbit splitting of the final virtual bound states in these transitions [24]. There accounts for 9 triplet features with triplet symmetries, e.g., 3T1g. The remaining 7 spectral features are assigned to non-degenerate singlet 1Ag, 1Eg, 1T1g and 1T2g features. The ordering of the singlets and triplets follows the T-S diagram for octahedral symmetry with 2 occupied strongly-correlated d-states. The spectrum is for an intermediate strength effective ligand field splitting defined by the 1Eg to 1T2g energy difference of 2.7±0.15eV and essentially the same as values in the Ti L2,3 spectrum.

Before presenting and analyzing the XAS spectra for the Magneli Phase TiO2n-1, and TiO2-HfO2 alloys, the 2nd derivative Ti L2,3 for Ti2O3 is presented in Figs. 4(a) and the second derivative Ti2O3 O pre K-edge spectra is displayed in Fig. 4(b). These spectra are obtained from a single crystal with the corrundum structure. As such, they include contributions for X-ray photons with components of the E-field aligned with both the c-axis in the z-direction, and two a-axis directions in the x-y base plane. Equally important, the formal valence state of Ti in Ti2O3 is +3 rather than +4 in TiO2. The ionic radius is increased from R(Ti4+) = 0.0745 nm to R(Ti3+) = 0.081 nm, equivalently the ratio of the +4 charge state to +3 charge state radii is 0.92.

The 2nd derivative spectra Ti L2,3 spectrum is in Fig. 4(a) and the 2nd derivative O K pre-edge spectrum in Fig. 4(b) spectra have been obtained with the X-ray beam at approximately normal incidence on the the base plane, and as such the electric field vector E is perpendicular to the c-axis. Qualitatively and quantitatively similar Ti L2,3 spectra have been obtained with the X-ray incident on a vertical face, with the E-vector perpendicular to both the c- and a-axis direction: these spectra are not shown. Values of ΔLF = 2.5±0.15 eV and ΔSO = 6.2±0.15 eV extracted from the Ti L2,3 vertical face spectrum of Ti2O3,are the same within the experimental uncertainty as those for of extracted from the Ti L2,3 base face spectrum of TiO2.

More significant, the value of ΔLF = 2.35±0.15 eV extracted from the TiO2 O pre-K-edge base face spectrum is different than the value of ΔLF = 2.7±0.15 eV obtained from the TiO2 O pre-K-edge
spectrum. The ratio of these values is 0.87±0.1, and close to the ratio of the ionic radii of Ti$^{4+}$ to Ti$^{3+}$, 0.92. Since $R$(Ti$^{4+}$) > $R$(Ti$^{3+}$), ΔLF is smaller. Finally, the spectral widths for the singlet and triplet transitions, respectively in the O K pre-edge spectrum, 4.0±0.1 eV and 3.0±0.1 eV, are the same as those determined by ab-initio calculations and are consistent with spectral widths from T-S diagrams [14].

4.2. XAS spectra for Magneli Phase $\text{Ti}_x\text{O}_{2n}$ and $(\text{TiO}_2)_x(\text{HfO}_2)_{1-x}$ alloys.

XAS spectra are presented analyzed for: (i) Magneli-phase alloys, $\text{Ti}_x\text{O}_{2n-1}$, $n$ is an integer 0≥n≥3, and (ii) $\text{TiO}_2$-$\text{HfO}_2$ mixed oxide alloys for $\text{TiO}_2$-rich (67% $\text{TiO}_2$), and $\text{HfO}_2$-rich (67% $\text{HfO}_2$) compositions. Emphasis is on respective Ti L2,3 spectra, and the extraction of ΔLF, and comparisons with ΔLF extracted from O K pre-edge spectra. The $\text{TiO}_2$ and $\text{Ti}_2\text{O}_3$ results are important for the interpretation of these comparisons since (i) the Magneli-phase alloys are mixtures $\text{Ti}^{3+}\text{TiO}_2$ and $\text{Ti}^{3+}\text{Ti}_2\text{O}_3$, (ii) the $\text{TiO}_2$-$\text{HfO}_2$ alloys display metallic hopping conductivity, similar to $\text{Ti}_2\text{O}_3$. Figure 5(a) is the second derivative Ti L2,3, spectrum for a Magneli-phase alloy written as $\text{TiO}_{2-x}$, x~0.15. This spectrum, including includes (A) and (R) connections. The stronger low photon energy component indicates mostly (R) edge-corner sharing. The following values have been extracted from the analysis: ΔLF = 2.40±0.15 eV, and ΔSO = 6.3±0.1 eV. ΔSO is essentially the same as the value for

