Oxygen diffusion and reactions in Hf-based dielectrics

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Oxygen transport in and reactions with thin hafnium oxide and hafnium silicate films have been investigated using medium energy ion scattering in combination with $^{18}$O isotopic tracing methods. Postgrowth oxidation of Hf-based films in an $^{18}$O$_2$ atmosphere at 490–950 °C results in O exchange in the film. The exchange rate is faster for pure hafnium oxides than for silicates. The amount of exchanged oxygen increases with temperature and is suppressed by the SiO$_2$ component. Films annealed prior to oxygen isotope exposure show complex incorporation behavior, which may be attributed to grain boundary defects, and SiO$_2$ phase segregation. © 2006 American Institute of Physics. [DOI: 10.1063/1.2221522]

Transition metal oxides and silicates with dielectric constant higher than that of SiO$_2$ are currently being investigated as potential gate dielectric materials in complementary metal-oxide-semiconductor (CMOS) devices. Many fundamental properties of O diffusion in hafnia remain unclear, in particular, the nature of the diffusing oxygen species, the role of oxygen vacancies, interstitial oxygen, and other defects. Previous experiments with ZrO$_2$ films and ultrafine grained ZrO$_2$, and density functional calculations of oxygen incorporation and diffusion energies in monoclinic hafnia have suggested that oxygen incorporates and diffuses in atomic (ionic, nonmolecular) form. Furthermore, $^{18}$O becomes a more thermodynamically stable interstitial by accepting two electrons. Calculations show that diffusion via oxygen lattice exchange should be the favored mechanism, however, the barriers for interstitial oxygen diffusion in HfO$_2$ are small, and defects could be mobile under high temperature processing conditions. In contrast, molecular oxygen incorporation is preferred for the less dense SiO$_2$ structure, with diffusion proceeding through interstitial sites.

We have studied the diffusion of oxygen in Hf-based dielectric thin films using an isotopic tracing approach. Dielectric films grown with the conventional ($^{16}$O$_2$) isotope were subsequently annealed in $^{18}$O$_2$ (98% isotopically enriched). Medium energy ion scattering (MEIS) was used to measure the $^{16}$O and $^{18}$O profiles to quantitatively determine the depth distribution of both oxygen species through the dielectric film. Factors in the Hf-based oxides and silicates affecting oxygen exchange such as film composition, phase separation, and crystallinity were examined. It is found that SiO$_2$ suppresses oxygen diffusion when present on the outer surface of the dielectric. Our data further indicate that HfO$_2$–SiO$_2$ phase separation results in the formation a SiO$_2$ enriched film close to the top surface of Hf silicate.

2–3 nm Hf oxide and silicate films were deposited on a 1 nm SiO$_2$/Si(001) film using atomic layer deposition (ALD) at 325 °C with O$_2$ as an oxidation agent. Reoxidation in $^{18}$O$_2$ was performed in situ in an UHV chamber (∼10$^{-9}$ Torr) by stabilizing the sample at a temperature in the ∼490–950 °C range (measured by an optical pyrometer), followed by $^{18}$O$_2$ gas introduction at a pressure of 0.01 Torr (30 min). In this letter we focus only on the exchange reaction in the Hf oxide and silicate films.

MEIS was used to determine the depth profile of all elements in the dielectric. We used a H$^+$ beam with an energy of 130 keV. Depth profiles of the elements were obtained by computer simulations of the backscattered ion energy distributions. The depth resolution was ∼3 Å in the near surface region and ∼8 Å at a depth of 30 Å.

Figure 1(a) shows the part of the backscattered ion spectrum corresponding to the O peak position for the as-deposited HfO$_2$ film, where the oxygen yield has contributions from both HfO$_2$ and the SiO$_2$ interfacial layers. The as-deposited HfO$_2$ films were found to be oxygen-rich HfO$_2$$_{2+0.05}$. Strong oxygen exchange is observed in the HfO$_2$ film at 490 °C (0.01 Torr), as shown in Fig. 1(a). There are no changes in the Si and Hf peaks (not shown), implying that no additional interfacial growth occurs and that atomic O diffusion through the interfacial SiO$_2$ layer is inefficient under these conditions. Based on a full analysis of the Si, $^{16}$O, $^{18}$O, and Hf peak shapes and energies, we conclude that the interfacial SiO$_2$ contains only $^{16}$O, as illustrated by the elemental depth distributions in the insert. Excess oxygen atoms, most likely stabilized as interstitials, remain in the hafnia film, as the total number of oxygen atoms remains the same after annealing at 490 °C.

Figure 1(b) shows the MEIS result for $^{18}$O reoxidation when it follows an UHV crystallization annealing at 750 °C for 40 min. [HfO$_2$ crystallization is expected and was reported at 750 °C (as well as at somewhat higher temperatures for Hf silicates).] After $^{18}$O$_2$ reoxidation of the “crystallized” HfO$_2$ film, we observe a different oxygen exchange profile, characterized by an $^{18}$O concentration gradi-
Several factors may also contribute to different exchanged oxygen distributions in the as-deposited and crystallized films. Presuming that the transported species are individual oxygen atoms (ions, not molecules), the availability of atomic oxygen at the surface is one of the factors affecting the extent of the exchange in the oxide. \( \text{O}_2 \) is expected to be adsorbed molecularly on perfect surfaces of \( \text{HfO}_2 \) and to dissociate primarily at O-vacancy defect sites. The amount of available atomic O depends on the rate of \( \text{O}_2 \) dissociation at the surface and is therefore related to the number of oxygen vacancies at the top surface. Additionally, as relaxation of atoms along the diffusion path is important for a lattice exchange mechanism, as-deposited disordered \( \text{HfO}_2 \) films might be expected to display a lower diffusion barrier than crystalline films.

