Oxygen species in HfO$_2$ films: An in situ x-ray photoelectron spectroscopy study

C. Driemeier$^a$

Instituto de Física, Universidade Federal do Rio Grande do Sul, Porto Alegre 91501-970, Brazil and University of Texas at Dallas, Richardson, Texas 75080, USA

R. M. Wallace

Materials Science and Engineering, University of Texas at Dallas, Richardson, Texas 75080, USA

I. J. R. Baumvol

CCET, Universidade de Caxias do Sul, Caxias do Sul 95070-560, Brazil and Instituto de Física, Universidade Federal do Rio Grande do Sul, Porto Alegre 91501-970, Brazil

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The chemical bonding of O atoms in HfO$_2$ films on Si was investigated by in situ x-ray photoelectron spectroscopy in the O 1s spectral region. In addition to trivial O forming only O-H$_2$ bonds, O 1s signals corresponding to nontrivial secondary O (O$_{sec}$) were also observed. By ruling out possible roles of impurities as well as by comparing O 1s signals for different thermochemical processing routes, O$_{sec}$ chemical origins were inferred. Moreover, angle-resolved photoelectron analysis was employed to quantitatively separate surface and bulk O$_{sec}$ contributions. Surface O$_{sec}$ was assigned to surface O-H groups generated either by room temperature water vapor exposure or by 600 °C H$_2$ annealing. Bulk O$_{sec}$ was assigned to O-O or O-H bonds and, as indicated by thermodynamic calculations and complementary structural analysis, is located in HfO$_2$ amorphous regions and grain boundaries. This bulk O$_{sec}$ can be partly removed by annealing in reducing atmospheres. For some of the processing routes employed here, we observed additional, water-induced bulk O$_{sec}$, which was attributed to dissociative water absorption in HfO$_2$ amorphous regions and O-depleted grain boundaries. © 2007 American Institute of Physics.

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I. INTRODUCTION

Continuous scaling of metal–oxide–semiconductor field-effect transistors (MOSFETs) led traditional SiO$_2$ and SiO$_2$/N$_x$ gate dielectric films to approach 1 nm thickness in Si-based integrated circuit technologies. Further MOSFET scaling is severely limited by an exponential increase in leakage currents through the gate dielectric due to direct electron tunneling. In order to overcome this limitation, high dielectric constant (high-k) materials will replace SiO$_2$ and SiO$_2$/N$_x$. High-k materials allow physically thicker films, which reduce leakage currents, while still increasing MOSFET capacitance density, as required for further MOSFET scaling. HfO$_2$ emerged as a leading high-k candidate due to its high dielectric constant ($k_{\text{HfO}_2} \approx 22 \gg k_{\text{SiO}_2} = 3.9$), thermal stability, and sufficient (>1 eV) band offsets to Si. However, HfO$_2$ gate dielectrics usually have high densities of electrically active defects, which degrade MOSFET performance.

Oxygen vacancies and interstitials are the energetically favored intrinsic defects in HfO$_2$, and first-principles calculations$^{9-11}$ provided strong evidence that gap states responsible for trap-assisted tunneling$^{12}$ and electron trapping$^{13}$ are related to oxygen vacancies in HfO$_2$. Besides intrinsic defects, extrinsic defects also play an important role. Water vapor present in the atmospheres where HfO$_2$ films are processed and handled is a ubiquitous potential source of extrinsic hydroxogenous defects because water vapor exposures are generally unavoidable in typical MOSFET fabrication facilities. Previous experiments showed that water-derived species can diffuse through HfO$_2$ at room temperature and may incorporate into HfO$_2$/Si thin film structures. Moreover, chemical instabilities during annealing of metal/HfO$_2$ structures were attributed to spurious, water-derived O-H groups present in HfO$_2$. In this scenario, identification of all O species in HfO$_2$ films is a key step in order to understand the origin and nature of O-related intrinsic and extrinsic defects. Due to its sensitivity to all elements (except H) in near surface (up to ∼5 nm deep) regions of a sample, as well as its capability to separate different chemical states of an element, x-ray photoelectron spectroscopy (XPS) is a powerful technique to investigate composition and chemical bonding of nanometric films for gate dielectric applications. However, XPS analysis of O signals from oxide films is usually jeopardized by spurious O-containing species that uncontrollably incorporate during film deposition or exposure to air.

We report here on in situ sputter deposition, annealing, water vapor exposure, and XPS analysis of nanometric HfO$_2$ films on Si. All processes were run in an ultrahigh vacuum (UHV) cluster system, without uncontrolled exposures to spurious O species. Analysis of the O 1s region of the pho-
toelectron spectra showed O atoms in HfO$_2$ which are in addition to trivial O forming only O-Hf bonds. Angle-resolved XPS analysis, variable processing routes, thermodynamic calculations, and complementary structural analysis were employed in order to infer about the nature of the nontrivial O in HfO$_2$.

