Gate dielectrics comprised of nanocrystalline HfO2 in gate stacks with thin SiO2/SiON interfacial transition regions display significant asymmetries with respect to trapping of Si substrate injected holes and electrons. Based on spectroscopic studies, and guided by ab initio theory, electron and hole traps in HfO2 and other transition metal elemental oxides are assigned to O-atom divacancies, clustered at internal grain boundaries. Three engineering solutions for defect reduction are identified: i) deposition of ultra-thin, < 2 nm, HfO2 dielectric layers, in which grain boundary formation is suppressed by effectively eliminating inter-primitive unit cell π-bonding interactions, ii) chemically phase separated high HfO2 silicates in which inter-primitive unit cell p-bonding interactions are suppressed by the two nanocrystalline grain size limitations resulting from SiO2 inclusions, and iii) non-crystalline Zr/Hf Si oxynitrides without grain boundary defects.
Intrinsic bonding defects in transition metal elemental oxides

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Abstract

Gate dielectrics comprised of nanocrystalline HfO$_2$ in gate stacks with thin SiO$_2$/SiON interfacial transition regions display significant asymmetries with respect to trapping of Si substrate injected holes and electrons. Based on spectroscopic studies, and guided by ab initio theory, electron and hole traps in HfO$_2$ and other transition metal elemental oxides are assigned to O-atom divacancies, clustered at internal grain boundaries. Three engineering solutions for defect reduction are identified: i) deposition of ultra-thin, < 2 nm, HfO$_2$ dielectric layers, in which grain boundary formation is suppressed by effectively eliminating inter-primitive unit cell π-bonding interactions, ii) chemically phase separated high HfO$_2$ silicates in which inter-primitive unit cell p-bonding interactions are suppressed by the two nanocrystalline grain size limitations resulting from SiO$_2$ inclusions, and iii) non-crystalline Zr/Hf Si oxynitrides without grain boundary defects.

1. Introduction

Densities of interfacial and bulk traps/fixed charge in high-k dielectrics are typically about one to two orders of magnitude higher ($\sim 10^{13}$ cm$^{-2}$) than in Si-SiO$_2$ devices. A crucial issue is to determine whether high-k defects are intrinsic and associated with the structure, nanocrystalline, non-crystalline, etc., or whether they are derived from processing, e.g., from chemical impurities. This paper presents spectroscopic studies of high-k gate dielectrics, with an emphasis on identification of electron and hole traps in gate stacks containing HfO$_2$ [1]. Asymmetry in hole and electron trapping represents a potentially significant limitation for the operation and reliability of CMOS circuits. Based on spectroscopic studies and ab initio molecular orbital (MO) theory, these differences in defect behavior are explained by different charge states of O-atom divacancy defects clustered at grain boundaries in nanocrystalline thin films prepared by remote plasma processing, RPECVD, reactive evaporation, RE, and atomic layer deposition, ALD. Spectroscopic studies have also been performed on nanocrystalline TiO$_2$, ZrO$_2$, HfO$_2$, and complex mixed oxides such as ZrTiO$_4$, LaAlO$_3$, and La$_2$Ti$_2$O$_7$, indicating qualitatively similar defects.

These grain boundary defects have been eliminated in several different ways: i) by limiting the size of nanocrystalline grains to < 2 nm by (a) limiting the dielectric film thickness to < 2 nm, and (b) limiting grain size in chemically phase separated silicates by SiO$_2$ inclusions, and ii) by deposition non-crystalline Zr/Hf Si oxynitrides without grain boundary defects; they are stable to temperatures of 1100°C, well above what is required for down-stream processing following gate film depositions. An emerging issue of importance is research into alternative dielectric for Ge and GaAs.
Figure 1. Energy band of Ti/Hf elemental oxides. Valence (solid squares) and conduction band states (solid dots). Defects are indicated by open circles.

Figure 2(a). SXPS valence band spectrum of HfO₂. 5d-state and defect features are identified.

Figure 2(b). SXPS valence band spectrum of TiO₂. 5d-state and defect features are identified.

Figure 3(a). O K₁ edge XAS spectrum of HfO₂. 5d-state features are identified.

Figure 3(b). O K₁ edge XAS spectrum of TiO₂. 3d-state features are identified.