In order to quantify and discuss the amount of \( ^{18}\text{O} \) incorporated into the high-\( \kappa \) layer, we calculate the \( ^{18}\text{O} \) exchange fraction as the ratio of \( ^{18}\text{O} \) to the total oxygen \( ^{16}\text{O} + ^{18}\text{O} \) MEIS areal density in an \( n(\text{HfO}_2)m(\text{SiO}_2) \) film (excluding any interfacial \( \text{SiO}_2 \)). Representative exchange fractions for selected as-deposited and crystalline Hf oxide and silicate films are listed in Table I. This comparison shows that when \( \text{SiO}_2 \) is introduced into \( \text{HfO}_2 \) films during the growth, the exchange process slows dramatically and is almost completely suppressed for 50% \( \text{SiO}_2 \) content (under our reoxidation conditions: 490 °C, 10\(^{-2} \) Torr, and 30 min).

Upon vacuum annealing to \( \approx 850 \) °C some changes were observed in the Hf and Si peak shapes (Fig. 2) and therefore in their depth distributions [in the \( (\text{HfO}_2)_x\text{SiO}_2 \) film]. The Hf peak increases in height and decreases in width, with the Hf areal density remains constant at \( (3.60\pm0.15) \times 10^{15} \) Hf atoms/cm\(^2\). While the Si distribution is uniform in as-deposited \( (\text{HfO}_2)_x\text{SiO}_2 \), after annealing the

![Image](https://example.com/image.png)
Si yield becomes larger closer to the top surface. This change can be a signature of phase segregation of the silicate layer with SiO₂ enrichment in the top surface layer. The corresponding depth profile (insert) is illustrative only, because strong lateral inhomogeneities are expected in this case. After reoxidation at 490 °C, only the O exchange reaction is observed, with no appreciable net increase in oxygen. The oxygen exchange fraction for recrystallized silicate is in the 0.07–0.11 range and is lower than for the as-deposited film. Since a crystallization annealing should lead to phase segregation in the Hf silicates, the lower O exchange fraction results from a lower surface area of HfO₂ exposed to oxygen, or a suppression of the diffusion through the silica enriched grain boundary regions.

Figure 3 shows the increase of the ¹⁸O exchange fraction in a (HfO₂)₂SiO₂ film as a function of reoxidation temperature in the 490–950 °C range. This exchange fraction increase is driven by several factors. First, the ¹⁸O₂ dissociation rate at the surface goes up as the temperature increases. Second, more oxygen species will diffuse towards the interface and will be trapped there due to chemical reactions with the Si substrate (if there is no barrier layer at the interface). Only exchange is observed at 490 °C; at higher temperatures (≥610 °C), interfacial SiO₂ growth is apparent, as others have observed under similar conditions.

In order to understand the suppression of the O exchange in Hf silicates after crystallization annealing, and how it affects O₂ diffusion and dissociation, we deposited an ∼2 ML thick SiO₂ layer on top of the HfO₂ film. The ∼2 ML SiO₂ on top of the HfO₂ film was achieved by two SiO₂ ALD deposition cycles at 410 °C. We find that the exchange rate at 490 °C is reduced to almost zero (last line, Table I) indicating that the oxygen diffusion is stopped by the thin SiO₂ layer. This is consistent with our results in Fig. 1, which shows no exchange in the interfacial SiO₂ film while atomic O is in abundance in the adjacent hafnia film. Alternatively, the top SiO₂ layer is expected to suppress O₂ dissociation by eliminating Hf bonded defect sites on the top surface thus reducing supply of atomic O.

These data suggest that the suppression of O exchange in Hf silicates discussed above may be caused by the segregation of SiO₂ to the top surface that accompanies the phase separation which is known to occur in Hf silicates under the high temperature annealing.¹²¹⁵ Indeed, as both Si–O and Hf–O bonds are present on the surface of Hf silicates, the ¹⁸O₂ dissociation rate is expected to be lower for silicates with higher SiO₂ content. Nevertheless, within a simple assumption that the Hf–O/Si–O bond ratio at the surface is the same as in the (HfO₂)m(SiO₂)n film bulk, the exchange rate should drop by less than a factor of 2 by going from HfO₂ to HfO₂SiO₂. However, a much more dramatic exchange rate decrease points to a nonuniform Hf:Sı surface distribution with a higher SiO₂ content (SiO₂ segregation) close to the top surface, probably due to its lower surface energy.¹⁶¹⁷ This surface layer enrichment with SiO₂ can significantly reduce and even block O₂ diffusion at low temperatures. A second effect is the suppression of oxygen lattice exchange in the Hf silicate due to the presence covalent Si–O bonding, as compared to the more ionic hafnium oxide.

In summary, we have studied oxygen exchange in Hf-based dielectric films by high-resolution ion profiling with isotopic tracing. Our results indicate that atomic oxygen diffusion via oxygen lattice exchange is the predominant diffusion mechanism in hafnia, consistent with theoretical calculations.² We further show that the exchange rate scales with temperature. Finally, we show that the addition (and surface segregation) of SiO₂ to hafnium oxide and Hf silicate suppresses O incorporation in the dielectric.

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7. We define oxygen exchange as substitution of the oxygen atoms within the framework of the thin film by oxygen coming from the gas phase. The number of atoms gained from the gas phase equals to the number of oxygen atoms lost, so the total oxygen content of the dielectric remains constant during exchange. This exchange process has to be differentiated from interfacial incorporation and growth, where oxygen reacts with the film or the substrate, increasing the total oxygen content.


14. The fluctuations in the exchange fraction for crystalline films may come from sample-to-sample variations in the crystallite size distribution or from surface SiO₂ segregation.


17. A. A. Demkov (private communication).