II. EXPERIMENTAL DETAILS

$P$-type Si(100) wafers (100 mm diameter) were cleaned by piranha etch (H$_2$SO$_4$/H$_2$O$_2$, 3:1) followed by HF strip and Radio Corporation of America cleaning (NH$_4$OH/H$_2$O$_2$/H$_2$O, 1:1:5+HCl/H$_2$O$_2$/H$_2$O, 1:1:6). Additional dipping in 2% HF for 1 min followed by 1 min rinsing in 18.1 MΩ de-ionized water was performed immediately before wafer insertion into the UHV cluster system.

The Si wafers were oxidized in situ for 60 min using a room temperature ultraviolet/ozone (UV/O$_3$) process. In this oxidation process UV radiation from a Hg vapor, quartz envelope lamp interacts with O$_2$ molecules generating O$_3$ and O$^+$ radicals that oxidize the Si surface, resulting in 1 nm thick, high-quality SiO$_2$/Si.$^{17}$ Oxidation was run with 600 mbar O$_2$ in the UV/O$_3$ chamber and the Hg vapor lamp was placed close (~1 cm) to the polished wafer surface. As the next step, HfO$_2$ was deposited in situ by sputtering from a HfO$_2$ target (99.9%) using 70 sccm, 0.016 mbar Ar as the sputtering gas. The base pressure in the sputtering chamber was $<10^{-8}$ mbar and sputtering power density was 0.5 W/cm$^2$.

Selected wafers were annealed at 600 °C for 5 min in 3×10$^{-3}$ mbar of O$_2$ in an attached annealing chamber (base pressure $<10^{-8}$ mbar). Following this first annealing step, selected wafers were further annealed for 30 min at (i) 600 °C in 600 mbar N$_2$, (ii) 600 °C in 370 mbar forming gas (H$_2$:N$_2$:1:9, hereafter called FG) or (iii) 800 °C in UHV (10$^{-10}$ mbar). All annealed samples presented hydrocarbon contamination that was partly removed by an additional 300 °C, 5 min, UHV (10$^{-10}$ mbar) final anneal, as determined by XPS analysis. The processes applied to the five samples of this study (as-deposited, O$_2$ only, O$_2$+N$_2$, O$_2$+FG, and O$_2$+vac) are summarized in Table I.

After the annealing steps, room temperature water vapor exposures were performed in an attached chamber. With the chamber initially in static vacuum ($<10^{-8}$ mbar), a valve to a glass ampule containing liquid water in equilibrium with its vapor is opened for a few seconds, allowing water vapor to enter into the chamber and to interact with the samples. The vapor is pumped away after 15 min of water vapor exposure. The water used in these experiments is 99.9% enriched in the $^{2}$H isotope aiming at performing isotopic tracing experiments to be reported elsewhere.

XPS analysis was performed in situ (analysis chamber at $<10^{-10}$ mbar), either before or after water vapor exposures, using a monochromatic Al $K\alpha$ ($h\nu=1486.6$ eV) x-ray source and a hemispheric electrostatic electron energy analyzer.$^{19}$ Spectra were taken at photoelectron take-off angles of 20°, 45°, and 55° (measured between analyzer axis and sample normal). Before acquiring each spectrum, samples were aligned by maximizing photoelectron count rate. Analyses are run with Si substrates electrically grounded to the electron analyzer and the binding energy scale was calibrated$^{20}$ using Au 4f$_{7/2}$ (83.96 eV), Ag 3d$_{5/2}$ (368.21 eV), and Cu 2p$_{3/2}$ (932.62 eV) photoelectron lines.

Grazing-incidence x-ray diffraction (GIXRD) was performed ex situ using a Rigaku Ultima III diffractometer with Cu Ka x-ray source and 0.5° x-ray incidence angle. In addition, high-resolution transmission electron microscopy (HR-TEM) was performed for the O$_2$ only sample. HfO$_2$ film thickness of 4.7 nm was measured from the HRTEM cross-section images.

III. RESULTS

A. O 1s peak fitting

The O 1s region of the photoelectron spectra for the O$_2$+N$_2$ sample is shown in Fig. 1, illustrating the general features observed for all samples. The components of the O1s spectra were deconvoluted by peak fitting using the XPS-PEAK 4.1 code,$^{21}$ performing Shirley background subtraction and assuming that each spectrum is composed by two features: the main peak at $\sim$531.8 eV (Ref. 22) and the secondary peak at binding energies 1.4–1.6 eV higher than the main peak. We hereafter refer to O contributing to these peaks as O$_{\text{main}}$ and O$_{\text{sec}}$ respectively. Meanwhile, O$_{\text{main}}$ can be straightforwardly attributed to trivial O forming only O-Hf bonds in HfO$_2$.$^{23,24}$ the chemical origins of O$_{\text{sec}}$ are unknown and are purpose of this work.

