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Intrinsic Electronically-Active Defects in Transition Metal Elemental Oxides

Gerald Lucovsky[1], Hyungtuk Seo[1], Les B Fleming[1], Marc D Ulrich[1] and Jan Lüning[2]

[1]NC State University, Department of Physics
2700 Stinson Drive, Raleigh, NC 27695-8202, USA
Phone: +01-919-515-3301 E-mail: lucovsky@ncsu.edu
[2]Stanford Synchrotron Radiation Laboratory
2575 Sand Hill Road, Menlo Park, CA 94025, USA

1. Introduction

Densities of interfacial and bulk defects in high-k dielectrics are typically an order of magnitude higher than in Si-SiO_2 devices. An asymmetry in hole and electron trapping represents a significant limitation for CMOS operation and reliability [1]. A crucial issue is whether these defects are intrinsic, or associated with processed introduced impurities. Spectroscopic studies on high-k gate dielectrics have identified intrinsic defect states in Ti, Zr and Hf elemental oxides [2]. Based on these studies and molecular orbital theory, this asymmetry is explained by different O-atom vacancies clustered at nanocrystalline grain boundaries.

2. Experimental Results

Our experiments [2], yield the *same asymmetric trapping* as in Ref. 1. Traps are present in films prepared by ALD, reactive evaporation and remote plasma deposition. Electrical studies indicate: i) relatively shallow electron traps, ~0.5 eV below the conduction band edges of HfO_2 and ZrO_2, as well as ii) deep hole traps below the valence band edge of Si, and ~3 eV above the HfO_2 and ZrO_2 valence band edges.

Soft x-ray photoelectron spectroscopy (SXPS), near edge x-ray absorption spectroscopy (NEXAS), visible and vacuum ultra-violet spectroscopic ellipsometry (vis-VUV SE), and vacuum ultra-violet photoemission spectroscopy (UPS) studies have been performed on Ti, Zr and Hf dioxide films. Figure 1 presents SXPS spectra for TiO_2 and HfO_2 indicating occupied defect states above the valence band edge. Figure 2 displays a vis-VUV SE ε_2 spectrum for ZrO_2, displaying features ~1 to 3 eV below the lowest band gap d-state [3]. Figure 3 indicates a ZrO_2 O K_1 NEXAS spectrum with a defect state below the conduction band edge. The studies have been used to create the electron energy level diagram for Hf(Zr)O_2 in Fig. 4. Photoconductivity and cathode-luminescence spectral results (Fig. 5) support the intrinsic nature of these defect states [3].

2. Discussion

The character of these defects has been identified by comparing MO calculations for octahedrally coordinated Ti^{4+} atoms in TiO_2, with the electronic states of Ti^{3+} in $Ti(H_2O)_6^{3+}$ clusters, and Ti_2O_3 crystals (see Fig. 1). Defects are consistent electron transfer from a Ti-atom of a divacancy into two *vacated* O-atom sites. The comparisons include E_g and T_{2g} state degeneracy removal by Jahn-Teller (J-T) distortions. The inherent properties of these defects are: i) electronic states that fall that within the energy gap of the Ti^{4+}-O bonding in TiO_2, ii) relative energies that are not changed by J-T splitting of the TiO_2 states, iii) partially-occupied T_{2g} states at the valence band edge, and iv) unoccupied E_g states at the conduction band edge. The degeneracies of these defects states are removed by J-T distortions. The T_{2g} states are occupied and act as traps for substrate hole injection, whilst the E_g states are empty, and act as traps for transport associated with substrate injection of electrons [1,2], and sub-band-gap photoconductivity [3].

Similar energy level diagrams apply to differences between $Zr^{4+}(Hf^{4+})$ band states, and Zr^{3+} (Hf^{3+}) defect states. The primary difference between the Ti^{3+} and Zr^{3+}/Hf^{3+} defects is the symmetry of the defect and band d-states. The occupied defect states near the valence band edge for Zr^{3+}/Hf^{3+} are J-T term-split E_g states, and the states near the conduction band are J-T term split T_{2g} states.

Two *engineering solutions* for elimination of intrinsic defects are identified, and extended EOT to ~0.7 nm. One involves suppression of defects in ultra-thin (< 2nm) HfO_2 layers [4]. These reductions are associated with effective elimination of nanocrystalline grain boundaries in these ulta-thin films, and/or in part by 700°C annealing in N-containing ambients. [4]. The second is by deposition of non-crystalline Zr/Hf Si oxynitrides, that are Si_3N_4 rich (~40%) with approximately equal and lower concentrations of Zr(Hf)O_2 and SiO_2, (~30%) [5]. These Zr/Hf Si oxynitride alloys show no chemical phase separation to 1100°C.

Acknowledgements
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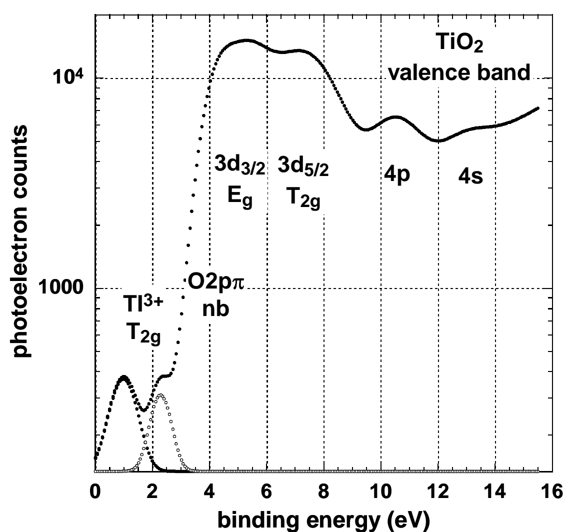