Figure 4. Ti L₃ edge XAS spectrum of TiO₂. Ti 3d J-T term split states are identified.
Figure 5(a). $E_2$ spectrum from SE measurements for TiO$_2$. Ti 3d and defect state features are marked.

Figure 5(b). $E_2$ spectrum from SE measurements for ZrO$_2$. Zr 4d and defect state features are marked.

Figure 6(a). Plot of 3d-state energies from O K$_1$ XAS spectrum of TiO$_2$ versus 3-state energies from Ti L$_3$ XAS spectrum of TiO$_2$. The slope for this plot is 1.

Figure 6(b). Plot of 3d-state energies from $E_2$ spectrum of TiO$_2$ versus 3-state energies from Ti L$_3$ XAS spectrum of TiO$_2$. The slope for this plot is 1.

Figure 7(a). O K$_1$ edge XAS spectrum of HfO$_2$ for a film with a physical thickness of 4 nm. The two J-T contributions to band edge Hf 5d$_{3/2}$ state are evident.

Figure 7(a). O K$_1$ edge XAS spectrum of HfO$_2$ for a film with a physical thickness of 2 nm. The band edge Hf 5d$_{3/2}$ state appears a single feature with no J-T splitting.
2. Spectroscopic results and data reduction

Soft x-ray photoelectron spectroscopy (SXPS), near edge x-ray absorption spectroscopy (NEXAS), have detected defect states in nanocrystalline ZrO2 and HfO2 [2]. These spectra have been used to generate the energy level diagrams display in Fig. 1. This section of the paper address three different regions identified in Fig. 1: i) the electronic structure of the valence bands using HfO2 and TiO2 as examples of symmetry driven changes in transition metal (TM) d-states that derive from approximately cubic and octahedral coordination, ii) the electronic structure of TM conduction band states, and in particular the equivalence of TM d-state features for excitations from (a) localized O-atom non-bonding π-states at the top of the valence band, and (b) the localized O 1s core level state, and finally iii) intrinsic defect states within the forbidden bands that derive from O-atom vacancies that are clustered at nanocrystalline grain boundaries.

Figure 2 presents SXPS spectra for (a) HfO2 and (b) TiO2, each indicating the d-state features in the valence band, as well as occupied defect states above the respective valence band edges. Figure 3 presents O K1 edge spectra for HfO2 in 3(a) and TiO2 in 3(b) indicating d-states, as well as σ p states features, that mirror those in the valence spectra of Figs. 2(a) and (b), respectively. The markers indicate Jahn-Teller term splittings of the respective crystal field split doublet and triplet E and T-symmetry d-states. Figure 4 gives the Ti L3 spectrum for oxidations from the Ti 2p3/2 state to Ti 3d states. This spectrum also indicates five distinct that reflect the Jahn-Teller term splittings of the T2g (triplet) and Eg (doublet) crystal field degenerate states. Figure 5 displays vis-VUV SE ε2 spectra for TiO2 and ZrO2 [2]. These spectra indicates the energies of d-state features obtained by differentiation, as well as additional defect state features, ~1 to 3 eV below the respective d-state band edge features. Figure 5 includes the spectra of the Jahn-Teller split d-state energies in the O K1 spectrum for TiO2, as a function of the energies of the corresponding d-state features in the TiO2 (a) L3 spectrum, and (4) the ε2 spectrum derived from the SE studies. The plots in Figs. 6(a) and 6(b) each indicate a linear scaling relationship with slope of very nearly. At this stage of the paper, this is the basis for using d-state energies extracted from O K1 edges of HfO2 and ZrO2, in combination with defect state features in the SXPS valence band and VUV SE ε2 spectra, to locate energies of defect states within the forbidden energy gaps of TiO2, ZrO2 and HfO2 as shown in Fig. 1. Analysis of spectroscopic data for ZrO2 yields 4d-state and defect state features with only relative small shifts, ~0.2-0.4 eV, in energy with respect to the valence and conduction band edges as for HfO2. As an example, photoconductivity (PC) and cathodo-luminescence spectra support the intrinsic character of these defect.

3. Discussion

Electrical measurements on metal-oxide semiconductor capacitors (MOSCAPs) by our group [3], yield the same asymmetric trapping as disclosed in Ref. 1. In summary, the analysis of electronic data, e.g., capacitance-voltage, C-V, and current-voltage, J-V, indicate: i) relatively shallow electron traps, ~0.5 eV below the conduction band edges of HfO2 and ZrO2, as well as ii) deep hole traps below the valence band edge of Si; ~ 3 eV above the HfO2 valence band.