By assuming that all nontrivial O contributes to O$_{\text{sec}}$ peaks, we do not claim that O$_{\text{sec}}$ corresponds to a single chemical species. Possible diversity of contributions to O$_{\text{sec}}$ peaks is addressed in the fitting procedure by leaving peak parameters free from fitting constrains, allowing the diversity of contributions to appear, for example, as broader peaks. O$_{\text{main}}$ peaks, on the other hand, correspond to O-Hf bonds only, and therefore fitting constrains were applied to this feature. From the four fitting parameters that characterize a

<table>
<thead>
<tr>
<th>Process</th>
<th>UV/O$_3$</th>
<th>Sputter HfO$_2$</th>
<th>600 °C 5 min</th>
<th>600 °C 30 min</th>
<th>600 °C 370 mbar FG</th>
<th>800 °C 30 min</th>
<th>300 °C 5 min</th>
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<tbody>
<tr>
<td>as-dep</td>
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<td>✓</td>
<td>✓</td>
<td>✓</td>
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<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>O$_2$ only</td>
<td>✓</td>
<td>✓</td>
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<td>✓</td>
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<tr>
<td>O$_2$+N$_2$</td>
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<tr>
<td>O$_2$+FG</td>
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<tr>
<td>O$_2$+vac</td>
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</table>

TABLE I. Processes applied for the different samples.
peak, viz., binding energy, intensity (peak area), full width at half maximum (FWHM), and Lorentzian ratio (peaks are a Lorentzian–Gaussian mix), we constrained FWHM and Lorentzian ratio of \( O_{\text{main}} \) peaks to be unique for a given applied process, independent on photoelectron take-off angles.

The \( O_{\text{main}} \) intensities before water exposures are the same (within 5%) for the different processing routes, being reduced by 5%–10% after water exposures, which is attributed to water-induced surface layers attenuating \( O_{1s} \) signals coming from underlying \( O_{\text{main}} \). Nevertheless, in the following angle-resolved XPS analysis the only fitting outputs employed are \( O_{\text{sec}} \) relative intensities, \( R \), defined as \( O_{\text{sec}}/O_{\text{main}} \) intensity ratios. Uncertainties in \( R \) are estimated by varying background subtraction and peak fitting and checking for corresponding variations in \( R \). Error bars shown for \( R \) correspond to estimates of \( \pm 2\sigma \), accounting for about 95% probability that the actual \( R \) lies within the error bars.

### B. \( O_{1s} \) angle-resolved analysis

The depth distribution of \( O_{\text{sec}} \) was investigated by analyzing \( R \) as a function of photoelectron take-off angle. Assuming that (i) HfO\(_2\) is thick enough to be considered semi-infinite regarding the \( O_{1s} \) signals, (ii) \( O_{\text{sec}} \) and \( O_{\text{main}} \) are uniformly distributed through HfO\(_2\) with concentrations \( [O_{\text{sec}}]_{\text{bulk}} \) and \( [O_{\text{main}}]_{\text{bulk}} \) (in atoms/cm\(^3\)), respectively, and (iii) \( O_{\text{sec}} \) is also at a surface delta layer with density \( [O_{\text{sec}}]_{\text{surf}} \) (in atoms/cm\(^2\)), one derives (see the Appendix)

\[
R = \frac{[O_{\text{sec}}]_{\text{bulk}}}{[O_{\text{main}}]_{\text{bulk}}} + \frac{[O_{\text{sec}}]_{\text{surf}}}{[O_{\text{main}}]_{\text{bulk}}} \lambda \cos(\theta),
\]

where \( \lambda \) is the attenuation length of \( O_{1s} \) photoelectrons in HfO\(_2\) and \( \theta \) is the photoelectron take-off angle. The validity of the assumptions underlying Eq. (1) is discussed in Sec. IV.

By plotting \( R \) vs \( 1/\cos(\theta) \), Eq. (1) corresponds to a straight line in the \( \gamma \)-intercept/slope mode, where \( [O_{\text{sec}}]_{\text{bulk}}]/[O_{\text{main}}]_{\text{bulk}} \) is the \( \gamma \) intercept and \( ([O_{\text{sec}}]_{\text{surf}})/[O_{\text{main}}]_{\text{bulk}}) \lambda \) is the slope. Assuming \( [O_{\text{main}}]_{\text{bulk}} \) as the O concentration in stoichiometric bulk HfO\(_2\) with a density \( 9.8 \text{ g/cm}^3 \), one has \( [O_{\text{main}}]_{\text{bulk}}] = 5.6 \times 10^{22} \text{ cm}^{-3} \). In addition, following procedures developed for calculating \( \lambda \), one derives \( \lambda = 13 \text{ Å} \) for \( O_{1s} \) photoelectrons (kinetic energy \( \sim 954 \text{ eV} \)) in HfO\(_2\). With these values for \( [O_{\text{sec}}]_{\text{surf}} \) and \( \lambda \), intercepts and slopes can be proportionally converted to bulk \( O_{\text{sec}} \) concentrations, \( [O_{\text{sec}}]_{\text{bulk}} \), and surface \( O_{\text{sec}} \) densities, \( [O_{\text{sec}}]_{\text{surf}} \), respectively. Table II shows the factors that apply for these conversions. Conversion factors accuracies are estimated to be within 20% for intercepts and 30% for slopes.

