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Spectroscopic Studies of Electronic Structure of Intrinsic O-atom Vacancy Defects in Hf Dioxide and Other Transition Metal (TM) Oxides

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1. Introduction

Theoretical calculations of the Robertson and Shluger groups places occupied defect states of mono-vacancies near mid-gap, whilst experimental studies indicate occupied defects just above the valence band edge of TiO_2, ZrO_2 and HfO_2. Three specific issues are addressed: (i) the occupied electronic states of the two electrons/removed O-atom, (ii) the *dimensionality* of the O-atom vacancies: mono- or di-vacancies, and (iii) a novel quantitative way for distinguishing between immobile and mobile defects.

2. Experimental Approach

The TM elemental oxides addressed in this study, TiO_2, HfO_2 and ZrO_2, are nano-crystalline thin films, typically 2 to 6 nm thick. These films have been deposited by remote plasma-assisted CVD onto passivated Si and Ge substrates, and annealed in Ar at 700 to 900°C [1,2].

Soft X-ray absorption spectroscopy (XAS) was used to obtain O K edge spectra at the Stanford Synchrotron Radiation Lightsource [1,2]. O K edge spectra are in the pre-edge regime, < 530 eV below the conduction band edge, ~ 530-545 eV, and the vacuum continuum, > 545 eV.

3. Spectroscopic Data and Data Reduction

Figure 1(a) presents XAS O K edge spectra for HfO_2 films 2.0 nm, 3.0 nm and 4.0 nm thick annealed at 900°C [1,2]. The 2 nm thick film shows no spectroscopic evidence (E_g spittling) for a monoclinic Jahn-Teller (J-T) distortion. It is *X-ray amorphous*, and has a defect density about ten times lower than the 3.0 nm and 4.0 nm films. These films display spectroscopic evidence in the first spectral peak for a J-T distortion [1,2]. Figure 1(b) indicates defect-related features in pre-edge XAS O K edge 2nd derivative spectra for 2 nm and 4 nm thick films. The spectral widths of these features differ by a factor of ~50%, and distinguish between mobile (~0.8 eV) and immobile (~1.2 eV) vacancies, with different numbers of Hf atoms at the respective vacancy sites.

Figure 1(c) includes defect absorptions, the first four features, as well as Hf 5f states associated with molecular orbital states that are required by 7-fold Hf coordination in monoclinic m-HfO_2, and 8-fold Hf coordination in tetragonal t-HfO_2. Differences between these 7 features reflect the differences in local symmetry between tetragonal and monoclinic nano-grains that contain J-T distortions; the tetragonal films show a two-fold symmetry axis.

4. Discussion

Conduction band edge traps in HfO_2 have been attributed by the Robertson and Shluger groups to O-atom mono-vacancies as distinct from di-vacancies [3,4], and by the Lucovsky group to di-vacancies [1,2]. The former assignments were based on theoretical calculations, whilst the latter were based on the multiplicity of occupied states at the valence band edge detected by soft X-ray photoelectron spectroscopy (SXPS) [1,2]. Valence band edge defects are not predicted by calculations in Refs. [3,4], which place the occupied defect states in $Hf(Zr)O_2$ at, or above mid-gap.

A second issue relates to the electronic states of the two electrons/removed O-atom. In Refs 3 and 4, these have been assumed to be delocalized; however, this model cannot account for the properties of the electrons in either mono-vacancies or di-vacancies. Figure 2(a) gives the local bonding of mono-vacancies in TiO_2 and $Hf(Zr)O_2$, and di-vacancies in $Hf(Zr)O_2$. The new model in Fig. 2(b) is based on digital occupation of TM d-states, similar to the occupied Si atom states in Si divacancies. The new model is based on an equivalent d^n representation: e.g., a d^2 occupancy for a Ti mono-vacancy and a d^4 occupancy for a Hf di-vacancy. This model provides an unambiguous way to differentiate between mono- and di-vancies by counting, as well as immobile (or fixed) and mobile vacancies by spectral width.

The spectra in Fig. 1(b) are d-d' transitions associated with d-state occupancies in Fig. 1(a), and the spectra in Fig. 1(c) are d-d* transitions, with anti-bonding d* states are in the virtual bound state regime. The Table in Fig. 2(b) indicates another feature of the model. The width of the d-states in Fig. 2(a) is equal to the crystal field (C-F) splitting, which is less than the band-gap, the ratios of the C-F splitting to the band gap, and the ratios of the d-band width to the band-gap are consistent with this model, and the differences between these values for TiO_2, and ZrO_2 and HfO_2 and TiO_2 distinguish between mono- and di-vancancies as well. The di-vacancy geometry for $Hf(Zr)O_2$ has axial symmetry, consistent with the electron spin resonance results of the Barklie group in Dublin [5]. Figure 3 is a defect state energy level diagram for HfO_2.

