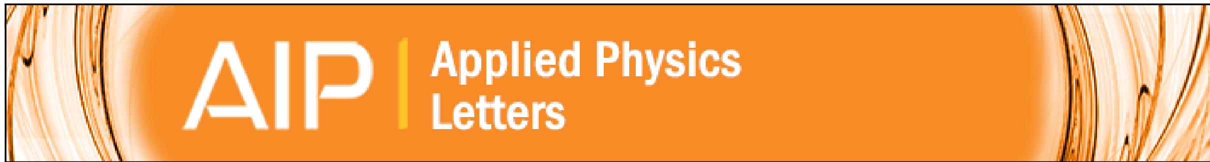

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Room temperature interactions of water vapor with HfO_2 films on Si

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$HfO_2/SiO_2/Si(001)$ thin film structures were exposed at room temperature to water vapor isotopically enriched in ^2H and ^{18}O followed by quantification and profiling of these nuclides by nuclear reaction analysis. We showed (i) the formation of strongly bonded hydroxyls at the HfO_2 surface; (ii) room temperature migration of oxygen and water-derived oxygenous species through the HfO_2 films, indicating that HfO_2 is a weak diffusion barrier for these oxidizing species; (iii) hydrogenous, water-derived species attachment to the SiO_2 interlayer, resulting in detrimental hydrogenous defects therein. Consequences of these results to HfO_2-based metal-oxide-semiconductor devices are discussed. © *2006 American Institute of Physics*.
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Scaling Si-based metal-oxide-semiconductor field-effect transistors (MOSFETs) pushed the usual SiO_2 gate dielectric layer to its ultrathin limits.[1–3] Hafnium oxide emerged as the leading candidate for SiO_2 replacement because of several desirable HfO_2 properties, including a dielectric constant much higher than that of SiO_2 ($k_{HfO_2}=22, k_{SiO_2}=3.9$).[2] This allows employing substantially thicker HfO_2 films while keeping the same metal-oxide-semiconductor capacitance achieved with ultrathin SiO_2. Hence, HfO_2 gate dielectrics allow further downscaling of Si-based MOSFETs for several forthcoming device generations. However, since for every generation device requirements become progressively stricter,[1] previously negligible factors will become increasingly important for device understanding at the appropriate level of detail. The ubiquity of water vapor and its potential role on detrimental Si oxidation, threshold voltage shifts, and hydrogenous defects[4–6] highlight the importance of the here reported room temperature water uptake in nanoscopic HfO_2 films on Si.

HfO_2 films of 2.5, 5, and 9 nm thick were deposited by metal-organic chemical vapor deposition on 1.5 nm thick SiO_2 films thermally grown on *p*-type Si(001). Although such "thick" SiO_2 interlayer would not be of practical use for state-of-the-art devices, it was here employed in order to provide a barrier to uncontrolled Si oxidation. The resulting $HfO_2/SiO_2/Si$ structures were annealed for 30 min at 800 °C in vacuum (10^{-7} mbar), employing a LN_2 cold finger to remove residual water vapor from the furnace atmosphere. This annealing, herein called *activation*, has the purpose of desorbing water which was incorporated during exposure of the structures to air. Postdeposition annealing, such as the here employed activation, is known to be necessary in order to achieve high quality HfO_2 layers because of thermal healing of deposition-related metastable defects.[2] However, such annealing also unavoidably crystallizes HfO_2 films[7,8] even when performed at considerably lower temperatures. Following activation, the water-desorbed samples were cooled down in vacuum and then exposed at room temperature to water vapor ($D_2\,^{18}O$) isotopically enriched in ^2H (D) and ^{18}O. The low natural abundances of these isotopes assure that measured D and ^{18}O effectively come from the isotopically enriched atmospheres. D isotopic enrichment of this vapor is about one order of magnitude lower than the 90% ^{18}O enrichment, according to mass spectrometer analyses. The employed $D_2\,^{18}O$ static pressure (10 mbars) is equivalent to ~30% relative humidity at 25 °C and an incident rate of about 10^7 ML/s (ML denotes monolayers). Exposure time was 30 min, unless when explicitly stated. Between $D_2\,^{18}O$ exposure and nuclear reaction analysis (NRA) samples were stored in air. In order to inspect for air-induced instabilities, control samples were stored in air for different periods of time at room temperature or, alternatively, immediately quenched and stored at 77 K, yielding identical results. The surface morphology of 9 nm HfO_2 films after activation and $D_2\,^{18}O$ exposure was accessed by atomic force microscopy (not shown), which evidenced flat surfaces (rms roughness <3 Å) with no evidence of pinholes.