Figure 2(a) shows \( O_{\text{sec}} \) relative intensities before water exposures \( (R_{\text{before}}) \) as a function of \( 1/\cos(\theta) \) for all the applied processes. The experimental data are fitted with straight lines and derived intercepts and slopes are shown in Figs. 2(b) and 2(c), respectively. Error bars for intercepts and slopes correspond to linear propagation of error bars for \( R \). Additional \( O_{\text{sec}} \) relative intensities after water exposures \( (R_{\text{after}} - R_{\text{before}}) \) as a function of \( 1/\cos(\theta) \) are shown in Fig. 3(a). Linear fitting to the data was performed, with derived intercepts and slopes shown in Figs. 3(b) and 3(c), respectively. The chemical origins of the observed intercepts and slopes, corresponding to bulk and surface \( O_{\text{sec}} \), respectively, are discussed in Sec. IV.

### C. Controlling impurities

Within typical XPS detection limits (\( \sim 1 \text{ at. %} \)), C is the only extraneous element present in the samples. The highest \( C_{1s} \) intensity [see Fig. 4(a)] corresponds to 2 at. % C. Angle-resolved analysis (not shown) indicates that this C is at surfaces. Nevertheless, the \( C_{1s} \) signals observed at \( \sim 286 \text{ eV} \) correspond to C-H bonds.29 Signals at \( \sim 290 \text{ eV} \), corresponding to C-O bonds, were not observed, indicating

![Diagram](image-url)

**FIG. 1.** \( O_{1s} \) spectra (symbols) and peak fitting (lines) for the \( N_2 + O_2 \) sample measured at 20° and 55° take-off angles, either before or after water vapor exposure. Gray-filled peaks correspond to \( O_{\text{sec}} \) and percentages are \( O_{\text{sec}} \) relative intensities.

**FIG. 2.** (a) Linear fitting (solid lines) and experimental (symbols) \( O_{\text{sec}} \) relative intensities before water vapor exposure \( (R_{\text{before}}) \) as a function of \( 1/\cos(\theta) \) for the different applied processes. (b) Intercepts and (c) slopes derived from the linear fitting in (a).

### TABLE II. Conversion factors from linear fitting coefficients to \( O_{\text{sec}} \) amounts.

<table>
<thead>
<tr>
<th>Intercept coefficient</th>
<th>( O_{\text{sec}} ) location</th>
<th>Coefficient → ( O_{\text{sec}} ) amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>Bulk</td>
<td>1% → 5.6×10(^{20}) ( O_{\text{sec}} ) cm(^{-3})</td>
</tr>
<tr>
<td>Slope</td>
<td>Surface</td>
<td>1% → 7.2×10(^{13}) cm(^{-2})</td>
</tr>
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</table>

\( [O_{\text{sec}}]_{\text{bulk}}]/[O_{\text{main}}]_{\text{bulk}} \) is the \( \gamma \) intercept and \( ([O_{\text{sec}}]_{\text{surf}})/[O_{\text{main}}]_{\text{bulk}}) \lambda \) is the slope. Assuming \( [O_{\text{main}}]_{\text{bulk}} \) as the O concentration in stoichiometric bulk HfO\(_2\) with a density 9.8 g/cm\(^3\), one has \( [O_{\text{main}}]_{\text{bulk}}] = 5.6 \times 10^{22} \text{ cm}^{-3} \). In addition, following procedures developed for calculating \( \lambda \), one derives \( \lambda = 13 \text{ Å} \) for \( O_{1s} \) photoelectrons (kinetic energy \( \sim 954 \text{ eV} \)) in HfO\(_2\). With these values for \( [O_{\text{sec}}]_{\text{surf}} \) and \( \lambda \), intercepts and slopes can be proportionally converted to bulk \( O_{\text{sec}} \) concentrations, \( [O_{\text{sec}}]_{\text{bulk}} \), and surface \( O_{\text{sec}} \) densities, \( [O_{\text{sec}}]_{\text{surf}} \), respectively. Table II shows the factors that apply for these conversions. Conversion factors accuracies are estimated to be within 20% for intercepts and 30% for slopes.

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C-O concentrations below 0.5 at.%. This implies that the several percent O$_{sec}$ relative intensities (Fig. 2) is not consistent with an assignment to C-O bonds. The same conclusion is derived from the C 1s spectra taken after water vapor exposures (not shown).

Considering possible contribution of Si-O bonds to the O 1s spectra, we first note that, in contrast with previous studies that employed thinner HfO$_2$ and assigned the secondary O 1s peak to interface Si-O bonds, the HfO$_2$ films employed here are thick enough to suppress O 1s signals from Si-O bonds in the interface region (see Sec. IV). Moreover, we modeled what would be the contribution to the Si 2p spectrum if 1% of the O atoms in HfO$_2$ would be bonded to spurious Si [see Fig. 4(b)]. For this modeling we used Eq. (2) (see the Appendix), calculated values for \( \lambda \), and a Si 2p peak at binding energies 1.7 eV lower than the SiO$_2$ peak (corresponding to Si-O diluted in HfO$_2$). It is clear from the comparison between model and experiment that the Si-O relative concentration in HfO$_2$ must be below the modeled 1%, implying that the several percent O$_{sec}$ relative intensities (Fig. 2) is not consistent with an assignment to Si-O bonds. Figure 4(b) only shows the Si 2p spectrum for the O$_2$+N$_2$ sample, but the same conclusion holds for the other samples as well (not shown).

