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Interaction of HfO₂/SiO₂/Si structures with deuterium gas

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HfO₂ films (2.5 to 12 nm) deposited on thermal SiO₂ (1.5 nm) on Si were annealed in deuterium gas at 400–600 °C and incorporated D amounts were quantified using the D(³He,*p*)⁴He nuclear reaction. We found $\sim 10^{13}$ D cm⁻² in the SiO₂ interlayer region and up to 2.2×10^{14} D cm⁻² near the HfO₂ surface, whereas D amounts in the bulk of the HfO₂ films were determined to be below 10^{13} cm⁻². However, analyses employing the ¹H(¹⁵N,*αγ*)¹²C nuclear resonant reaction showed much more spurious H present in the bulk of HfO₂ films. Mechanisms of D incorporation and desorption as well as contribution of the present results to the understanding of HfO₂-based devices are discussed. © 2006 American Institute of Physics. [DOI: [10.1063/1.2168501](https://doi.org/10.1063/1.2168501)]

Annealing in hydrogen atmospheres is a final processing step in the fabrication of metal-oxide-semiconductor field-effect transistors (MOSFETs) owing to the H ability to passivate electrically-active Si dangling bonds (*P_b*-type defects) present at the SiO₂/Si interface.¹ Moreover, H introduced either intentionally or unintentionally into MOSFET structures, in particular into the gate dielectric, plays a fundamental role on device reliability.^{2,3} At present, MOSFET technology is searching for an alternative, high permittivity (high-*k*), reliable, and process-compatible oxide to replace SiO₂ as the gate dielectric material.^{4,5} Among various alternative materials studied so far, HfO₂ has emerged as one of the most promising candidates due to its considerable high dielectric constant (*k* \sim 25 versus *k* = 3.9 for SiO₂) and good thermal stability on Si. In this scenario, the role of hydrogen in structures employing HfO₂ as gate dielectric is a central matter. Previous work points to the existence of *P_b*-type defects at HfO₂/Si(001) interface either similar⁶ or identical⁷ to those found at SiO₂/Si(001) interfaces. Passivation of these dangling bonds by annealing in H₂ was also demonstrated, leading to improved electrical performance.^{7–9} The role of H on negative bias temperature instability,¹⁰ radiation-induced instabilities,¹¹ and fixed charges¹² were also investigated for HfO₂-based MOSFETs.

We report here on the quantitative investigation of H in HfO₂/SiO₂/Si structures, giving special attention to D incorporation during annealing in D₂ gas. Sample preparation started with clean *p*-type Si(001) wafers submitted to thermal

oxidation in O₂ at 600 °C to grow a 1.5 nm thick SiO₂. HfO₂ films were then deposited on SiO₂ by a metalorganic chemical vapor deposition (MOCVD) process run at 550 °C. Variable HfO₂ deposition times led to HfO₂ films 2.5, 5, 9, and 12 nm thick, as determined by Rutherford backscattering spectrometry (RBS). High-resolution transmission electron microscopy images (not shown) showed that as-deposited HfO₂ films with thickness in the 2.5–12 nm range have abrupt and flat interfaces.

Annealing sequences started with 800 °C, 30 min vacuum anneal aiming at establishing a common most-aggressive thermal step for all samples which serves also to desorb deposition residuals and impurities absorbed from air. Samples were then annealed in static, 60 mbar D₂ gas (H₂ 95% enriched in the ²H \equiv D isotope). The D-enriched gas is chemically identical to H₂ and allows us to distinguish hydrogen atoms coming from the D₂ annealing atmosphere from those previously existent in the films or absorbed from air. Selected samples were also annealed in vacuum after D₂ exposure. Exposure to spurious gases, either during or between annealing, was avoided by keeping samples inside the furnace (10^{-7} mbar base pressure) during the whole annealing sequences and by placing a LN₂ cryogenic trap in contact with the furnace atmosphere (far from the heating region).

D amounts in the samples were determined *ex situ* by nuclear reaction analyses (NRA) using the highly selective and sensitive ($\sim 10^{12}$ cm⁻²)D(³He,*p*)⁴He nuclear reaction induced by ³He⁺⁺ ions at 700 keV.¹³ The technique integrates D amounts detected to a depth of approximately 2 μm below the surface. Since D in the Si substrate contributes negligibly ($< 10^{12}$ cm⁻²) owing to the low D solubility in *c*-Si,¹⁴ D amounts here quantified are mostly in the overlying films and

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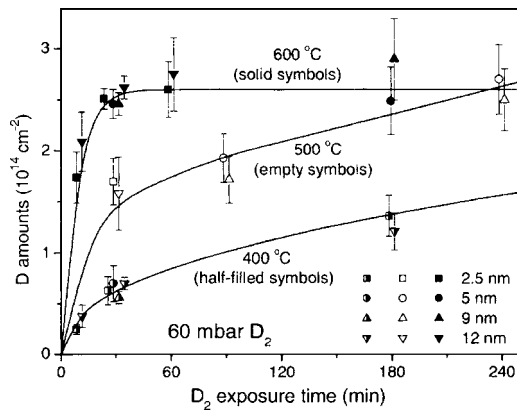


