Spectroscopic Studies of Electronically-Active Defects in Transition Metal Oxides for Advanced Si Devices

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Abstract. Based on spectroscopic studies, and guided by ab initio theory, the electron and hole traps in HfO\textsubscript{2} and other transition metal elemental oxides e.g., TiO\textsubscript{2}, are assigned to O-atom divacancies, clustered at internal grain boundaries. Engineering solutions for defect reduction are identified: i) deposition of ultra-thin, < 2 nm HfO\textsubscript{2} and phase separated Hf silicate dielectrics, in which grain boundary formation is suppressed by effectively eliminating inter-primitive unit cell \(\pi\)-bonding interactions, and ii) non-crystalline Zr/Hf Si oxynitrides without nanocrystalline grain boundaries.

Keywords: transition metal oxides, x-ray absorption spectroscopy, grain-boundary defects, engineering solutions

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INTRODUCTION

Densities of electrically active defects in high-k dielectrics are typically about 10-100 time higher than in Si-SiO\textsubscript{2} devices. A crucial issue is to determine if these defects are intrinsic or if they are derived from processing, e.g., chemical impurities. Spectroscopic studies of high-k gate dielectrics are used to identify electron and hole trapping states in HfO\textsubscript{2} gate stack dielectrics [1]. An asymmetry in hole and electron trapping is a significant limitation for operation and reliability of Si integrated circuits. Based on spectroscopic studies, asymmetries are explained by different charge states of O-divacancies clustered at grain boundaries in nano-crystalline (na-) films. These films are prepared at 30-300°C by remote plasma processing, RPECVD, and reactive evaporation, RE, and processed at higher temperatures (700-900°C) for device integration. Spectroscopic studies have also been performed on na-TiO\textsubscript{2} and -ZrO\textsubscript{2}, and complex oxides, e.g., La\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7}, with similar results.

EXPERIMENTAL RESULTS

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) have been applied to na-Ti, -Zr and -Hf elemental dioxides. Figure 1(a) presents SXPS spectra for HfO\textsubscript{2} and TiO\textsubscript{2}, indicating occupied defect states above the respective valence band edges. Figures 2(a) and (b) compared vis-VUV SE \(\varepsilon_2\) spectra for TiO\textsubscript{2} and ZrO\textsubscript{2}, each displaying features ~1 to 3 eV below the respective d-state band edges [2]. A comparison between the energies of d-state features extracted from the second derivative of spectra of the TiO\textsubscript{2} O K\textsubscript{1} spectrum, with energies of d-state features in the TiO\textsubscript{2} \(\varepsilon_2\) spectrum yields a linear scaling relationship with a slope of 1 providing the rationale for using d-state energies extracted from O K\textsubscript{1} edges of HfO\textsubscript{2} and ZrO\textsubscript{2}, in combination with defect state features in the XPS valence band and VUV SE \(\varepsilon_2\) spectra, to locate the energies of defect states within the forbidden energy gaps of TiO\textsubscript{2}, ZrO\textsubscript{2} and HfO\textsubscript{2}. The correspondence between d-state features in O K\textsubscript{1} and \(\varepsilon_2\) spectra is supported by hole localization in the respective final states: i) a core hole in the O 1s state, and ii) a localized hole in previously doubly occupied valence band edge O-atom 2p \(\pi\) state.

The results of this analysis have been used to create electron energy level diagrams for HfO\textsubscript{2} and TiO\textsubscript{2} that are in excellent agreement with molecular orbital (MO) calculations applied to transition metal ion clusters [3]. Spectroscopic data for ZrO\textsubscript{2} yields essentially the same defect states as for HfO\textsubscript{2}, with relatively small energy shifts. Photoconductivity and cathode-luminescence data support the intrinsic nature of these defects [2].

Experiments by our group [4], yield essentially the same asymmetric trapping as in Ref. 1. These traps are present in films prepared by RE and RPECVD, and
atomic layer deposition, ALD, as well. Analysis of capacitance-voltage (C-V) and current voltage (J-V) 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; ~3 eV above the HfO$_2$ valence band.

**DISCUSSION**

The nature of the intrinsic defects in na-films has been identified by comparing MO calculations for octahedrally coordinated Ti$^{4+}$ atoms in TiO$_2$ with Ti$^{3+}$ in Ti(H$_2$O)$_6^{3+}$ clusters and Ti$_2$O$_3$, as well [3]. The defect electronic structure is consistent with the trap being a divacancy. Initial comparisons were based on crystal field splittings, but these have been extended to include $E_g$ and $T_{2g}$ state degeneracy removal by Jahn-Teller (J-T) distortions. The inherent properties of the divacancy defects are: i) electronic states of Ti$^{3+}$ that fall within the energy gap of the Ti$^{4+}$-O states in TiO$_2$, and J-T degeneracy removal for ii) partially-occupied $T_{2g}$ states at the valence band edge, and iii) unoccupied $E_g$ states at the conduction band edge. The $T_{2g}$ states of Ti$^{3+}$ are partially occupied and act as traps for substrate hole injection, whilst $E_g$ states are empty, and act as traps for transport via substrate injection of electrons [1], and sub-band-gap photoconductivity [2].

Similar energy level schemes apply to i) Zr(Hf)$^{3+}$ defects at grain-boundary clustered divacancies, and ii) Zr(Hf)$^{4+}$ states in bulk Zr(Hf)O$_2$ where the symmetries of the defect d-states are reversed: occupied states near the valence band are J-T term-split $E_g$ states, and those near the conduction band, J-T term split $T_{2g}$ states.

**Engineering solutions** for elimination of these intrinsic defects have been identified. Two involve suppression of defect states in ultra-thin HfO$_2$ films HfO$_2$ films, and chemically-phase separated high HfO$_2$ content silicates. The third uses the deposition of non-crystalline Si$_3$N$_4$-rich Ti(Zr,Hf) Si oxynitrides: e.g.,

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**FIGURE 1.** SXPS valence band spectra for na-HfO$_2$ and na-TiO$_2$, prepared by reactive evaporation.

**FIGURE 2.** $\varepsilon_2$ spectra from vis-VUV-SE for (a) na-TiO$_2$ and (b) na-ZrO$_2$ films prepared by reactive evaporation.
[Si₃N₄] ~33-40%, with approximately equal [SiO₂] and [Ti(Zr,Hf)O₂] concentrations of 33 to 30%.

In i) ultra-thin (<2 nm) nc-HfO₂, and ii) high HfO₂ (~80%) phase separated Hf silicates, J-T splitting of band edge Eg (5d₃/2) anti-bonding π-states is suppressed by decoupling π-bonding interactions between strings of metal and oxide atoms in neighboring primitive unit cells (Figs. 3(a) and (b) and 4(a) and (b)). The ~2 nm scale of order is too small for grain boundaries; however, broadening of band edge states occurs, and may effect transport properties.

Studies of O K₁ and N K₁ edges of Zr Si oxynitrides indicate 4-fold coordinated Zr with O nearest-neighbors, and Si, O and N bonding similar to Si₂O₅N₂. Si₃N₄ rich Zr/Hf Si oxynitrides are stable against phase separation up to 1100°C [5].

Electrical measurements show that ultra-thin HfO₂ annealed in N₂ or NH₃ at 700°C, and Zr/Hf Si oxynitrides, have low defect densities, and additionally can be scaled to EOT values of 0.7-0.8 nm, thereby extending device scaling below the 0.45 nm node [6].

REFERENCES