From SiO$_2$ and substrate Si intensity ratios, Si 2p spectra also allow determining the thicknesses of interfacial SiO$_2$ layers (see Ref. 32 for the equation and parameters employed). The SiO$_2$ thickness is 1.0 nm for the as-deposited (as-dep) sample. It grows to 1.6 nm by annealing in O$_2$ (O$_2$ only sample) and it remains constant after subsequent 800 °C annealing in UHV (O$_2$+vac sample). On the other hand, SiO$_2$ thicknesses grows to 2.1 nm by additional annealing in N$_2$ or FG (O$_2$+N$_2$ and O$_2$+FG samples), indicating presence of oxidizing residuals in these annealing atmospheres. Room temperature water vapor exposures did not promote measurable (>0.2 nm) SiO$_2$ growth in any sample.

**D. Structural analysis**

Figure 5(a) shows GIXRD patterns for all the samples of this study. While for the as-dep sample the pattern is smooth, indicating fully amorphous HfO$_2$, for the annealed samples there are diffraction peaks, identified with monoclinic (m-HfO$_2$) and tetragonal (t-HfO$_2$) phases. Among the annealed samples, those submitted to a second high-temperature anneal (O$_2$+N$_2$, O$_2$+FG, and O$_2$+vac) have diffraction patterns indistinguishable from one another, but which differ (especially for \( 28° < 2\theta < 32° \)) from the pattern for the O$_2$ only sample. This difference is attributed to incomplete HfO$_2$ crystallization (indicating remaining amorphous HfO$_2$) for the sample only annealed in O$_2$, while further high-temperature annealing completes crystallization. This behavior agrees with the observed onset for HfO$_2$ crystallization at \( \sim 600 \) °C.\(^{25,33}\)

Figure 5(b) shows the HRTEM cross-section image of the O$_2$ only sample, indicating the presence of HfO$_2$ and SiO$_2$ layers as well as the crystalline Si substrate. The electron beam, which was aligned with the Si [100] direction, also appears to have been incidentally aligned with an axis or plane of a HfO$_2$ crystallite. When this happens, one may observe a single HfO$_2$ crystallite and determine an approximate grain dimension parallel to the interfaces, \( L \), as shown in Fig. 5(b). An average \( L \) of 6.0 nm with standard deviation of 2.5 nm was determined from HRTEM images taken at different spots.
E. Hf 4f features

The inset of Fig. 6 shows the Hf 4f spectrum for the O_{2}+N_{2} sample, illustrating the features observed for all the samples. One observes a single Hf component, corresponding to O-Hf bonds, with the 1.65 eV spin-orbit splitting between Hf 4f_{7/2} and Hf 4f_{5/2} photoelectrons. The same spectrum with intensity multiplied by 20 evidences no additional Hf 4f features. Figure 6 also shows the Hf 4f_{7/2} FWHM (as derived from peak fitting) for the different applied processes. The observed higher Hf 4f_{7/2} FWHM for the as-dep and O_{2} only samples are attributed to amorphous HfO_{2} present in these samples, as detected by GIXRD. Correspondingly higher FWHM for O_{main} peaks (in the O 1s spectra) could not be established due to worse O_{main} peak width precision.

IV. DISCUSSION

A. Validity of the angle-resolved model

The validity of the assumptions underlying the angle-resolved model for O_{sec} relative intensities is discussed later.

(i) HfO_{2} is semi-infinite regarding O 1s signals – This assumption is supported by the absence of significant O 1s signal coming from the interfacial SiO_{2} layers. Since O in SiO_{2} leads to O 1s peaks at binding energies close to those observed for O_{sec}, if the underlying SiO_{2} contributed to the O 1s spectra, then one should observe a component of R approximately proportional to the attenuation due to the HfO_{2} overlayer, \( R \sim \exp\left[-t/\lambda \cos(\theta)\right] \), where t is the HfO_{2} thickness and \( \lambda \sim 3 \). Judging from the data in Fig. 2(a), any contribution to R with such behavior is negligibly small.

(ii) Bulk O_{sec} and O_{main} concentrations are independent with depth – First, deposition conditions and thermal budgets are constant through the HfO_{2} films examined, which is a necessary condition to assume that film chemistries do not depend on depth. Moreover, we observed R_{before} independent on take-off angle.

B. Surface O_{sec}

Water-induced surface hydroxylation is a common phenomenon in transition metal oxides, is well established for atomic layer deposition techniques that use water as a HfO_{2} deposition precursor, and was observed by exposing HfO_{2} films to water vapor at room temperature, leading to an O 1s peak at binding energies close to those of O_{sec}. Based on these facts, we assign the additional surface O_{sec} due to water exposure to surface hydroxylation. It was proposed that a H_{2}O molecule decomposes by attaching an O-H group to surface Hf and the remaining H to a neighbor surface O, forming two hydroxyls for each dissociatively adsorbed water molecule. This reaction was calculated to be exothermic by 90–180 kJ mol^{-1} at the m-HfO_{2}(001) surface and by 60–86 kJ mol^{-1} at the m-HfO_{2}(111) surface.