D quantification[9] was achieved by counting proton products from the $D(^3He,p)^4He$ nuclear reaction induced by 700 keV $^3He^{+2}$ ions. For ^{18}O quantification[10] the counted products were alpha particles from the $^{18}O(p,\alpha)^{15}N$ nuclear reaction induced by 730 keV H^+ ions. D and ^{18}O amounts were determined by comparing reaction yields from samples and calibrated standards. Sensitivities of 10^{12} D cm^{-2} and 10^{13} ^{18}O cm^{-2} are achieved. Since D and ^{18}O amounts in the Si substrate contribute negligibly, nuclear reaction yields ef-

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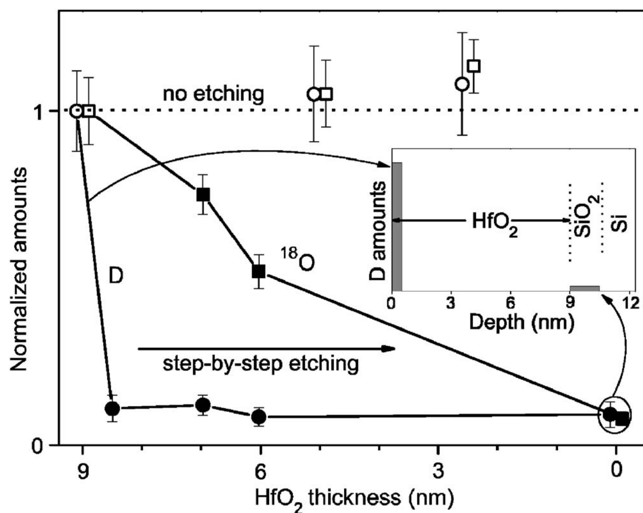

FIG. 1. Normalized D (circles) and ^{18}O (squares) amounts after activation and $D_2{}^{18}O$ exposure for nonetched HfO_2 films of variable thicknesses (empty symbols) and for 9 nm thick HfO_2 samples thinned by step-by-step chemical etching (filled symbols). HfO_2 film thicknesses were determined by measuring Hf amounts by Rutherford backscattering spectrometry and converting to nanometers assuming 9.8 g/cm^3 HfO_2 density. Normalizing amounts are 1.0×10^{15} ^{18}O cm^{-2} and 1.0×10^{14} D cm^{-2}, reflecting mainly the difference of ^{18}O and D isotopic enrichments. The inset sketches D depth distribution.

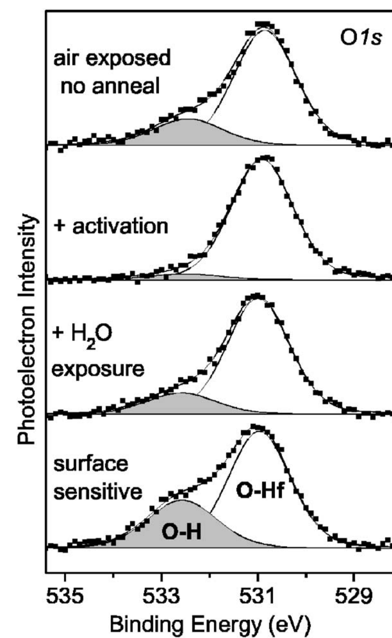

FIG. 2. O1s photoelectron spectra taken for (from top to bottom) (i) an air exposed, nonannealed 9 nm HfO_2 sample; (ii) same sample after *in situ* activation; (iii) same sample after *in situ* reexposure to water vapor; and (iv) same sample as in (iii) but collecting photoelectrons at surface-sensitive, grazing angle detection.

fectively measure elemental amounts in the HfO_2 and SiO_2 films. For activated samples exposed to $D_2{}^{18}O$ at room temperature we observed that D and ^{18}O amounts are independent of (i) $D_2{}^{18}O$ exposure time (30 min–15 h) and (ii) HfO_2 film thickness (Fig. 1). These facts point out, respectively, to (i) incorporation of $D_2{}^{18}O$-derived species self-saturating in a time interval shorter than 30 min and (ii) negligible D and ^{18}O incorporation in bulklike HfO_2 regions.