The spectroscopic measurements described above indicate electronic structure that is consistent with the local character of the Ti, Zr and Hf, and d and 5d states making strong contributions to: i) the valence band, ii) the conduction band, and iii) the defects within the forbidden energy gap. These states are mixed with O-atom 2p σ- and 2p π-states. The states at the top of the valence band are always derived from O non-bonding π-states independent of the bonding geometry and symmetry of the transition metal atom. More detailed discussions of the energy band structure of octahedral and tetrahedral bonding of group IVB TMs, Ti, Zr and Hf, to O are presented in Refs. 3, 4 and 5. These references address the differences in crystal field d-state splittings for octahedral and tetrahedral coordination, and include the extension to cubic coordination as well. Reference 5 provides particularly good insight in the separation of the valence band states into π- and σ-bonding contributions, highlighting the π-bonding contributions at the top of the valence and their atomic parentage, TM d-states, T2g for octahedral coordination, and Eg for tetrahedral coordination, and contrasting this with hybridisation or mixing atomic TM states for σ-bonding, e.g., a mixture of Ti 4s, 4p(σ) and 3d1/2 or Eg states for octahedrally-coordinated Ti, and a equivalent mixture 4s + 4p + 5d1/2 or Eg for the 7-fold coordination of monoclinic ZrO2. As noted above, the conduction band or final states for optical transitions mirror the valence band structure. The spectral resolution and intrinsic line-widths of these final states make it possible to identify the J-T term split states that derive from departures from ideal octahedral, tetrahedral and cubic bonding [4,6]. For Ti and Sc, the core hole life-times in 2p atomic states are sufficiently long to resolve both crystal field and Jahn-Teller splittings in the 3d states in the L3 spectrum, whilst for Zr and Hf, the core life-times are significantly shorter, and it is not possible to resolve J-T term split states in either ZrO2 or HfO2; in these oxides, as noted above, these splittings can be extracted from O K1 edge spectra by differentiation.

The nature of the intrinsic nanocrystalline defects
oxynitride, as-deposited. The $E_g - T_g$ splitting of < 2 eV is indicative of a 4-fold tetrahedral bonding of Ti to O-atoms.

Figure 9(a). Ti L$_3$ spectrum for a low, 16% Si$_3$N$_4$ Ti Si oxynitride, as-deposited. The $E_g - T_g$ splitting of < 2 eV is indicative of a 4-fold tetrahedral bonding of Ti to O-atoms.

Figure 9(b). Ti L$_3$ spectrum for a high, 42% Si$_3$N$_4$ Ti Si oxynitride, as-deposited. The $E_g - T_g$ splitting of < 2 eV is indicative of a 4-fold tetrahedral bonding of Ti to O-atoms.

Figure 9(c). Ti L$_3$ spectrum for a high, 42% Si$_3$N$_4$ Ti Si oxynitride, as-deposited. The $E_g - T_g$ splitting of < 2 eV is indicative of a 4-fold tetrahedral bonding of Ti to O-atoms.

Figure 9(d). Ti L$_3$ spectrum for a high, 42% Si$_3$N$_4$ Ti Si oxynitride, 900°C anneal. The $E_g - T_g$ splitting of < 2 eV is indicative of a 4-fold tetrahedral bonding of Ti to O-atoms.

Figure 8(a). O K$_1$ edge XAS spectrum of a 2 nm phase separated Hf silicate film. The band edge Hf 5d$_{3/2}$ is a single feature with no J-T splitting.

Figure 8(a). O K$_1$ edge XAS spectrum of a 4 nm thick phase separated Hf silicate film. The Hf 5d$_{3/2}$ feature is stronger than in the 2 nm film, but with no J-T splitting.
has been identified by comparing ab initio calculations for octahedrally coordinated Ti$^{3+}$ atoms in TiO$_2$ with Ti$^{2+}$ in Ti(H$_2$O)$_6$$^{2+}$ clusters and Ti$_2$O$_3$ [3]. The defect electronic structure is consistent with electron transfer from a Ti-atom of a divacancy into two vacant O-atom sites. These comparisons include crystal field splittings, but neglect of E$_g$ and T$_{2g}$ states at the valence band edge with degeneracy lifted by a local J-T distortion, and unoccupied E$_g$ states at the conduction band edge with the degeneracy lifted. The T$_{2g}$ states of Ti$^{3+}$ are occupied and act as traps for substrate hole injection, whilst E$_g$ states are empty, and act as traps for substrate trapping states for transport, e.g., substrate electron injection [1], and band edge photoconductivity [7].