![Fig. 4. XAS spectra for single crystal corundum Ti2O3: (a) 2nd derivative Ti L2,3; (b) 2nd derivative O pre-K edge.](image-url)

![Fig. 5. XAS spectra for Magneli-phase $\text{Ti}_x\text{O}_{2n-1}$ alloy second derivative: (a) Ti L2,3; and (b) O K pre-edge.](image-url)
TiO$_2$, and other Ti-oxides reported in this article. The value of $\Delta L = 2.40 \pm 0.15$ eV is smaller compared to $\Delta L = 2.70 \pm 0.1$ eV for TiO$_2$, but not as small as the value for Ti$_2$O$_3$, 2.4$\pm$0.15 eV. As discussed above, the values of $\Delta L$ from Ti L2,3 spectra reflect the average properties of the nano-grains, and distribution of Ti$^{3+}$ and Ti$^{4+}$ atomic radii. The $\Delta L$ from O K pre-edge spectra are determined by a similar average over the valence of the Ti-atoms that are directed into the vacated O-atom bonding site.

Figure 5(b) is the second derivative TiO$_{2-x}$ O K pre-edge spectrum. The number and ordering of symmetry designated singlet and triplet terms is the same is essentially the same as those in TiO$_2$ and Ti$_2$O$_3$. More significant are the spectral widths of singlet and triplet states: 4.0 eV and 3.0 eV, respectively and the same as those for Ti$_2$O$_3$ and TiO$_2$.

Fig. 6. Second derivative Ti L2,3 (TiO$_2$)$_x$(HfO$_2$)$_{1-x}$: (a) x = 0.67; and (b) x = 0.33.

Moving on, results are presented for TiO$_2$-HfO$_2$, (TiO$_2$)$_x$(HfO$_2$)$_{1-x}$ alloys. This are of interest because differences in ionic radii and local bonding coordination are too large for mixed Ti-O and Hf-O bonding in the same nano-grain within a thin film alloy. The spectral features are addressed for two alloys with different Ti to H ratios, H is 2 for x = 0.67, and 0.5 for x = 0.33. Figures 6(a) and 6(b) are respectively the 2nd derivative Ti L2,3 plots in (a) for an alloy with 67% TiO$_2$ and 33% HfO$_2$, and in (b) for a mirror-image alloy with 33% TiO$_2$ and 67% HfO$_2$. These alloys display metallic hopping conductivity, so that hopping induced multi-valency is a contributor to the 16 features in the respective L3 and L2 regimes. Since there is a relatively strong dependence on alloy concentration, a second contributing mechanism also involve grain size Ti multi-valency is strain-induced by the large radius difference between Hf$^{4+}$ and Ti$^{4+}$ contributing to Ti$^{3+}$ bonding as well as Ti$^{2+}$ bonding. This explanation requires a larger size for rutile (R) nano-grains. This is correlated with the higher fraction of TiO$_2$, and consistent with the XAS spectra. The extracted values from Ti L2,3 spectra, $\Delta SO = 6.4$ eV, and $\Delta L = 2.4$ eV are effectively the samethose of the Magneli-phase TiO$_{2-x}$ and Ti$_2$O$_3$ films. The values of $\Delta SO' = 6.0$ eV are also effectively the same as those for the TiO$_2$, and the TiO$_{2-x}$ and Ti$_2$O$_3$ films, when experimental uncertainties are included. In contrast the $\Delta L = 2.4$ eV, including experimental uncertainties is close to those of the TiO$_{2-x}$ and Ti$_2$O$_3$, and smaller than $\Delta L = 2.70$ for TiO$_2$. 

![](image)
Independent of the detailed models that apply to the specific alloys, the metallic conduction in each of the alloys, the Magneli-phase TiO$_2$ alloy, and the TiO$_2$-HfO$_2$ alloys must both be considered as candidate thin film materials for memory, switching and other emerging device technologies.