Besides surface O_{sec} due to water, there is a O_{sec} surface density of 1.4±0.6×10^{14} cm^{-2} [from Fig. 2(c) and Table II] for the O_{2}+FG sample before water exposure. This surface O_{sec} is attributed to O-H groups created by reaction of the HfO_{2} film surface with H_{2} from the 600 °C FG annealing. This is in reasonable agreement with a 2.2±0.1×10^{14} 2H cm^{-2} observed to incorporate at HfO_{2} surfaces by annealing in 2H_{2} (600 °C, 30 min), as well as in qualitative agreement with O-H groups that form at ZrO_{2} chemically similar to HfO_{2} surfaces by annealing in H_{2}. Moreover, dissociative H_{2} adsorption (forming O-H and Zr-H bonds) was calculated to be exothermic by 17.8 kJ mol^{-1} at the HfO_{2}(101) surface.

C. Bulk O_{sec} – Location

We describe the HfO_{2} films as consisting of ordered regions, corresponding to HfO_{2} within crystallites (with or without point defects), and disordered regions, corresponding to HfO_{2} amorphous regions, grain boundaries, surfaces, and interfaces. First of all, bulk O_{sec} cannot be assigned to [Fig. 2(a), the exception for the O_{2}+FG sample is explained later], which would not be observed if O chemistries depended on depth.
defect-free crystallites because O atoms in ideal r-HfO₂ and m-HfO₂ are all derived from equivalent O atoms in c-HfO₂ and would not lead to an O_{sec} peak shifted from O_{main} peak by considerable 1.4–1.6 eV.

Moreover, considering the presence of O vacancies and interstitials within HfO₂ crystallites, the equilibrium relative concentration of the point defects can be approximated by exp(−E±μ₀/k_BT), where E is the formation energy of the defect (referred to half the energy of an isolated O₂ molecule), μ₀ is the chemical potential for O atoms, k_B is the Boltzmann constant, and T is the temperature in Kelvin. The “±” holds for interstitials and the “−” for vacancies. Such a simple thermodynamic model assumes that the presence of the intrinsic defects is not controlled by reaction kinetics, which is supported by fast O diffusion observed in HfO₂.42,43

First-principles calculations determined E=1.6 eV for O interstitials3 and E=6.4 eV for O vacancies.4,44 Moreover, considering μ₀ to be that of an ideal O₂ gas,

$$\mu_0 = \frac{1}{2} k_B T \ln \left( \frac{P \cdot (2\pi \hbar^2 / m_O k_B T)^{3/2}}{k_B T} \right),$$

and calculating μ₀ for a pressure (P) of 10⁻³ mbar of O₂ and T=873 K (600 °C), which is a typical experimental condition employed here, one obtains μ₀=−2.1 eV. Applying μ₀ and E to the exponential factor leads to relative defects concentrations of ~10⁻²² for O interstitials and ~10⁻²⁵ for O vacancies. Performing similar calculation for H interstitial in HfO₂ [using E=2.0 eV (Ref. 45) and P_H₂ =10⁻⁸ mbar], one derives relative H concentration of ~10⁻²⁵. Since all considered defects are expected in relative concentrations far lower than the few percent relative concentrations observed for bulk O_{sec}, it is very likely that bulk O_{sec} is not within HfO₂ crystallites. Instead, bulk O_{sec} is in disordered HfO₂, i.e., in amorphous regions and grain boundaries.

Considering a polycrystalline oxide, the ratio between O concentration at grain boundaries and inside crystallites can be approximated by

$$\frac{[O_{\text{boundary}}]}{[O_{\text{inside}}]} \sim \frac{\sigma A}{\rho L},$$

where σ is the density of O atoms at a HfO₂ surface, ρ is the concentration of O atoms in HfO₂, A is a typical grain area, and V is a typical grain volume. Assuming σ~ρ²/³ and A/V~1/L, where L is a typical grain dimension parallel to the interfaces, and using ρ=5.6×10⁻²² O cm⁻² (as previously used for [O_{main}]) and L=6.0 nm (average L from HR-TEM images), one obtains [O_{boundary}]/[O_{inside}]~4%. This percentage is in good agreement with observed bulk O_{sec}/O_{main} ratios before water vapor exposure [Fig. 2(b)], further supporting O_{sec} location in disordered regions such as grain boundaries. In the case of the as-dep HfO₂, which is amorphous (fully disordered according to our description), most O still contributes to the O_{main} peak, implying that in disordered regions not all O atoms correspond to O_{sec}, but rather that O_{sec} and O_{main} coexist.

D. Bulk O_{sec} – Removal by FG annealing

It is worth comparing the O₂+N₂ and O₂+FG samples, both with fully crystallized HfO₂, because they were exposed to identical thermal budgets and, therefore, should have very similar distribution of crystallites and grain boundaries. Nevertheless, one observes lower bulk O_{sec} concentration for the O₂+FG sample [Fig. 2(b)], indicating that bulk O_{sec} from grain boundaries was partly removed by the reducing FG annealing. Such O_{sec} removal might leave O-vacancy-like defects at HfO₂ grain boundaries.

