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Final state effects in VUV and soft X-ray absorption spectra of transition metal oxides and silicate alloys: comparisons between experiment and ab initio calculations

G. Lucovsky*, Y. Zhang, C.C. Fulton, Y. Zou, R.J. Nemanich, H. Ade, J.L. Whitten

North Carolina State University, College of Physical and Mathematical Sciences, Raleigh, NC 27695-8202, USA

Abstract

This paper uses X-ray absorption spectroscopy and vacuum ultra-violet spectroscopic ellipsometry to study the electronic structure of high-*k* transition metal (TM) oxide gate dielectrics. The results are applicable to TM and rare earth (RE) silicate and aluminate alloys, as well as complex oxides comprised of mixed TM/TM and TM/RE oxides. These studies identify the nature of the lowest conduction band d^* states, which define the optical band gap, including their relationship to the band gap, E_g, of the oxide.

Keywords: Transition metal oxides; X-ray absorption spectra; Intra- and inter-atomic transitions; Spectroscopic ellipsometry

1. Introduction

The paper presents a study electronic structure in high-*k* TM oxides by X-ray absorption spectroscopy and vacuum ultra-violet spectroscopic ellipsometry. Combined with X-ray photoelectron spectroscopy and Auger electron spectroscopy, these results are applied to band alignments at Si-high-*k* dielectric interfaces, not only for the Ti, Zr and Hf oxides, but to other TM/RE oxides and their silicate and aluminate alloys [1,2]. The paper differentiates between XAS spectra probe intra-atomic and inter-atomic transitions. Most importantly correlations are made between the final states in OK_1 spectra and the lowest conduction band states of the corresponding high-*k* dielectrics.

2. Experimental results

Fig. 1(a)–(d), present respectively $ZrM_{2,3}$, ZrK_1, OK_1 and band edge optical absorption constants for crystallized thin film ZrO_2. The $ZrM_{2,3}$ spectrum in Fig. 1(a) is an intra-atomic spectrum. The energy differences between the spectral peaks of two d-states, $\Delta(d_1^*,d_2^*)$, and the spectral peak of the first d^* state and the s^* state $\Delta(d_1^*,s^*)$ are in good agreement (±0.3 eV) with ab inito calculations based on small clusters with central Zr atoms, and two shells of atomic neighbors. The relative intensities of the d^* and s^* features are markedly different, and are consistent with the radial wave functions of the initial and final states in this transition. There also contributions for $Zr5p^*$-states in these spectra. Since these are in the same spectral regime of the $5s^*$-state contributions, they have not been highlighted. Moreover these states do not contribute to the band-gaps or band offset energies discussed below. The ab initio calculations also provide equally excellent agreement with respect to the Zr–O bond length, and the spectral peaks of features in the valence band as determined by UV photoemission spectroscopy. The ZrK_1 and OK_1 spectra in Fig. 1(b) and (c) are inter-atomic with final states reflection the mixing $O2p^*$ and $Zr4d^*$ and $5s^*$ states. Agreement with ab initio calculations is approximately ±0.3 eV as well. The ZrK_1 spectrum for ZrO_2 is similar to spectra presented in [3]. Since transitions from the Zr1s-state to $Zr4d^*$ and $5s^*$ states are not dipole-allowed, the ZrK_1 edge spectrum is qualitatively similar to the OK_1 edge spectrum in which the final states are a mixture of: (i) $Zr4d^*$ and $5s^*$ states, and (ii) $O2p^*$

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* Corresponding author. Tel.: +1 919 515 3301; fax: +1 919 515 7331.
E-mail address: lucovsky@ncsu.edu (G. Lucovsky).

