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Compositional stability of hafnium aluminates thin films deposited on Si by atomic layer deposition

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We have used nuclear reaction analyses and Rutherford backscattering spectrometry to investigate quantitatively the compositional stability of hafnium aluminates thin films deposited on Si(001) by atomic layer deposition using HfCl₄/H₂O and Al(CH₃)₂/H₂O precursors. It was found that increasing Al/Hf deposition cycles ratio leads to increasing oxygen deficiency in the as-deposited films as well as to increasing metal losses (up to ~15%) from the films after rapid thermal annealing at 1000 °C. Furthermore, isotopic substitution experiments, showed that incorporation of oxygen from the gas phase is eased in the cases where deposition conditions failed to supply enough oxygen to complete oxides stoichiometry. © 2005 American Institute of Physics. [DOI: 10.1063/1.1940130]

There is currently an intensive search for insulating materials holding high dielectric constant (high k) as alternatives to SiO₂ or Si₃N₄ gate dielectrics in metal-oxide-semiconductor field-effect transistor (MOSFET) devices. Any candidate to gate dielectric material should satisfy extreme requirements which include films and interfaces with low density of defects (such as suboxidized species and impurities), resistance to degradation during postdeposition thermal processing steps, and subnanometer thickness control of the high-k film itself as well as of the interfacial low-k oxide (typically SiO₂) that may be intentionally or unintentionally grown between the high-k layer and the Si substrate. Among the various alternative materials considered for gate dielectric application, probably Al₂O₃ and HfO₂ are those which received more attention so far. A good trade-off between the characteristics of these two materials can be achieved by forming (HfO₂)(Al₂O₃)ₓ₋ₓ mixed oxides, either homogeneous in composition or in nanolaminated structures. A convenient approach for depositing such films (oxides and mixed oxides) is the atomic layer deposition (ALD) technique, where self-saturating surface chemical reactions are employed. This approach has been successfully applied to control chemical reactions at the Si/high-k and high-k/gate electrode interfaces, as well as to obtain (HfO₂)(Al₂O₃)ₓ₋ₓ structures retaining sufficiently high dielectric constant and remaining amorphous up to high processing temperatures. Metastable defect configurations owing to the low-temperature film deposition process can be suppressed by postdeposition annealing. In particular, postdeposition annealing in oxygen containing atmospheres has been widely shown to improve electrical response of high-k dielectrics.

We report here on the quantitative investigation of the composition and thermal stability of hafnium aluminates ultrathin films deposited on Si by ALD, as well as on oxygen incorporation and transport in these structures. After standard wet chemical cleaning of the Si(100) substrates (two solutions employed in sequence, namely NH₄OH–H₂O₂–H₂O followed by HCl–H₂O₂–H₂O. For details see Ref. 12), a thin layer of SiO₂ grown by rapid thermal annealing (RTA) in O₂ was produced. (HfO₂)(Al₂O₃)ₓ₋ₓ/SiO₂/Si structures were then grown layer by layer by ALD using Al(CH₃)₃/H₂O (AO) and HfCl₄/H₂O (HO) as precursors at a substrate temperature of 300 °C. We varied AO/HO cycles ratio and the total number of cycles. The ALD sequences are given in the first column of Table I. Compositional stability and oxygen transport in these structures were investigated in selected samples (see Table I) by RTA in atmospheres of low pressure (between 0.1 and 10 mbar) O₂ at two typical temperatures of MOSFET processing, namely postdeposition annealing at

<table>
<thead>
<tr>
<th>ALD sequences</th>
<th>Selected samples</th>
<th>Metal loss (2A/Hf + 3/2A/Al) (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>xHO</td>
<td>x=92, HfO₂</td>
<td>5</td>
</tr>
<tr>
<td>x(1AO+5HO)</td>
<td>x=15, Hf₆Al₂O₁₅</td>
<td>9</td>
</tr>
<tr>
<td>x(1AO+1HO)</td>
<td>x=30, Hf₆Al₂O₁₅</td>
<td>14</td>
</tr>
<tr>
<td>xHO+5AO+xHO</td>
<td>x=46, HfO₂/Al₂O₃/HfO₂</td>
<td>8</td>
</tr>
</tbody>
</table>

TABLE I. Atomic layer deposition (ALD) sequences and number of cycles (x) used in the selected samples for rapid thermal annealing (RTA). The last column shows the metal losses in each one of the selected samples after RTA at 1000 °C for 10 s in ¹⁸O₂. Typical errors in the determination of metal losses are approximately 10%.