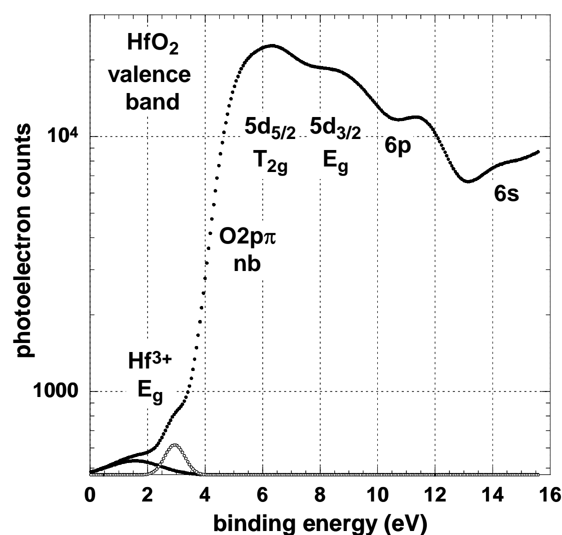

Fig. 1. SXPS valence band spectra of TiO_2 and HfO_2 indicating similar band edge defects.

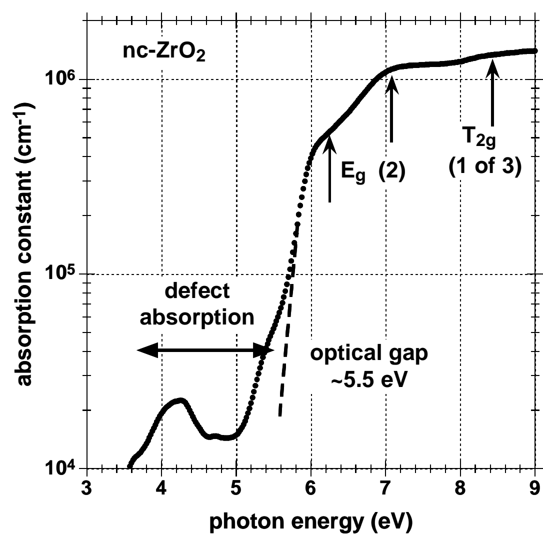

Fig. 2. Vis-VUV SE absorption for ZrO_2.

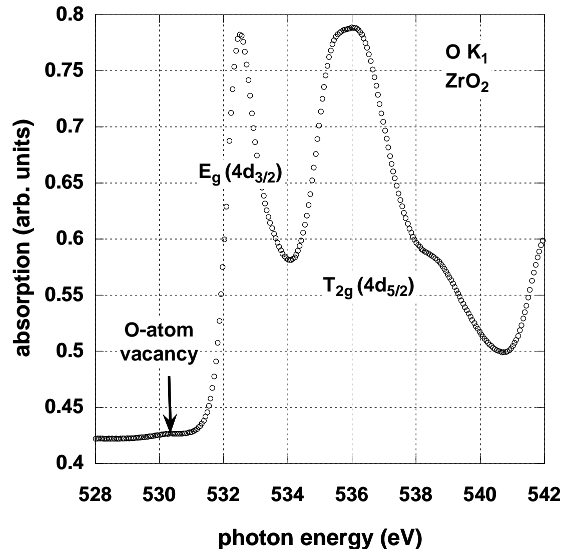

Fig 3. O K_1 NEXAS for ZrO_2

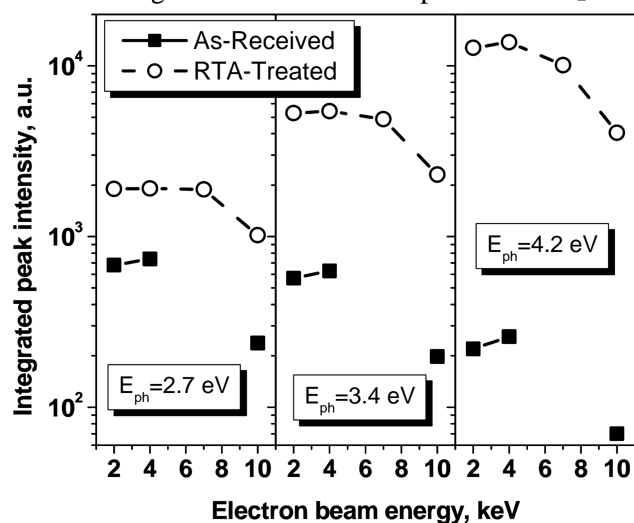

Fig. 4. CLS spectral features in HfO_2.

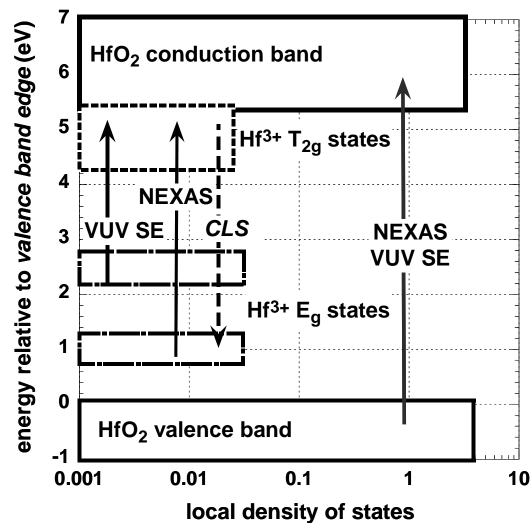

Fig 5. Band energy electronic states of HfO_2.