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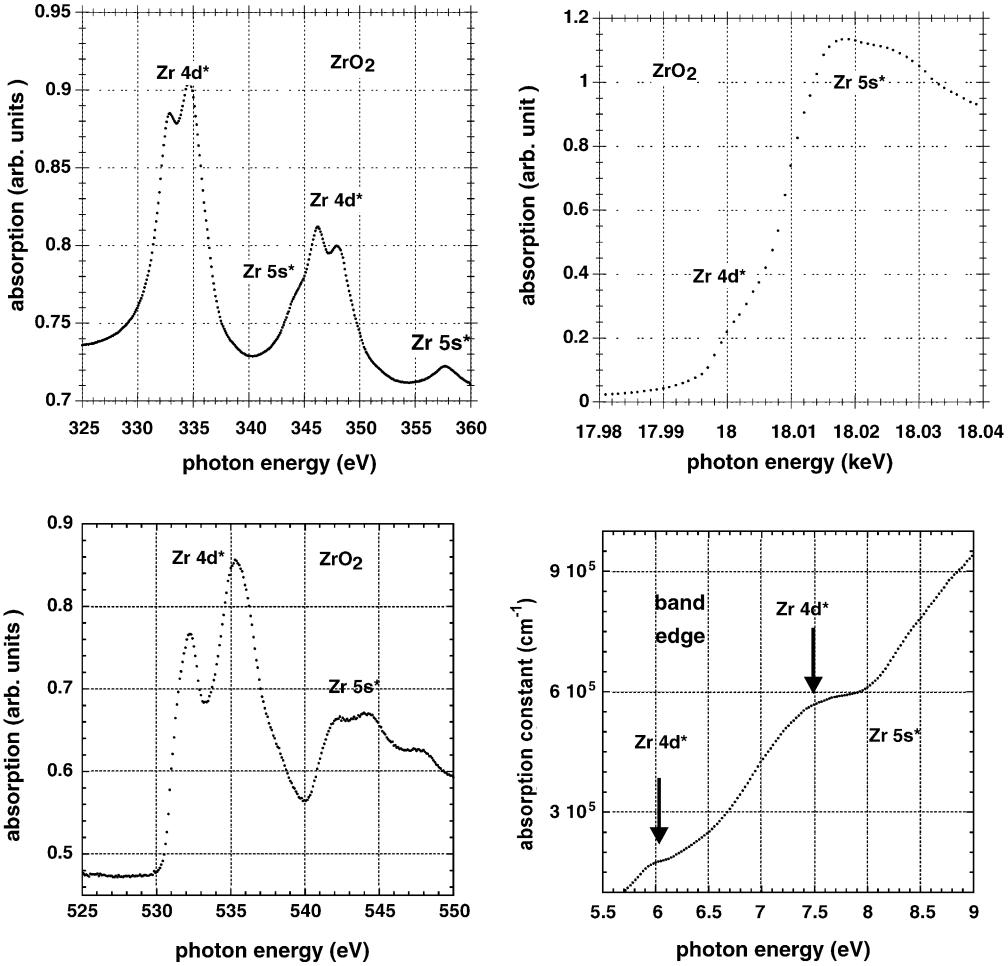

Fig. 1. Electronic structure spectra for ZrO_2: (a) $ZrM_{2,3}$, (b) ZrK_1, (c) OK_1 and (d) band edge optical absorption constant.

states. The doublet $4d^*$ features are not resolved in Fig. 1(b), nor in [3]. The average d^*–s^* energy difference is ∼10 eV. Fig. 1(d) presents the band edge absorption constant, determined from spectroscopic ellipsometry data, for ZrO_2. The energy difference between the two d^* features, and their relative spectral width are in excellent agreement with the calculations to ±0.2 eV. The calculations for the OK_1 edge and band edge final states utilized clusters centered on O-atoms.

Qualitatively similar spectra have been for the p-state absorption in TiO_2 and HfO_2, the $TiL_{2,3}$ and $HfN_{2,3}$, edges, and the respective OK_1 edges as well. The relative intensities of features within the individual spectra, and between these spectra and the corresponding $M_{2,3}$ edge of Zr are all consistent with the intra-atomic character of these transitions. In contrast, the OK_1 spectra show differences in the relative amplitudes of the respective d^* features consistent with the 6-fold coordination of Ti, and the 8-fold coordination of Zr and Hf. In addition, the differences in energy between the first d^* peaks are the same to within an experimental uncertainty of ∼0.3 eV as the differences in the experimentally determined band gaps [4]. There is also a direct correlation between the features in the OK_1 spectra of TiO_2, ZrO_2 and HfO_2 and the energy of the atomic states for the electronic configuration appropriate to oxides, $nd^2(n+1)s^2$, where $n = 3$, 4 and 5, respectively for Ti, Zr and Hf [5]. As discussed below this has important implications for the scaling of optical band gaps, E_g, and conduction band offset energies with respect to Si, E_B.