5. Theory of Defect Spectra - Vacated O-atom Site Transitions

Two theory-based models have been proposed for the electronic structure of O-vacancy states. The Robertson and Shlugger groups have applied density functional theory (DFT) based models primarily to HfO$_2$ and ZrO$_2$, in many instances using cubic phases with a CaF$_2$ lattice structure. These models have identified singlet O-vacancy (VO), and interstitial O-atoms (IO) states in the band gap [9,11]. Determined in this way the band gap is significantly smaller than that reported in experimental studies of X-ray photoemission spectroscopy (XPS) for ground state energies, and O pre-edge XAS [11]. There are modifications to ΔFT theory in which photons, corresponding to band gaps, are added to the ground states. These approaches do not take into account the holes created by optical or thermal excitation. A detailed critique of these additions to DFT theory is beyond the scope of this article. In contrast, Lucovsky and co-workers have applied two-electron T-S diagrams in this article and other cited references [12] to: (i) two Si(Ge) dangling bond states with d-symmetries projecting into the vacated O-atom site in SiO$_2$ and GeO$_2$, respectively, and (ii) two dangling bond states in TM oxides taking note of different local site symmetries for vacancy sites and the TM sites as well [5-7]. This model for SiO$_2$ and GeO$_2$ predicts singlet states and triplet terms after a significant relaxation that reduces the repulsion between NN dangling bond defects [12,14]. This approach and ΔFT yield different ground state energies in the lower half of the band-gap, as well as different energies of singlet state trapping states in the upper half of the band gap. After a structural relaxation in the tetrahedrally-bonded vacancy site in the DFT calculations, two electrons are distributed equally over four TM dangling bonds.

In contrast in the quantum chemistry ab-initio calculations and supported by measurements, there are displacive motions invacated O-atom sites yielding different ground states for singlet and triplet spin states. The displacive motion leads a small separation between the singlet and triplet ground states and explains the observable singlet and triplet features in the excited 2nd derivative O K pre-edge spectra.

In SiO$_2$ and GeO$_2$, the pair of dangling bonds in located within a rigid and ordered cluster comprised of 6-member rings with 1 nm dimensions [14]. The vacant site reduces local strain with in the cluster. The clusters are imbedded in compliant, and more disordered matrix of 5- and 7-member rings. The vacant O-atom sites in nano-grain TM oxides are qualitatively different, and have been addressed in two recently published chapters of a monograph dealing with the Jahn–Teller effect [6,7]. Based on results in those papers, and the more recent understanding of the properties of dangling on the 2 Si- and Ge-atoms bordering a vacated, two fold coordinated bonding O-bonding site, the electronic structure for vacancies in (a) TiO$_2$ and (b) HfO$_2$ with tetragonal, and mixed tetragonal-monoclinic textures are addressed. The focus is on the local symmetry and coordination of the TM atoms, and the coordination(s) of the O-atoms which assumed to be within the nano-grains with 2 nm to 5 nm dimensions. Ab-initio calculations are currently being performed on model bonding geometries for the O-atom vacated sites: e.g., 4-fold coordinated sites in tetragonal HfO$_2$, as well as 3-fold coordinated O-atom sites in monoclinic HfO$_2$ and ZrO$_2$, and in rutile and anatase TiO$_2$. Two theory-based models have been proposed for the electronic structure of O-vacancy states. The Robertson and Shlugger groups have applied density functional theory (DFT) based models primarily to HfO$_2$ and ZrO$_2$, in many instances using cubic phases with a CaF$_2$ lattice structure. These models have, identified singlet O-vacancy (VO), and interstitial O-atoms (IO) states in the band gap [9,11]. Determined in this way the band gap is significantly smaller that what has been reported in experimental studies of X-ray photoemission spectroscopy (XPS) for ground state energies, and O pre-edge XAS [11]. There are some modifications to DFT theory in which photons, corresponding to band gaps, are added to the ground states. These approaches however do not take into account the holes created by optical or thermal excitation. A detailed critique of these additions to DFT theory is
beyond the scope of this article.

In contrast, Lucovsky and co-workers have applied two-electron T-S diagrams in this article and other cited references [12] to: (i) two Si(Ge) dangling bond states with d-symmetries projecting into the vacated O-atom site in SiO2 and GeO2, respectively, and (ii) two dangling bond states in TM oxides taking note of different local site symmetries for vacancy sites and the TM sites as well [5-7]. This model for SiO2 and GeO2 predicts singlet states and triplet terms but only if there is a significant relaxation that reduces the repulsion between NN dangling bond defects [12,14].

