Many-electron charge transfer multiplet theory: O-atom vacancies in high-k dielectrics

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1. Introduction

The performance and reliability of high-k dielectrics being considered for aggressively scaled CMOS is limited by intrinsic bonding defects, e.g., O-atom vacancies. The objectives of this research are: (i) the spectroscopic identification of O-vacancy occupied and final states, including negative ion states, (ii) the interpretation of spectroscopic data in the context of a new model for the O-vacancy electronic states that is consistent with Hund's rule d-state occupancy, and (iii) the interpretation of other spectroscopic studies, and electrical measurements in the context of the new model quantified in this paper. X-ray absorption and photoemission spectroscopies (XAS and XPES), performed at the Stanford Synchrotron Research Lightsource (SSRL), are used to identify conduction band edge states, and O-vacancy occupied and empty defect states in nano-crystalline HfO_2, ZrO_2, and Y_2O_3, and Gd_2O_3 and Lu_2O_3 from AMI, Aachen DE, and also in non-crystalline dielectrics including Gd and Lu silicates and Hf Si oxynitrides [1].

2. Electronic States of O-atom Vacancies

Previous density functional theory (DFT) studies of O-vacancy defects in HfO_2 and ZrO_2 have assumed that the two electrons associated with a neutral vacancy are distributed uniformly over the Hf and Zr d-states bordering the vacancy in a way inconsistent with Hund's rule occupancy, e.g., in doubly occupied ground and negative ion states [2]. This has lead to quantitative errors in interpreting defect state energies in spectroscopic ellipsometry (SE) studies by assuming that spectral feature energies could be referenced to the top of the valence band. The electronic structure proposed in this paper is qualitatively different and is successful in interpretation of SE and electrical measurements, as well [1].

The removal of neutral O-atom results in two non-bonding electrons that must be localized in the immediate vicinity of the missing O-atom. In the quantitative new model, these electrons are localized in a high spin d^2 ground state, with the ground state energies localized above the Fermi level of the oxide in close proximity to the top of the valence band. These levels are consistent with the electron occupancy of dn states of first row transition metal oxides, e.g., the d^2 states of V^{3+} in V_2O_3 [3]. Based on Tanabe-Sugano diagrams for intra d-state transitions [4], the neutral excited states and negative ion states span a significant portion of the forbidden band gap between the top of the valence band and the bottom of the conduction band. Figure 1 is a schematic energy level diagram showing the excited states of a neutral O-vacancy in HfO_2. The excited state energies have been confirmed by cathodoluminesce measurements [5]. Hole trapping is produced by removal of an electron from one of the high-spin occupied states, and electron trapping is associated with electron localization in negative ion states at energies higher than any of the allowed dipole transition energies. It is import to distinguish between occupied and empty defect states, and energies of transitions falling within the band gap. The labeled dipole excitation energies are not states within the energy gap, but are transition energies, and such XAS measurements, combined with XPES studies have been used to confirm the predictions of the d^2 model, in particular the placement of occupied and negative ion states, respectively, relative to (i) the top of the valence band, and (ii) the lowest d-state energies of transition metal
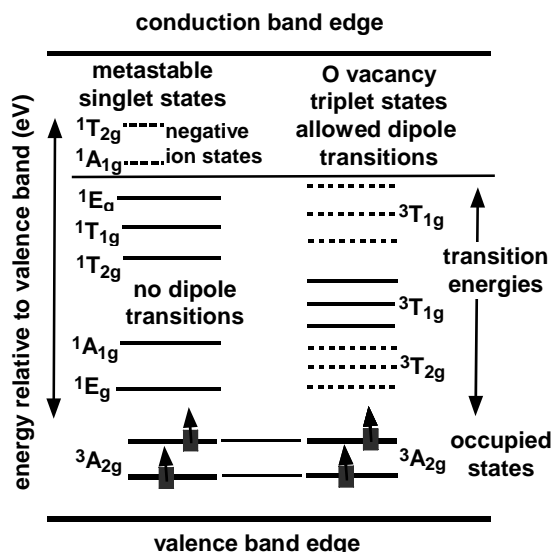

Fig. 1. Tanabe-Sugano energy levels for d^2 tetrahedral O-vacancy bonding geometry

atoms at the bottom of the conduction band [1].