FIG. 1. D amounts determined by NRA as a function of D_2 exposure time. Data points were shifted in time (~ 1 min) for better visualization. Line for 600 °C exposures is a fit to the data with a saturating exponential function. Lines for 400 and 500 °C exposures are only guides for the eyes.

interfaces. Relative precision in D amounts are given by error bars (1σ) in the figures below. Moreover, H profiling was accomplished by using the resonance at 6385 keV in the cross section curve of the $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ nuclear reaction.¹⁵

D incorporation kinetics at 400, 500, and 600 °C are shown in Fig. 1. The chosen temperature range encloses usual ~ 400 °C H_2 passivation annealing as well as alternative, high-temperature (500–600 °C) annealing reported^{8,9} to improve interface passivation in poly-Si/HfO₂/Si structures. Since appreciable D content in the bulk of HfO₂ films would lead to D amounts depending on HfO₂ thickness, and since such dependence is never observed (Fig. 1), a higher limit to D amounts in the bulk of HfO₂ films can be established. Bulk D amounts below 10^{13} cm⁻² are deduced considering the precision of our data. Therefore, D is located mainly in HfO₂ surface regions and/or in the SiO₂ interlayer regions.

In order to determine how much D is present in the HfO₂ surface region we removed near-surface HfO₂ layers and then determined D amounts after this removal. HfO₂ films (5 nm thick) exposed to D_2 (600 °C, 30 min) were sputtered *ex situ* using a 5 keV Ar⁺ beam (45° incidence) scanned over the sample to assure sputtering uniformity in the whole sample area. D amounts after removal of 0.5–1 nm HfO₂ (typical range of possible beam-induced roughness and layer mixing) are $2\text{--}3 \times 10^{13}$ cm⁻² (Fig. 2). Since sputtering may also cause D loss due to desorption of D atoms present in the SiO₂ interlayer region, it is important to verify the above result by an independent method. D quantification after removal of near-surface HfO₂ layers (verified by RBS) by chemical wet etching performed in a hot (210 °C) concentrated H₂SO₄ solution confirmed remaining D amounts around 3×10^{13} cm⁻².

The difference between D amounts before and after removal of HfO₂ near-surface layers yields 2.2×10^{14} D cm⁻² within 0.5–1 nm from the HfO₂ film surface. One speculates that this D is bonded to the outermost HfO₂ layer. Furthermore, since around $2\text{--}3 \times 10^{13}$ D cm⁻² remain after removal of near-surface layers but less than 10^{13} cm⁻² is in the HfO₂ film bulk, D incorporation of $\sim 10^{13}$ cm⁻² in the SiO₂ interlayer region is also deduced. The inset of Fig. 2 summarizes the above conclusions. D losses for longer sputtering times (>60 min) in Fig. 2 are attributed to Ar⁺ beam-induced desorption of D present in the SiO₂ interlayer region.

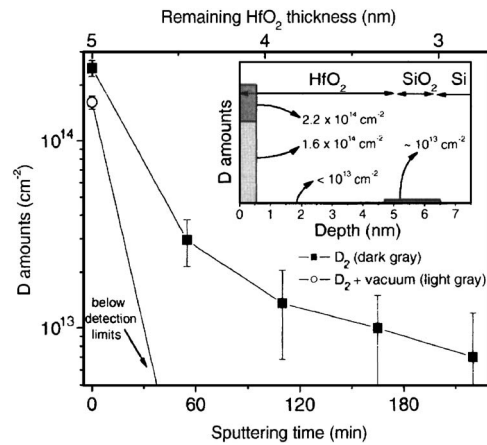


FIG. 2. D amounts determined by NRA vs sputtering time for the 5 nm HfO₂ sample. Remaining HfO₂ thickness was determined by RBS. Lines are only guides for the eyes. The inset shows proposed D amounts in HfO₂ surface, bulk, and SiO₂ interlayer region quoted in units of cm⁻².