This approach and the the DFT yield different ground state energies in the lower half of the band-gap, as well as different energies of singlet state trapping states in the upper half of the band gap. In addition after a structural relaxation in the tetrahedrally-bonded vacancy site, the two electrons are distributed equal over the four TM dangling bond.

In constrast and supported by measurements, there are displacive motions in vacate O-atom sites in the quantum chemistry ab-initio calculations which yield two different electron ground states for singlet and triplet spin states. These displacive motions lead to at most a small separation between the singlet and triplet ground states, thereby accounting for the singlet and triplet features in the excited state spectra as determined from the 2nd derivative of the O K pre-edge spectra.

Proceeding in this way and using SiO2 as an example, as the distance between the bordering atoms is increased, the exchange energy for triplet terms is decreased, and the overlap energy, associated with two electron symmetric radial wave function for singlet sates is decreased as well, This has a profound effect on the spectrum; e.g. it promotes increased mixing of singlet and triplet excited states, and eventually makes it possible to observed singlet and triplet states in the same O K pre-edge spectrum.

If Si and/or Ge atoms bordering the vacated O-site atoms relax completely to relieve local-strain then singlet and triplet features, as indicated in T-S diagrams, occur with approximately equal weighting factors in the defect spectrum. For SiO2 and GeO2, the respective Si and Ge neutral dangling bonds are located in small, ordered molecular locally-rigid clusters identified from their respective FSDPs in X-ray diffraction measurements [32]. The degree of relaxation which makes the triplet and singlet ground state energies effectively equal comes from the compliant covalent random bonding present in the non-crystalline matrix in which encapsulates the clusters [12,14]. A more limited relaxation dangling bond-states with partial overlap of nearest-neighbor dangling bonds applies the nanograin TM oxides of this final contract report [8,9], limits the observed spectral to the singlet transitions identified in the appropriate, local coordination and symmetry T-S diagrams [15,16].

The O-vacancy sites in nanograin TM oxides are qualitatively different, and have been addressed in two recently published chapters of a monograph dealing with the Jahn-Teller effect [6,7]. Based on results in those papers, and the more recent understanding of the properties of dangling on the 2 Si- and Ge-atoms bordering a vacated, two fold coordinated bonding O-bonding site, the electronic structure for vacancies in (a) TiO2 and (b) HfO2 with tetragonal, and mixed tetragonal-monoclinic textures are addressed in this final chapter. For TM oxides, the focus is on the local symmetry and coordination of the TM atoms, and the coordination(s) of the O-atoms. Ab initio calculations are currently being performed on model bonding geometries for the O-atom vacated sites: e.g., 4-fold coordinated sites in tetragonal HfO2, as well as 3-fold coordinated O-atom sites in monoclinic HfO2 and ZrO2, and in rutile and anatase TiO2. The same model holds for the defect states since they are atom-dependent; i.e. associated with neutral dangling bonds projecting in to the O-atom vacated with of the respective defect centers.

6. Discussion: (i) Scales of order of Ligand Field Spittings, and (ii) Vacated O-atom states in TM oxides and Application in Device Technology.

Several different splittings of final states in XAS spectra have been addressed for ZrO2 and HfO2, which provide model systems for comparing a larger number of Ti-elemental and complex/mixed oxides which include multivalency in formal Ti-atoms charges as well. These splittings include transitions from core level occupied p-states to virtual bound final states derived from symmetry adapted combinations of d-states in one energy regime, and s-states in a second. This core level
splitting accounts for the separation of the final states into two energy regimes for the d-state features. In TiO$_2$ are two energy regimes: a lower energy L3 regime, and a higher energy L2 regime. There is also a separate and distinct regime at higher energies above the L2 regime for the transitions to virtual bound s-derived states.

The average L$_3$-L$_2$ differences in Ti-oxide Ti L2,3 spectra has been determined for TiO$_2$, Ti$_2$O$_3$, Magneli-phase alloys, Ti$_n$O$_{2n-1}$, and HfO$_2$-TiO$_2$ alloys all values so obtained are in excellent agreement with the spin-orbit splitting to the limit of experimental uncertainty, the 2p core-level splitting, $\Delta SO = 6.4\pm0.15$ eV.