Abbreviations: AO, Al(CH₃)₃/H₂O; HO, HfCl₄/H₂O; RTA, rapid thermal annealing.
different sequences of ALD cycles. Ideal, stoichiometric HfO2 versus hafnium plus aluminum (2A_{Hf}+3/2A_{Al}) areal densities for the different as deposits samples in the inset are plotted the areal densities of (\(^{16}\text{O}+^{18}\text{O}\)) vs (2A_{Hf}+3/2A_{Al}) after rapid thermal annealing (RTA) at 1000 °C in \(^{18}\text{O}_2\).

600 °C and dopant activation annealing at 1000 °C. The oxygen atmosphere in RTA was O\(_2\) enriched to 97% in the \(^{18}\text{O}\) isotope (\(^{18}\text{O}_2\)).

Hf and \(^{16}\text{O}\) contents in the films were simultaneously determined by Rutherford backscattering spectrometry in channeling geometry (c-RBS) and detection at grazing angle.\(^{13,15}\) Figure 1(a) shows a set of such spectra, where the Hf and \(^{16}\text{O}\) signals are indicated. The Al signal overlaps the substrate-Si signal in these spectra and therefore Al in the films had to be independently quantified. The \(^{27}\text{Al}(p,\gamma)^{28}\text{Si}\) nuclear reaction near the resonance in the cross section curve at 992 keV was used for that purpose as performed in Ref. 5. These methods give precisions for Hf, Al and O areal densities of about 3%, 10% and 10%, respectively. The calculated, ideal approximate stoichiometries are given in the second column of Table I.

Figure 1(b) is a plot of the amount of oxygen (A\(_{O}\)) versus hafnium plus aluminum (2A_{Hf}+3/2A_{Al}) from the different sequences of ALD cycles. Ideal, stoichiometric (HfO\(_2\))\(_2\)(Al\(_2\)O\(_3\))\(_{1-x}\) mixed oxide films should yield a straight line of unit slope crossing the origin. Linear fits to the data were made taking into account: (i) interfacial O amounts consistent with 1.1 nm SiO\(_2\) interlayer determined by transmission electron microscopy (not shown), (ii) aluminum-rich Hf\(_x\)Al\(_{1-x}\)O\(_2\) films are evidently poorer in O when compared to Hf-richer samples and thus they were fitted separately. The fitting-derived slopes point to oxygen deficiency in as-deposited films. Previous results in HfO\(_2\) films described in the literature\(^{17}\) qualitatively support these findings. One observed that HO cycles performed on an aluminum oxide layer produced in an immediately precedent AO cycle lead to larger amounts of Hf incorporation per HO cycle as compared to HO cycles on HfO\(_2\), a fact that is also observed in Ref. 7. On the other hand, O deficiency increases with the Al content. Thus, one can associate O deficiency mainly with corresponding excessive Hf incorporation in HO cycles.

We performed rapid thermal annealing of the selected samples of Table I in the low pressures of \(^{18}\text{O}_2\) range mentioned above, at 600 °C for 60 s and at 1000 °C for 10 s. \(^{16}\text{O}\) areal densities were determined using the \(^{18}\text{O}(p,\alpha)^{15}\text{N}\) nuclear reaction in a plateau region of the cross section curve near 730 keV.\(^{18,19}\) Typical precision in \(^{18}\text{O}\) amounts is 5%. Elemental amounts for samples annealed at 1000 °C in 0.1 and 1 mbar in \(^{18}\text{O}_2\) are plotted in the inset of Fig. 1(b). The data points in the inset of Fig. 1(b) are at or above the stoichiometry, unitary slope line (solid line), indicating elimination of previously O-deficient sites as well as some eventual interface oxidation during oxygen annealing. Quantification of Hf and Al, after RTA in \(^{18}\text{O}_2\) or in vacuum at 1000 °C for 10 s showed (Table I) substantial metal losses. A tendency to higher metal losses in films containing more Al is manifested. Since we found that increasing Al content is related to increasing O deficiency, we propose that metal losses during RTA is also a mechanism of eliminating O-deficient sites remaining from film deposition.

Narrow resonance nuclear reaction profiling (NRP)\(^{18,19}\) was also employed to determine \(^{18}\text{O}\) profiles using the narrow (\(\Gamma=100\) eV) resonance at 151 keV in the cross section curve of the \(^{18}\text{O}(p,\alpha)^{15}\text{N}\) reaction, with an approximate depth resolution of 0.7 nm in near-surface regions. Excitation curves and the corresponding simulated concentration profiles (insets) are shown in Figs. 2(a)–2(d) for the homogeneous, mixed oxides of Table I, as well as for a 7 nm Al\(_2\)O\(_3\) film grown by ALD on SiO\(_2\)/Si(100) for comparison purposes. Arrows indicate the approximate position of the high.