D profiling in the 9 nm HfO_2 sample after activation and $D_2{}^{18}O$ exposure was achieved by step-by-step removal of HfO_2 layers by chemical wet etching in a concentrated H_2SO_4 solution at 210 °C followed by D quantification after each removal step. One observes (Fig. 1) a major D signal loss after removal of the outermost HfO_2 layer, indicating that most D is bound in the HfO_2 surface region. Additional removal of HfO_2 layers does not bring new D loss, indicating no measurable incorporation of D in the bulk of the HfO_2 films by exposure to $D_2{}^{18}O$. Thus, the high hydrogen content found in the bulk of HfO_2 films in previous work[11] cannot be attributed to absorption of water. Moreover, since about one-tenth of the initial D and ^{18}O remains in the samples after complete removal of the HfO_2 film and considering that the chemical solution etches HfO_2 selectively, without removing the SiO_2 underneath, one assigns the remaining D and ^{18}O to be bound to the SiO_2 interlayer.

Analyses of the HfO_2 surface region by x-ray photoelectron spectroscopy using Mg $K\alpha$ x-ray source and photoelectron takeoff angle of 30° relative to sample normal evidence that the O1s photoelectron region has two components (Fig. 2). The assignment of the signal at 532.6 eV to surface hydroxyls is based on the reported O1s binding energy difference between surface hydroxyls and bulklike Zr–O bonds in ZrO_2 films.[12] Activation promoted desorption of surface hydroxyls, while subsequent *in situ* exposure to saturated water vapor reestablishes the hydroxylated surface. The stronger O–H signal for grazing (60°) takeoff angle (surface sensitive) confirms the hydroxyls surface location. We speculate that H_2O dissociates at HfO_2 surface by attaching an O–H group to a surface Hf and donating a H to a nearby O, thus forming two hydroxyls for each dissociatively adsorbed H_2O.[13] This process is reversible, according to the observed adsorption-desorption cycling shown in Fig. 2. Hence, surface D observed after $D_2{}^{18}O$ exposure (Fig. 1) is attributed to chemisorbed surface hydroxyls.

Figure 1 also evidences that ^{18}O depth distribution is remarkably different from D. In order to observe that in detail, ^{18}O profiling with nanometric depth resolution was achieved using nuclear resonant reaction profiling[14,15] (NRP) employing the narrow (Γ_R=80 eV) resonance in the cross section curve of the $^{18}O(p,\alpha)^{15}N$ nuclear reaction. In this technique, by scanning the proton beam energy above the resonance energy (151 keV) we are sampling for the presence of ^{18}O at increasingly deeper layers of the $HfO_2/SiO_2/Si$ structures.

In Fig. 3 we show the experimental excitation curves and simulated ^{18}O profiles for the 9 nm HfO_2 film after activation and room temperature exposure to $D_2{}^{18}O$ and, alternatively, to $^{18}O_2$ for comparison purposes. After both $D_2{}^{18}O$ and $^{18}O_2$ exposures one observes (i) near surface peaks in the ^{18}O concentration, (ii) constant, smaller ^{18}O concentrations in bulklike HfO_2 regions, and (iii) near interface ^{18}O peaks. The migration of ^{18}O into HfO_2 films is due to entropy-driven $^{16}O-{}^{18}O$ isotopic exchange[2,16] and although the easy migration of oxygen at higher temperatures is well recognized, no such easy room temperature oxygen migration was reported to date. If all ^{16}O in the HfO_2 film had equal probability of participating in this room temperature $^{16}O-{}^{18}O$ isotopic scrambling process, then one would expect a constant ^{18}O concentration throughout the HfO_2 film. This was not observed, meaning that only a fraction of the ^{16}O, probably those loosely bound present near defective sites (e.g., interfaces and grain boundaries), participate in this room

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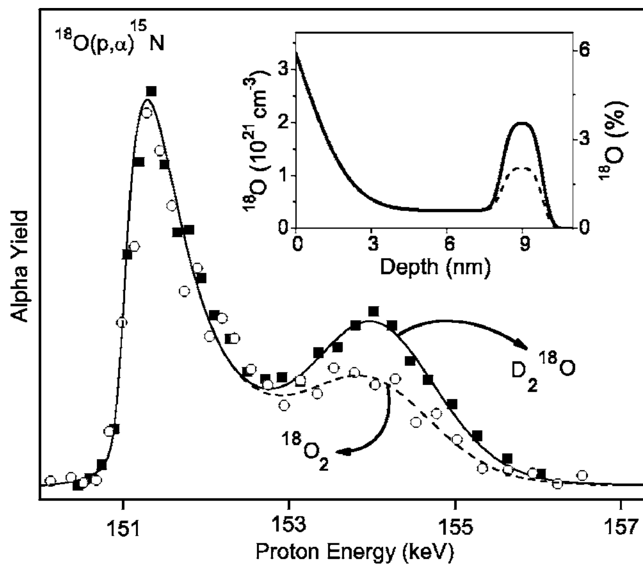

FIG. 3. Experimental excitation curves of the $^{18}O(p,\alpha)^{15}N$ nuclear reaction near the resonance at 151 keV and ^{18}O profiles (inset) for 9 nm HfO_2 samples after activation and exposure either to $D_2{}^{18}O$ (filled squares, solid line) or $^{18}O_2$ (empty circles, dashed line). Lines are the simulated excitation curves using the ^{18}O profiles from the inset. The right vertical axis from the inset shows the ^{18}O concentration as the O fraction calculated for HfO_2.