The group theoretical formalism for determining the number and symmetry of the final states is based on CTM approaches in Refs. 24 and 25. Since defect states in vacated O-sites leave the site neutral, the sites have two singly occupied dangling bond states projecting into the vacancy site. This means the multiplets have two-electron ground states, as well as singlet and triplet excited state two electron terms.

The ground state splittings for these transitions are replicated with a different splitting, in this article $\Delta SO'$, in virtual bound that requires a three-electron state for transitions form the O 1s$_2$ core-level. The three electron transition is coherent with three transitions occurring simultaneously. These are: (i) a first transition from the O 1s$_2$ state to a resonant virtual bound state above the ionization threshold for the O-core state, and generally reduced in energy by an bond-ionicty determined positive shift of the ground state energy, this is followed by; (ii) a radiative decay from two p-derived states in the valence band separated by an energy defined here as $\Delta SO'$ and replicated in the O K-edge spectra, generally smaller than the core level $\Delta SO$ (in ZrO$_2$ and HfO$_2$), and at most equal to $\Delta SO$ (in Ti-oxides); and finally (iii) the energy difference between the X-ray photon, and the virtual bound state is in the energy regime above the O-atom ionization energy. This differences from the commonly-accepted and incorrect characterization of empty conduction band states which are simply-filled by electrons. In contrast the virtual bound states, or virtual molecular orbital states require a compensated hole for each electron-occupied virtual bound state. These holes are in the core level state, the valence band, or an electrode that is either tunneling or direct contact with the this energy regime.

The more interesting energy difference in the ligand field splitting, $\Delta LF$, defined by energy separation between d-state derived eg and t$_2g$ states in final state spectral features. The focus on this paper is the relationship between and feature in the final states of excitations with the vacated atom sites. For example, to a very good approximation limited by experimental uncertainy, the values of $\Delta LF$ in Ti-oxides, and both elemental and alloy, is the same in three spectra: (i) the Ti L2,3 spectrum, (ii) the O K-edge spectrum, and (iii) the O pre-K-edge spectrum as well.

6.1 Scales of Order for Ligand Field Splittings.

The observation of the same Ti and Hf ligand field splittings, $\Delta LF$, in the respective Ti L2,3 and Hf O5,6 spectra, in the O K edge spectra, and the O pre-K edge defect state spectra has been found within experimental uncertainties. This observation, and the application of the Tanabe-Sugano diagrams is in consistent with with the historical evolution from crystal field splitting ($\Delta CF$) to the ligand field splittings. Following the discussion in Ref. 16: (i) Hans Bethe developed a crystal field theory in which the bonding was 100% ionic and defined a crystal field splitting, $\Delta CF$, accordingly. Van Fleck pointed out that “even in the case of highly covalent bonding, which is best treated by molecular orbital theory, the symmetry properties and requirements remain exactly the same for the crystal field model and the ligand field model”. Finally Cotton, showed that whenever molecular orbital theory applies, and when there was sufficient chemical ordering to extend beyond SRO, bond-lengths and bond-angles, extend into the MRO domain. This regime includes dihedral angles, and correlations among them. In this case, $\Delta LF$ is non-vanishing, but is atom specific, and coordination and formal charge specific to the same degree as was noted and discussed with respect to Ti in Section 4.

Using Zr-oxides and Hf-oxides as prototypical examples, the extraction of ligand field splitting from spectra is different for (i) the Ti
L2,3 core level transition, and the O pre-K-edge spectra, and (ii) the replication of the Ti L2,3 features in the so-called conduction band regime. The observability of a TM L2,3 spectrum, and the extraction of a value for $\Delta LF$, simply requires a range of order in the material extending into the MRO regime of at least 3-atom bond correlations as in dihedral angles, and generally to 4-atom bond correlations. This includes materials such as SiO$_2$ and GeO$_2$ nano-grain dimensions of order 1nm in chemically-ordered clusters imbedded in a more compliant completely disordered network without MRO. The same description also applies to hydrogenated amorphous Si with about 5 to 10 atomic percent H in monohydride (Si-H) arrangements. The detection of in nano-grain materials is dependent on grain-size for L2,3, M3,4 and O5,6 replication in O K-edge spectra, and independent of grain-size for the O pre-K-edge spectra for vacated O-atom defect sites. For example, $\Delta LF$ can be extracted from HfO$_2$ films 2 nm thick, if deposited on SiON passivated Si surfaces that have broad features, as well as in films 3.5 to 4 nm and thicker on the same passivated substrates which display sharper features in the "conduction band" regime of virtual bound states. This includes Jahn-Teller effect (JTE) degeneracy remove of "conduction band edge" degeneracies. In marked contrast, the detection of $\Delta LF$ in the excited state vacated O-vacancy sides depends only MRO at the defect site extending to at least 3rd NN, and sometimes 4th NN atom correlations, and is not correlated with the existence of larger grain sizes required for JTE band edge degeneracy removal.