3. Spectroscopic Studies of O-vacancy States

Figures 2(a) and 2(b) are respectively pre-edge O K edge spectra for tetragonal HfO_2, and bixbyite Lu_2O_3. The three-fold degeneracy of the Tanabe-Sagano energies states has been lifted by unit cell distortions, and the spectral features in these two figures are labeled according to symmetry designations obtained from Tanabe-Sugano diagrams for d^2 states, adjusted from octahedral to a distorted cubic symmetry [4]. The ground state symmetries are $^3A_{2g}$, and the allowed transitions are to triplet states derived from ^3F and ^3P many electron states. The negative ion states are derived from 1G and 1S states. These states span energy ranges of ~5 to 5.5 eV consistent with the Tanabe-Sugano (T-S) calculations, and cathodo-luminescence measurements [5]. Combined with SXPS measurements of the respective valence bands of transition metal oxides, these features span the band gaps of HfO_2 and Lu_2O_3. In addition they provide for a proper interpretation of the spectroscopic ellipsometry data, referencing spectral features to occupied d2 states above the valence band edge. The unoccupied negative ion states of O-vacancy defects participate in the trap-assisted tunneling (TAT) process in ZrO_2 and HfO_2 MOS structures for electron injection from n-type Si substrates [1].

4. Discussion

The conduction band states observed in O K edge X-ray spectroscopy have the same relative energies as those observed in SE (see Ref. 1 and spectra for TiO_2), and cannot be interpreted as a joint density of states as originally proposed in Ref. 2.

The Zr $M_{2,3}$ spectrum, and OK edge spectrum of ZrO_2, and the $L_{2,3}$ spectrum and O K edge of TiO_2 must be analyzed in terms CTM theory, contrary to the previous model proposed in Ref. 2.

In this paper O-vacancy defects are described by a theory that takes proper account of Hund's rule occupancy, and therefore DFT theories used previously are not valid [5]. The energy levels of the d- d′ transitions from the d_2 ground state, and negative ion states as well are obtained by application of Tanabe-Sugano energy level diagrams.

Differences in the band edge symmetry between non-crystalline SiO_2 and HfO_2 account for absence of trap-assisted tunneling in SiO2 and its observation in HfO_2. Gd_2O_3 and Lu_2O_3 display similar pre-edge O-vacancy defects in their O K edge spectra.

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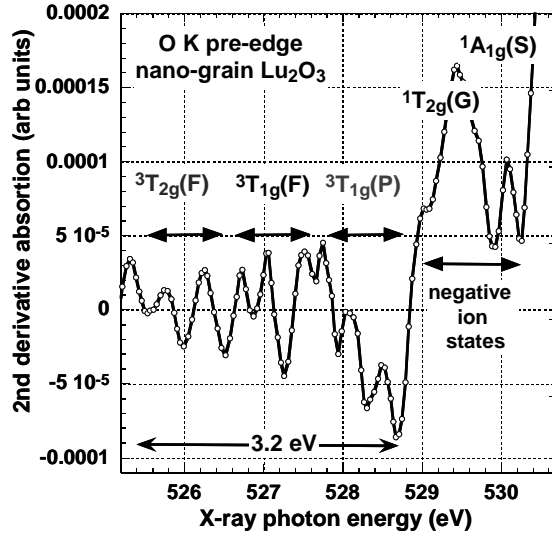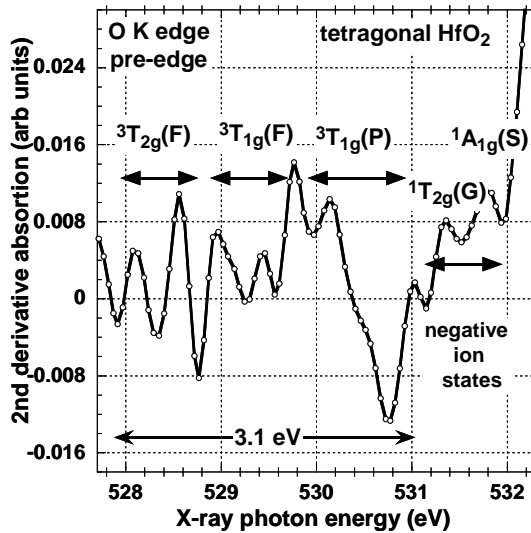
Pre-edge O K spectra for nano-grain (a) 900°C annealed HfO_2, and (b) as-deposited Lu_2O_3.