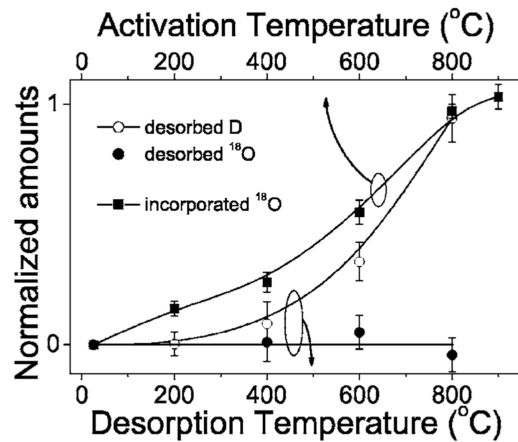

FIG. 4. *Desorbed* D and ^{18}O amounts as a function of temperature of the 30 min vacuum annealing performed *after* activation and $D_2{}^{18}O$ exposure (circles). *Incorporated* ^{18}O amounts as a function of temperature of the 30 min vacuum annealing performed *before* $D_2{}^{18}O$ exposure (squares). Normalizing amounts are 1.0×10^{15} ^{18}O cm^{-2} and 1.0×10^{14} D cm^{-2}.

temperature isotopic exchange and diffusion process. In $D_2{}^{18}O$ exposure, isotopic exchange takes place between ^{16}O initially in the HfO_2 films and ^{18}O incorporated via the self-saturating chemisorption of surface hydroxyls, whereas in $^{18}O_2$ exposure, ^{16}O from HfO_2 are directly exchanged for ^{18}O from the gas phase.

In contrast with ^{18}O in near surface and bulklike HfO_2 regions, near interface ^{18}O concentration is lower after $^{18}O_2$ than after $D_2{}^{18}O$ exposure, indicating that near interface ^{18}O in the latter case has an additional ^{18}O source. We attribute this excess of interfacial ^{18}O to species containing ^{18}O and D (Fig. 1), possibly hydroxyls, which migrated through the 9 nm HfO_2 at room temperature being attached to the SiO_2 interlayer. The sites to which these molecules attach may be either related to intrinsic interfacial mismatch or created during activation.[17,18] In addition, permeation of these water-derived molecules probably takes place through grain boundaries of the crystallized HfO_2 films.

By annealing in vacuum after activation and $D_2{}^{18}O$ exposure, we were able to investigate desorption of incorporated $D_2{}^{18}O$-derived species. D desorption, reflecting mainly desorption of surface hydroxyls, starts at temperatures above 200 °C and is complete after a 30 min, 800 °C annealing (Fig. 4). The need for considerable temperatures for D desorption indicates strong hydroxyls bonding. These surface hydroxyls passivate and induce dipoles[6] at the HfO_2 surface possibly influencing, respectively, adhesion and band lineup of metal gates on HfO_2. Differently from D, ^{18}O desorption was not observed because ^{18}O inwards diffusion through $^{16}O-^{18}O$ isotopic scrambling turned ^{16}O into the most probable oxygen isotope to be desorbed via surface hydroxyls. Moreover, by varying activation temperature *before* $D_2{}^{18}O$ exposure, we observed that *incorporated* ^{18}O amounts closely follow D amounts *desorbed* by annealing in vacuum *after* usual 800 °C activation and $D_2{}^{18}O$ exposure. This incorporation-desorption link arises from the *incorporation* of $D_2{}^{18}O$-derived species in sites where activation previously desorbed $H_2{}^{16}O$-derived species.

In summary, it was shown that exposing HfO_2 films on Si to water vapor at room temperature promotes diffusion of oxidizing, water-derived species through the polycrystalline HfO_2 films, attaching water-derived, hydrogenous species to the SiO_2 interlayer. Moreover, room temperature exposure to water forms strongly bonded hydroxyls at HfO_2 surface, which may affect adhesion and band alignment of metal gates on HfO_2. Therefore, carefully managing water vapor exposures and controlling the related effects constitute a critical issue for deep, quantitative, and precise understanding of HfO_2-based gate dielectrics to be used in future device generations.

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