3. Discussion

There has been a search for alternative dielectrics with significantly increased dielectric constants, k, with respect to SiO_2 to reduce direct tunneling in FETs with EOT < 1.5 nm. This allows increases in physical thickness proportional to k for a given gate dielectric capacitance, thereby providing the possibility of significantly reduce direct tunneling. However, *increases* in k are accompanied by *decreases* in E_g, E_B, and the electron tunneling mass, m^*_{eff}. These trade-offs are quantified in a tunneling figure of merit [6], Φ_m, given by Eq. (1),

$$\Phi_m = k[E_B m^*_{\text{eff}}]^{0.5} \tag{1}$$

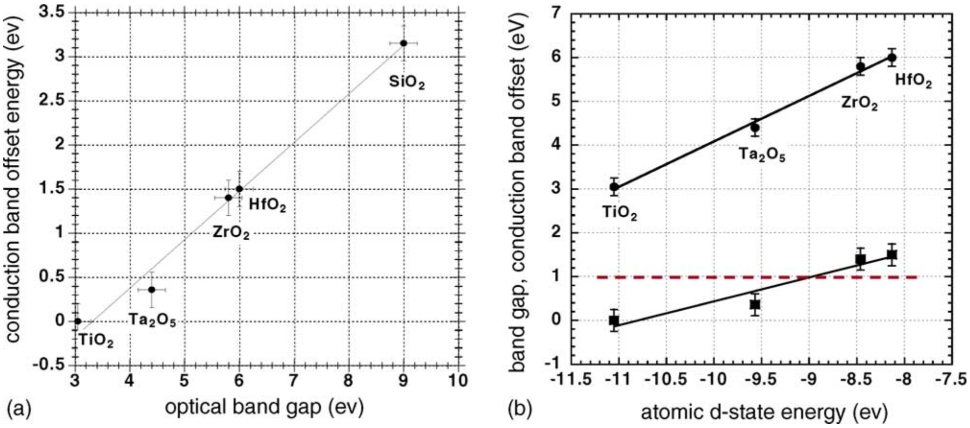

Fig. 2. (a) Conduction band offset energy, E_B, as a function of the optical band gap, E_g. (b) E_g and E_B as a function of atomic d-state energy.

Robertson has developed a model for obtaining band gaps and band offset energies for dielectrics including the high-*k* dielectrics of this paper [7]. These results yield an approximately linearly relation for E_B as a function of E_g. Fig. 2(a) and (b) contains plots, respectively of: (i) EB as a function of E_g, based on the calculations of [7]; and (ii) E_g and E_B as a function of atomic d state energy for a representative set of TM oxides. The scaling in Fig. 2 follows directly from the spectroscopic studies of this paper, and the ab initio calculations for OK_1 spectra that provide the correlation between optical band gaps and atomic d-state energies. A band offset energy of 1 eV or more is required for tunneling leakage current to be sufficiently low for scaled CMOS devices [8]. Using this criterion, the TM oxides with the highest dielectric constants, TiO_2, and Nb_2O_3 and Ta_2O_3, have offset energies below 1 eV that either correlate with high tunneling leakage, and/or electric field assisted injection into low-lying conduction band states associated with these atoms [9]. Based on this scaling with atomic d-states, (i) the oxides of Zr and Hf and (ii) the oxides of Y, La and the lanthanide RE oxides have conduction band offset energies >1.2 to 1.3 eV, and therefore, the potential for meeting roadmap targets for low tunneling leakage current [9], provided that the electron tunneling mass, m_{eff}, does not decrease significantly with decreasing E_B. Since the TM and RE d-states do mix with the lowest conduction band s states of Si and Al, the scaling argument can be extended to the silicate and aluminate alloys of the Zr, Hf, Y, La and the lanthanide RE atoms.

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