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 $^{18}O_2$ 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.[1] Many fundamental properties of O diffusion in hafnia remain unclear, in particular, the nature of the diffusing oxygen species, the role of oxygen vacancies,[2] interstitial oxygen, and other defects. Previous experiments with ZrO_2 films[3] and ultrafine grained ZrO_2,[4] and density functional calculations of oxygen incorporation and diffusion energies in monoclinic hafnia[5] (HfO_2) have suggested that oxygen incorporates and diffuses in atomic (ionic, nonmolecular) form. Furthermore, O^{2-} becomes a more thermodynamically stable interstitial by accepting two electrons. Calculations[5] 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.[6]

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 ^{18}O and ^{16}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[7] 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_3 as an oxidation agent. Reoxidation in $^{18}O_2$ was performed *in situ* in an UHV chamber ($\sim 10^{-9}$ Torr) by stabilizing the sample at a temperature in the $\sim$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[7] 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.[8–10] Depth profiles of the elements were obtained by computer simulations of the backscattered ion energy distributions. The depth resolution was $\sim$3 Å in the near surface region and $\sim$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 $HfO_{2.10\pm0.05}$. 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 $^{18}O_2$ 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).[11,12]] 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-

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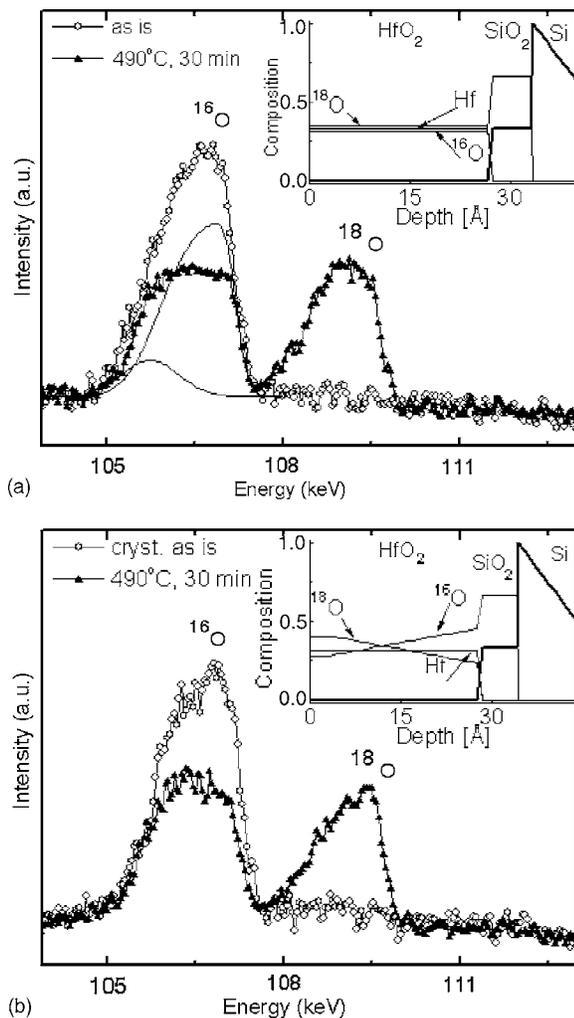
FIG. 1. The ^{16}O and ^{18}O energy range of MEIS spectra for HfO_2 films on Si (100) before (open circles) and after oxidation in $^{18}O_2$ (solid symbols) at 490 °C. Deconvolutions of the peak into HfO_2 and SiO_2 contributions are shown by the thin lines. The spectra were obtained with 130.3 keV protons in a channeling and blocking configuration. The HfO_2 film is amorphous in (a) and crystalline in (b). Inserts show best fit elemental depth distribution profiles for the samples after ^{18}O oxidation.

TABLE I. Areal densities of different oxygen isotopes before and after annealing in an $^{18}O_2$ atmosphere ($p_{^{18}O_2} = 10^{-2}$ Torr) at 490 °C for 30 min.

Sample	Total oxygen ($\times 10^{15}$ at./cm^2)	^{16}O loss (^{18}O gain) ($\times 10^{15}$ at./cm^2)	Exchange fraction
HfO_2	15.6	7.8(7.8)	0.50
$(HfO_2)_2SiO_2$	13.3	2.6(2.6)	0.20
HfO_2SiO_2	14	<0.5(0.5)	<0.04
HfO_2 (crystalline)	14.7	5.6(5.8)	0.40
$(HfO_2)_2SiO_2$ (crystalline)	13.2	0.9–1.5(1.1)	0.07–0.11
SiO_2/HfO_2	19.5	1.0(1.0)	0.07

the extent of the exchange in the oxide. O_2 is expected to be adsorbed molecularly on perfect surfaces of HfO_2 and to dissociate primarily at O-vacancy defect sites.[13] The amount of available atomic O depends on the rate of 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 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}O incorporated into the high-κ layer, we calculate the ^{18}O exchange fraction as the ratio of ^{18}O to the total oxygen ($^{16}O + ^{18}O$) MEIS areal density in an $n(HfO_2)m(SiO_2)$ film (excluding any interfacial 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 SiO_2 is introduced into HfO_2 films during the growth, the exchange process slows dramatically and is almost completely suppressed for 50% SiO_2 content (under our reoxidation conditions: 490 °C, 10^{-2} Torr, and 30 min).