Similar energy level diagrams apply to differences between the Zr(Hf) and Zr(Hf)$^{3+}$ and Zr(Hf)$^{4+}$ states in divacancies and bulk Zr(Hf)O$_2$, respectively. The primary difference between the Ti$^{3+}$ and Zr(Hf)$^{3+}$ defects is the symmetry of the d-states. The occupied states for Zr(Hf)$^{3+}$ are J-T term-split E$_g$ states, and empty states are J-T term split T$_g$ states.

### 4. Engineering solutions for defect elimination

Three materials engineering solutions for elimination of these intrinsic defects are presented. One involves suppression of defect states in ultra-thin (< 2 nm) HfO$_2$ layers by suppressing intra-primitive unit cell π-bonding interactions that couple Hf-atom 5d$^p$ states in one primitive cell with Hf atoms in at least two neighboring primitive cells [8]. The length scale for this is ~ 1.5-2.0 nm. The second is by chemically phase separation high HfO$_2$ content silicates by annealing at temperatures >700°C. In the instance, the inter-primitive unit cell π-bonding interactions are suppressed by the nanocrystalline grain size limitations resulting from SiO$_2$ inclusions. The third is by direct deposition of non-cristalline Ti, Zr and Hf Si oxynitride alloys, (Ti/Zr/Hf)$(O_x)_{(SiO_x)}_{(Si_3N_x)}_{(H_2O_x)}$, that are Si$_3$N$_4$ rich: x = 0.3-0.32 and 1-x-y = 0.36-0.4 [9].

Consider the first class of materials. The O K$_1$ edge spectra in Figs. 7(a) and 7(b) indicate a marked difference between the lowest 5d$_{x^2-y^2}$ ($E_y$) π-states. A J-T term splitting is clearly evident in Fig. 7(a) for the 4 nm thick sample, but this is not the case for the spectrum in Fig. 7(b) for the 2 nm film. Suppression of the J-T term splittings indicates a decoupling between the 5d$_{x^2}$ π-states in nearest neighbor primitive unit cells. This is accompanied by a broadening the band edge spectral feature, which renders the band edge grain boundary traps inactive.

Figures 8(a) and (b) compare the O K$_1$ spectra for two Hf silicate alloys with 80% HfO$_2$ and 20% SiO$_2$ after annealing at 700°C. In each case the J-T splitting of the band edge E$_g$ state is suppressed by the nature of the thin film morphology; SiO$_2$ inclusions that (a) limit nanocrystalline grain size to < 2 µm in films that are 2 nm, as well as 4 nm thick, , but (b) can not suppressing a narrowing the O K$_1$ edge feature when the film thickness is increases from 2 nm to 4 nm.

Studies of O K$_1$ and N K$_1$ edges of Zr Si oxynitrides indicate 4-fold coordinated Zr with O nearest-neighbors, and Si, O and N bonding similar to Si$_2$O$_4$: Zr/Hf Si oxynitride alloys are stable against phase separation up to 1100°C. The dependence on the Si$_2$O$_4$ content is illustrated in Figs. 9(a), (b), (c) and (d) for Ti Si oxynitrides. For the low Si$_2$O$_4$ Ti Si oxynitride, (TiO$_2$)$_{0.16}$(SiO$_2$)$_{0.42}$(Si$_3$N$_4$)$_{0.42}$, the Ti atom coordination, obtained from d-state crystal field and/or term splittings is four as deposited, and increases to six after chemical phase separation that includes SiO$_2$ and nanocrystalline TiO$_2$. In contrast, the coordination is four, for an as-deposited and annealed (900°C) Ti Si oxynitride with 40% Si$_3$N$_4$, and equal concentrations of TiO$_2$ and SiO$_2$, ~ 30%.

Electrical measurements indicate that ultra-thin HfO$_2$ annealed in N$_2$ or NH$_3$ at 700°C, and Zr/Hf Si oxynitrides can be scaled to EOT values to 0.7-0.8 nm, and extending scaling past the 0.45 nm node [8].

### References