6.2. Vacated O-atom states in TM oxides and Technology Applications

The O-vacancy sites in nano-grain TM oxides are qualitatively different than those of SiO$_2$, GeO$_2$ and GeS$_2$. The TM defects have been addressed in several previous publications in two recently published chapters of a monograph dealing with the JTE, but based on new insights required in unconstrained relaxation in nc-oxides and chalcogenides in a 0.1 0.2 nm regime. The TM oxides require additional considerations addressed below [5,6].

The TiO$_2$ O K-pre-edge spectra in Fig 3(d) is qualitatively similar to the pre-existing defect spectra in nc-SiO$_2$ and GeO$_2$. All three of these spectra have been analyzed in the context of the appropriate T-S diagrams. This is consistent with the partial overlap of the radial wave functions and the Fermion wave functions. These obey Pauli exclusion and explain the observed singlet and triplet features.

The sub-oxide Magneli phase alloys, e.g. Ti$_4$O$_7$ and the TiO$_{1.85}$ alloy of this report have similar band edge defects. Their position relative to the conduction and valence band edges makes ideal candidates for memory and thin film transistor applications.

The observation in the last paragraph holds for TiO$_2$-HfO$_2$ alloys. The Ti defects are lower in the band-gap determined by the TiO$_2$ fraction, and as such these alloys are also candidate materials for memory and thin film transistor applications.

The single states are important for applications based on electron transport, since they (a) can accept electrons with either spin-up or spin-down, and (b) provide near neighbor trapping for variable range hopping or Poole-Frenkel transport paths [30]. Multi-valency is also responsible the metallic conductivity of Ti$_2$O$_3$ above the insulator to metal transition temperature as discussed in Ref. 10. The significant aspect of alloy-controlled effective multivalency is that it provides a way of changing and/or controlling the density of O-vacancy defects in the two alloys of this study. Electrons can be injected into the singlet states near the band edge from negatively biased Si, Ge, and other semiconductor substrates, and metals, each with different offset energies [4-7]. Injection can occur over a considerable portion of the band-gap as well. The singlet states closest the conduction band edge serve as relatively shallow traps for injection into oxide layers. The deepest traps capture of injected charge provide an electrical basis for distinguishing between occupied and empty deep traps [30]. Fast erasing is initiated by injection of holes in the occupied singlet and triplet ground states. The transition form the negatively charge deep traps to these positively charged deep traps is radiative, effectively a “p to s” transition with a short life-time for recombination.

Two terminal devices with asymmetric current-voltage characteristics provide options for memory
The results of this paper are qualitatively different than mechanisms suggested elsewhere. These alternative mechanisms attribute the switching and memory effects to movement of O-atom vacancies of Magneli phases, rather than electron, and possibly hole-transport through electronic states associated with vacancies [4-7]. The proposed electronic transport mechanism is currently being tested in two terminal device structures with metal or doped semiconductor contacts optimized for injection of electron and holes.

Finally, it is significant to recognize the marked qualitative and quantitative differences between Ti L2,3 spectra of the (i) Ti elemental oxides, TiO2 and Ti2O3, and (ii) Magneli Phase Ti2O2n-1 and the (TiO2)x(HfO2)1-x alloys. TiO2 is an insulator with a band-gap of ~ 3.1 eV, and Ti2O3 is a narrow band-gap semiconductor with an insulator metal transition that is sensitive to the stoichiometry. In contrast, both the Phase Ti2O2n-1 and the (TiO2)x(HfO2)1-x alloys exhibit metallic hopping conductivity transport which results in increases the number of Ti formal charge states from Ti4+ to both Ti3+ and Ti2+. This in turn creates difference in ground state, and singlet state energies that can be used to provide electron and hole injection from two different electrodes provide a configuration that will result in controlled electron trapping to on-state, and controlled injection of holes to reduce trapping and provide the an off-state.

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