E. Bulk O_{sec} – Chemical nature

Having ruled out the presence of impurities (except H), we restrict the discussion of bulk O_{sec} bonding to three chemical elements: Hf, O, and H.

(i) Modified O-Hf bonds (bonds with nontrivial length and/or formed between atoms with nontrivial coordination numbers) are expected in HfO₂ disordered regions.46 Nevertheless, judging from surface disorder that does not lead to surface O_{sec} [Fig. 2(c)], and from the Hf 4f spectra, where disorder appears as broader, but not as separated peaks (Fig. 6), it is unlikely that bulk O_{sec} corresponds to modified O-Hf bonds.

(ii) O-O bonds lead to less negative net charges at O atoms, which typically imply higher binding energies for the corresponding O 1s photoelectrons. Such qualitative binding energy difference was observed between O_{sec} and O_{main}, indicating that bulk O_{sec} possibly corresponds to O-O bonds.

(iii) O-H bonds might be formed during HfO₂ deposition by reaction of O dangling bonds with H₂ molecules. Such reaction was observed in SiO₂ (Ref. 47) and the concentration of H₂ residuals in the deposition atmospheres is enough to explain O_{sec} relative concentrations.48 Moreover, binding energies of O_{sec} peaks are fully compatible with O-H bonds (e.g., surface O_{sec} assigned to O-H). Judging from the earlier-mentioned facts, it is likely that bulk O_{sec} observed before water exposure corresponds to O-H bonds.

Now consider the additional bulk O_{sec} that appears after water exposures [Fig. 3(b)]. Ruling out nondissociative water absorption because it typically leads to O 1s photoelectrons at binding energies 1.0–1.5 eV higher than those observed for O_{sec},35,49 we attribute water-induced bulk O_{sec} to dissociative water absorption (hydroxylation). Water-induced bulk O_{sec} was observed for the samples with HfO₂ amorphous regions (as-dep and O₂ only), whereas it was not observed for the O₂+N₂ and O₂+vac samples with fully crystallized HfO₂ [Fig. 3(b)]. A previous study13 observed water-induced bulk O-H groups in a HfO₂ film grown at low temperature (presumably amorphous), whereas not detecting such signal for HfO₂ grown at higher temperature (presumably crystallized). Another study15 failed to detect water absorption into 800 °C-vacuum-annealed, fully crystallized HfO₂ films. These previous results, as well as the results presented here, suggest that amorphous HfO₂ absorbs water, whereas polycrystalline HfO₂ does not.
However, the O$_2$+FG sample is an exception to this rule. In this case, the HfO$_2$ film is fully crystallized and water-induced bulk O$_{sec}$ [Fig. 3(b)] is attributed to hydroxylation of grain boundaries from where bulk O$_{sec}$ had been removed by the FG annealing. In general, we suggest that hydroxylation of HfO$_2$ amorphous regions and O-depleted grain boundaries relies on the presence of atomic-scale voids, which allow net incorporation of water-derived atoms while avoiding energy-costly displacements of neighbor HfO$_2$. Finally, typical MOSFET processing includes a ~1000 °C activation annealing. In general, we suggest that hydroxylation of the FG annealing. In general, we suggest that hydroxylation of HfO$_2$ surface hydroxyls induced either by room temperature analyses, is located in HfO$_2$ amorphous regions and grain boundaries. Moreover, this bulk O$_{sec}$ could be partly removed by annealing in reducing, H$_2$-containing atmospheres, which might leave O-vacancy-like defects. For HfO$_2$ films with amorphous regions or O-depleted grain boundaries we also observed additional, water-induced bulk O$_{sec}$ attributed to HfO$_2$ bulk hydroxylation. Finally, the presence of non-trivial O, either induced by water or not, indicates that HfO$_2$ amorphous regions and grain boundaries might contain O-related defects without counterparts within HfO$_2$ crystallites.

V. CONCLUSIONS

In summary, we performed in situ sputter deposition, annealing, room temperature water vapor exposure, and XPS analysis of HfO$_2$ nanometric films on Si. Each O 1s photoelectron spectrum was deconvoluted into two O peaks: one main peak, corresponding to trivial O forming O-Hf bonds, and one secondary peak, corresponding to nontrivial secondary O (O$_{sec}$) whose origins were investigated here.

Besides ruling out possible roles of impurities (except H) on O$_{sec}$ bonding, an angle-resolved XPS model was employed in order to quantitatively separate HfO$_2$ surface and bulk contributions to O$_{sec}$. Surface O$_{sec}$ was attributed to HfO$_2$ surface hydroxyls induced by room temperature water vapor exposure or by 600 °C H$_2$ annealing. HfO$_2$ surface hydroxylation might become significant for metal/HfO$_2$ interface engineering in HfO$_2$-based MOSFETs.