![FIG. 1](image1.png)

**FIG. 1.** (a) Rutherford backscattering spectra in channelled geometry (c-RBS). (b) Oxygen (A\(_{O}\)) areal densities vs hafnium plus aluminum (2A_{Hf}+3/2A_{Al}) after rapid thermal annealing (RTA) at 1000 °C in \(^{18}\text{O}_2\).

![FIG. 2](image2.png)

**FIG. 2.** Excitation curves of the \(^{18}\text{O}(p,\alpha)^{15}\text{N}\) reaction around the narrow resonance at 151 keV. The corresponding \(^{18}\text{O}\) profiles extracted from the simulation of the experimental curves are shown in the insets. The solid line in the excitation curve of Fig. 2(b) (HfO\(_2\)) represents a simulation performed assuming a constant \(^{18}\text{O}\) concentration profile, whereas the dashed line represents a simulation performed assuming the profile shown in the inset.
Al2O3/SiO2 interface, which is typical of diffusion-limited 18O incorporation. On the other hand, the rather flat 18O profiles in the “bulk” of the Hf-containing films [Figs. 2(b)–2(d)] and the propagation of the 18O front down to the interface are clear indicators that for Hf-containing films, even at such a low temperature as 600 °C, 18O diffusion is much faster than its incorporation into the films.

18O profiles from all films annealed (RTA) at 1000 °C are consistent with two regions with different characteristics. In near-surface regions, 18O profiles are flat (almost flat for Al2O3), indicating fast diffusion. In near-interface regions, the incorporated 18O results from the joint action of three mechanisms, namely 18O–16O exchange, oxidation of suboxided species and substrate-Si oxidation, which lead to 18O pileup shown in Figs. 1(b) and 1(d). Considering the flat 18O profiles in the “bulk” of the films, one notices that the 18O concentrations after RTA at 1000 °C, in 1 mbar of 18O2, are quite similar (∼1010 cm−3) for all studied stoichiometries, indicating that 18O incorporation rates into the films after RTA at 1000 °C are weakly dependent on stoichiometry. Furthermore, after RTA in 0.1 mbar of 18O2 at 1000 °C, the 18O concentration is significantly larger for the HfAl2O4 film, which was shown in Fig. 1(b) to be the most oxygen deficient one. The pressure independence of 18O incorporation is due to the high thermal energy supplied at 1000 °C, which makes reactions fast enough such that the films will readily go towards a low energy, O-filled configuration even in very small oxygen partial pressures, is incorporated to occupy O-deficient sites.

In Fig. 3 we compare the 18O profiles after RTA at 600 °C in 18O2 for HfO2 and HfO2/Al2O3/HfO2 film samples on Si. The only difference in the deposition of the two films is the intercalation of 5 AO cycles in the middle of the HfO2 film deposition (see Table I) for the HfO2/Al2O3/HfO2 nanolaminate. The Al distribution in the nanolaminate was determined by NRPS using the narrow (Γ=40 eV) resonance in the 27Al(p, α)24Si nuclear reaction cross section curve at 404.9 keV, whose excitation curve and the resulting 27Al profile are shown in Fig. 3(a). The 18O profiles in Fig. 3(b) clearly show a 18O pileup near the Al-containing layer. Details on width and shape of this accumulated 18O distribution cannot be precisely determined, but its existence is easily assured by the differences in shape of the two excitation curves. One can speculate that 18O pileup would take place in the HfO2 atomic layers deposited on the Al2O3 layer since these HfO2 layers are highly O deficient and this deficiency would favor 18O incorporation therein.

In summary, hafnium aluminate thin films of different thicknesses and stoichiometries were deposited on Si(001) by ALD using HfCl4/H2O and Al(CH3)3/H2O precursors. Quantitative analyses of the Hf, Al and O amounts in the films indicate that as-deposited films are highly deficient in oxygen, this deficiency being higher for aluminates with higher Al content. Removal of O deficiencies takes place during RTA of the films in O2 by two parallel mechanisms, namely metal losses and incorporation of oxygen from the gas phase in previously O-deficient sites. Removal of deposition-related, metastable defects in postdeposition thermal processing steps here investigated is mandatory for successful integration of any candidate to gate dielectric for future MOSFET technology.

1High-k Dielectrics, edited by M. Houssa (Institute of Physics, London, 2004).