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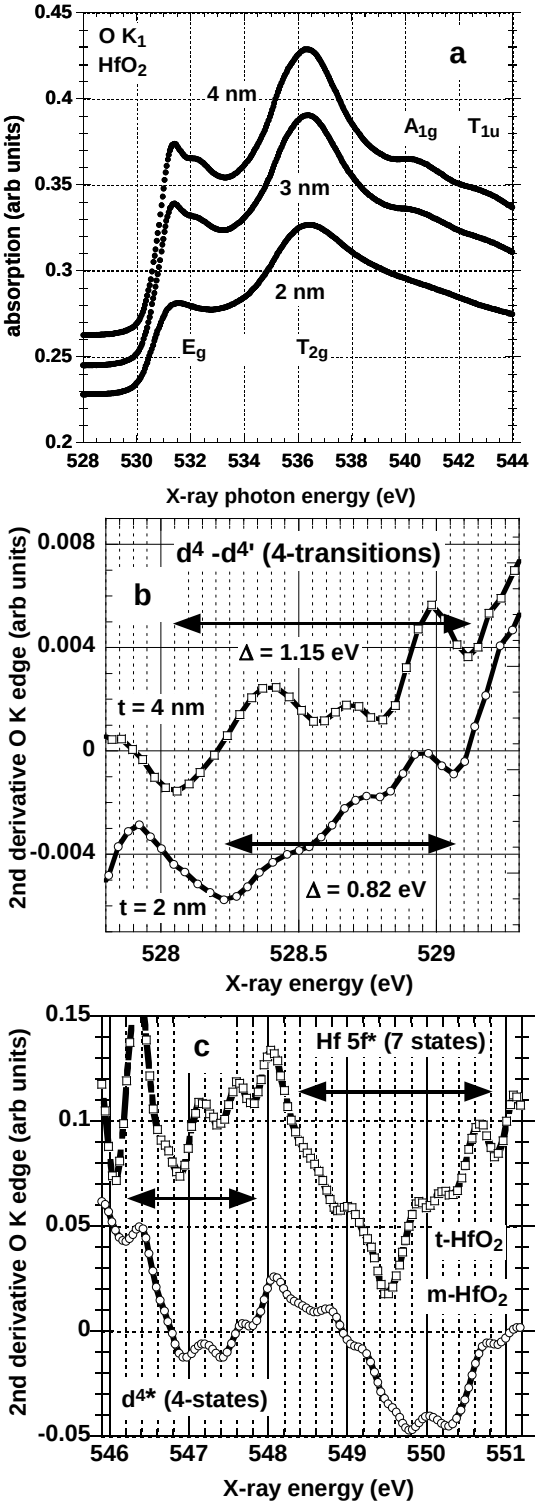
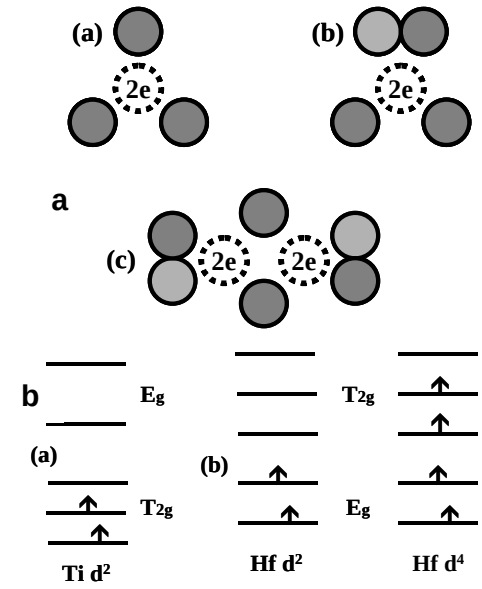


Fig. 1 XAS OK edge spectra. (a) HfO_2 as a function of thickness. (b) pre-edge spectra for 2 nm and 4 nm HfO_2. (c) virtual bound states resonances for t- and m-HfO_2.



c

oxide	crystal field spitting C-F (eV)	band gap E_g (eV)	ratio C-F/E_g	defect state width E_d (eV)	E_d/E_g
TiO_2	2.7	3.1	0.87	2.6	0.84
ZrO_2	3.7	5.5	0.67	3.6	0.65
HfO_2	3.9	5.7	0.68	3.7	0.65

all eV values ±0.2 eV

Fig. 2 d-state (a) geometry, and (b) occupancy of mono- and di-vacancies. (c) Crystal field, C-F, band gap and d-state widths for mono- and di-vacancies.

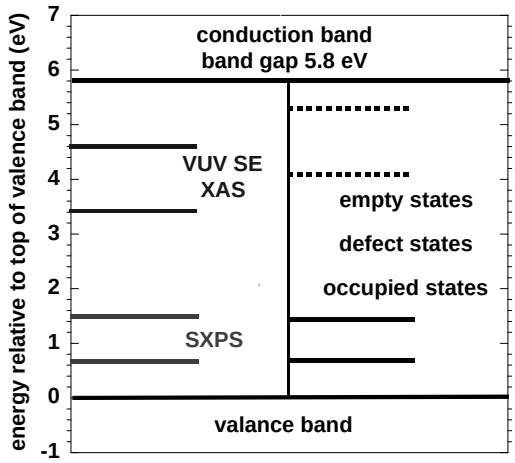


Fig. 3. Determination of defect states by spectroscopic ellipsometry, SE, XAS and SXPS (XPES); pre-edge XAS are d-d' transitions, and the energies of occupied and empty d-states.