Bulk O$_{sec}$ was attributed primarily to O-H bonds and, as indicated by thermodynamic calculations and structural analyses, is located in HfO$_2$ amorphous regions and grain boundaries. Moreover, this bulk O$_{sec}$ could be partly removed by annealing in reducing, H$_2$-containing atmospheres, which might leave O-vacancy-like defects. For HfO$_2$ films with amorphous regions or O-depleted grain boundaries we also observed additional, water-induced bulk O$_{sec}$ attributed to HfO$_2$ bulk hydroxylation. Finally, the presence of non-trivial O, either induced by water or not, indicates that HfO$_2$ amorphous regions and grain boundaries might contain O-related defects without counterparts within HfO$_2$ crystallites.

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APPENDIX

The intensity of an XPS signal (peak area) for a given chemical state X of a given element core level can be expressed as

$$I_X(\theta) = TXA_X\sigma_X L_X \int_0^\infty C_X(z) \exp\left[\frac{-z}{\lambda_X(\cos \theta)}\right] dz,$$

where $F$ is the x-ray photon flux, $TX$ is the transmission function of the electron analyzer, $A_X$ is the analysis area, $\sigma_X$ is the cross section of the photoemission process, $L_X$ is the asymmetry factor, $C_X(z)$ is the concentration of atoms in the chemical state X as a function of depth $z$ ($z=0$ at the surface), $\lambda_X(\cos \theta)$ is the attenuation length, and $\theta$ is the photoelectron take-off angle. All terms labeled with an X subscript depend on the core level under analysis. If one is interested only in the ratio $R$ between the intensities of two chemical states X and Y of the same core level, $R(\theta) = I_X(\theta)/I_Y(\theta)$, then $F$, $T$, $A$, $\sigma$, and $L$ cancel, since they are identical for X and Y. Moreover, if we further assume a homogenous media, then $\lambda$ has a single value for X and Y, independent on $z$, and $R(\theta)$ can be expressed as

$$R(\theta) = \frac{\int_0^\infty C_X(z) \exp\left[\frac{-z}{\lambda_X(\cos \theta)}\right] dz}{\int_0^\infty C_Y(z) \exp\left[\frac{-z}{\lambda_X(\cos \theta)}\right] dz}.$$  

If $C(z)=C$, independent on $z$, then the integrals simplify to

$$\int_0^\infty C \exp\left[\frac{-z}{\lambda_X(\cos \theta)}\right] dz = CL(\cos \theta).$$

Moreover, if $C(z)$ is a surface delta layer, $C(z)=D\delta(z-\epsilon)$, where $D$ is a surface atomic density (in atoms/cm$^2$), $\delta$ is the delta function, and $\epsilon$ is a positive infinitesimal quantity introduced to mathematically remove the delta peak from the lower integration limit, then the integral simplifies to

$$\lim_{\epsilon \to 0^+} \int_0^\infty D\delta(z-\epsilon) \exp\left[\frac{-z}{\lambda_X(\cos \theta)}\right] dz = D.$$  

Now consider that

$$C_X(z) = C_X + D_X\delta(z-\epsilon),$$

$$C_Y(z) = C_Y.$$  

By substituting $C_X(z)$ and $C_Y(z)$ from Eqs. (A5a) and (A5b) into Eq. (A2) and solving the integrals according to Eqs. (A3) and (A4), we obtain

$$R(\theta) = \frac{C_X\lambda(\cos \theta) + D_X}{C_Y\lambda(\cos \theta)} = \frac{C_X}{C_Y} + \frac{D_X}{C_Y\lambda(\cos \theta)}.$$  

Labeling $C_X$, $D_X$, and $C_Y$ as $[O_{sec}^{bulk}]$, $[O_{sec}^{surf}]$, and $[O_{main}^{bulk}]$, respectively, leads us to the expression of Eq. (1). The term between the equal signs in Eq. (A6) allows simple interpretation of the formula: $R$ is the ratio between effective densities (in atoms/cm$^2$) contributing to the XPS signal. Surface atoms contribute integrally, with a density $D$, while bulk atoms contribute up to an effective depth $\lambda \cos \theta$, with a density $C\lambda \cos \theta$.


25The pressure of the FG annealing atmosphere (370 mbar) was calculated based on 600 mbar reading (identical to N2 annealing) in a thermal conductivity pressure gauge. Because both pressure and temperature readings depend on the thermal conductivities of the annealing atmospheres, identical pressure reading assures that N2 and FG annealing are run at identical temperatures.


25Comparison with published spectra (see Refs. 23–25) suggests that binding energies are shifted by ~0.5 eV due to x-ray-induced positive charges in the SiO2 interfacial layer.


25For Si 2p photoelectrons we calculated λ(1486.6 eV) = 17.5 Å in HfO2 and λ(1486.6 Å) = 35.9 Å in SiO2.


25M. Ritala, in High-k Gate Dielectrics, edited by M. Houssa (Institute of Physics, Bristol, 2004), Chap. 2.1, pp. 17–64.


25A time-integrated flux of ~1010 H2 cm−2, which is comparable to ~2.5 × 1010 O cm−2 present in the HfO2 films, was calculated using kinetic gas theory and considering H2 as an important component of the 10−8 mbar base pressure of HfO2 deposition processes.