Upon vacuum annealing to $\geq$850 °C some changes were observed in the Hf and Si peak shapes (Fig. 2) and therefore in their depth distributions [in the $(HfO_2)_2SiO_2$ film]. The Hf peak increases in height and decreases in width, with the Hf areal density remains constant at $(3.60 \pm 0.15) \times 10^{15}$ Hf atoms/cm^2. While the Si distribution is uniform in as-deposited $(HfO_2)_2SiO_2$, after annealing the

ent decreasing from the top surface towards the interface with the substrate [insert, Fig. 1(b)].

Recent high resolution transmission electron microscopy (HRTEM) studies of HfO_2 films[2] indicated that there is O depletion in the grain boundary region after rapid thermal annealing. In other works on the analogous ZrO_2 case, faster diffusion was found to occur via the grain boundaries of nanocrystalline films, compared to the "bulk" of nanocrystallites, and was attributed to higher vacancy concentration in the oxygen sublattice in the grain boundary region.[4] Consolidation of nanocrystalline grains in as-deposited HfO_2 films into larger-size crystallites after vacuum anneals results in fewer grain boundaries. Therefore, the contribution of the bulk of the crystallites with slower diffusion becomes more prominent. The observed ^{18}O distribution can be considered characteristic of bulk HfO_2 crystallite (major fraction, slow) and grain boundary diffusion (minor, fast).

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

FIG. 2. The Hf and Si MEIS peaks for a $(HfO_2)_2SiO_2$ film before (solid line) and after annealing in vacuum for 30 min (850 °C, 10^{-9} Torr) (circles). Simulation profiles for Hf, Si, and O distributions for the annealed film are shown in the insets.
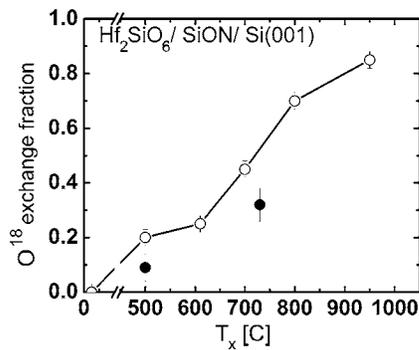
FIG. 3. The ^{18}O exchange fraction in a 29 Å thick $(HfO_2)_2SiO_2$ film as a function of oxidation temperature (30 min, $p_{18_{O_2}} = 10^{-2}$ Torr) for as-deposited (open circles) and crystallized or phase segregated (dark circles) films.

Si yield becomes larger closer to the top surface. This change can be a signature of phase segregation of the silicate layer with SiO_2 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 observable net increase in oxygen. The oxygen exchange fraction for recrystallized silicate is in the 0.07–0.11 range[14] 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 HfO_2 exposed to oxygen, or a suppression of the diffusion through the silica enriched grain boundary regions.

Figure 3 shows the increase of the ^{18}O exchange fraction in a $(HfO_2)_2SiO_2$ film as a function of reoxidation temperature in the 490–950 °C range. This exchange fraction increase is driven by several factors. First, the $^{18}O_2$ 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 ($\geq$610 °C), interfacial SiO_2 growth is apparent, as others have observed under similar conditions.[3]

In order to understand the suppression of the O exchange in Hf silicates after crystallization annealing, and how it affects O_2 diffusion and dissociation, we deposited an ~2 ML thick SiO_2 layer on top of the HfO_2 film. The ~2 ML SiO_2 on top of the HfO_2 film was achieved by two SiO_2 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 SiO_2 layer. This is consistent with our results in Fig. 1, which shows no exchange in the interfacial SiO_2 film while atomic O is in abundance in the adjacent hafnia film. Alternatively, the top SiO_2 layer is expected to suppress O_2 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 SiO_2 to the top surface that accompanies the phase separation which is known to occur in Hf silicates under the high temperature annealing.[12,15] Indeed, as both Si–O and Hf–O bonds are present on the surface of Hf silicates, the $^{18}O_2$ dissociation rate is expected to be lower for silicates with higher SiO_2 content. Nevertheless, within a simple assumption that the Hf–O/Si–O bond ratio at the surface is the same as in the $n(HfO_2)m(SiO_2)$ film bulk, the exchange rate should drop by less than a factor of 2 by going from HfO_2 to HfO_2SiO_2. However, a much more dramatic exchange rate decrease points to a nonuniform Hf:Si surface distribution with a higher SiO_2 content (SiO_2 segregation) close to the top surface, probably due to its lower surface energy.[16,17] This surface layer enrichment with SiO_2 can significantly reduce and even block O_2 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.[5] We further show that the exchange rate scales with temperature. Finally, we show that the addition (and surface segregation) of SiO_2 to hafnium oxide and Hf silicate suppresses O incorporation in the dielectric.

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