Exposure of SiO₂/Si to D_2 at 450 °C leads to $\sim 10^{14}$ cm⁻² D accumulation in a region ~ 4 nm thick in the SiO₂ side of the interface, without any detectable D near the SiO₂ surface.^{13,16} On the other hand, annealing monoclinic and tetragonal zirconia in H_2 in the same temperature range of the present work¹⁷ was shown to promote an increase in surface OH signal detected by infrared spectroscopy. Hence, the observed near-surface and near-interface D accumulations in our structures are in qualitative agreement with similar systems reported in the literature. In Fig. 2, one also observes that the HfO₂/SiO₂/Si structure annealed in vacuum (600 °C, 30 min) after D_2 exposure (600 °C, 30 min) has no remaining D once near-surface HfO₂ layers were removed. This fact points to complete D desorption from bulk HfO₂ and SiO₂ interlayer region during the vacuum anneal. At the same conditions (600 °C, 30 min) complete D desorption from SiO₂/Si structures^{13,16} and from P_b -type defects¹⁸ also take place. We remark that H-passivated P_b -type defects account only for a fraction of the H found in the SiO₂/Si interface region.

Figure 3 shows excitation curves of the $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ nuclear reaction near the resonance at 6385 keV for 73 nm thick HfO₂ films. Excitation curves bring information about depth distribution of ^1H atoms,¹⁹ since ^1H atoms at progressively deeper layers contribute to reaction yield at corre-

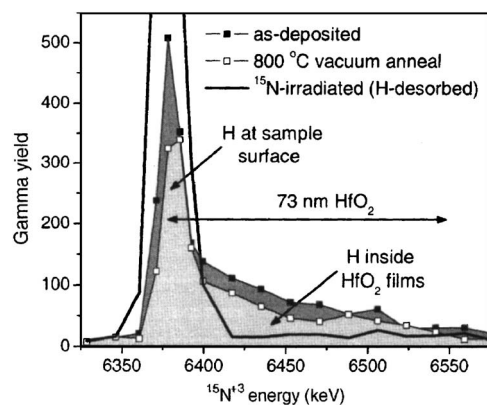


FIG. 3. Excitation curves of the $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ nuclear reaction near the resonance at 6385 keV for as-deposited, vacuum-annealed, and irradiated 73 nm HfO₂ sample.

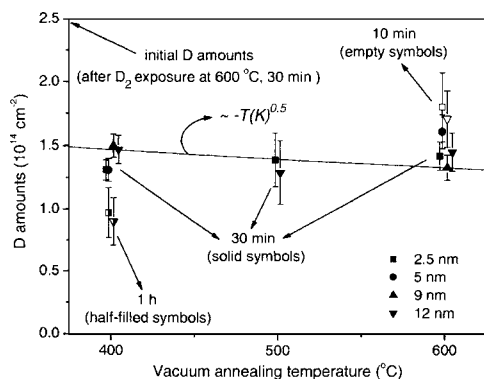


FIG. 4. D amounts determined by NRA remaining in samples annealed in vacuum after D_2 exposure at 600°C for 30 min. Data points were shifted in temperature ($\sim 1^\circ\text{C}$) for better visualization.

sponding progressively higher ^{15}N beam energies. In Fig. 3, one observes: (i) Surface ^1H peaks arising mainly from adsorbed hydrocarbon due to atmospheric air exposure and (ii) H content inside HfO_2 films in amounts comparable to the surface peaks, a fact also reported for HfSiO and HfSiON films on Si.¹⁵ Calibrating against a polystyrene H standard (subtracting background and surface contamination contributions) one determines H amounts of $7 \times 10^{15} \text{ cm}^{-2}$ inside the as-deposited HfO_2 film and $4 \times 10^{15} \text{ H cm}^{-2}$ inside the 800°C -annealed film. Deposition residuals (CH_x groups from MOCVD precursors) and adsorbed water molecules may be explanations for this bulk H content. H desorption from the bulk of the films induced by the impinging ^{15}N ion beam was unavoidable, in contrast with the analyses with ^3He incident beam in which D desorption was never observed. The seventh excitation curve taken on an as-deposited sample analyzed seven successive times at the same spot (^{15}N irradiated) is shown in Fig. 3. We notice that the bulk-H signal is at the background level, whereas an enhanced surface peak appears due to irradiation-induced hydrocarbon deposition at the sample surface.

Since D is located mostly near HfO_2 surfaces, information about the D chemistry in this region can be obtained by analyzing the determined total D amounts. If D incorporation near HfO_2 surface was governed by a first-order single-step chemical reaction, than one would expect D amounts following an increasing exponential function saturating in time. We tried to fit D incorporation kinetics (Fig. 1) with such exponential function. At 600°C , this fit is possible, but data availability before saturation is too poor to withstand any conclusion. However, for D_2 exposures at 400 and 500°C the fit does not agree with experimental data. Possibly we are facing multipath D incorporation, reflecting the diversity of bonding sites near the surface of the polycrystalline HfO_2 films.

Desorption of D by annealing in vacuum was also investigated (Fig. 4). Besides an expected decrease in D concentration with increasing annealing time, we found an unexpected independence on annealing temperature. The latter behavior suggests the possibility of spontaneous (not activated) rate-limiting reactions which would typically lead to a reaction rate (and also rate time integral, which is the quantity actually measured) proportional to a fractional power of the temperature T (in Kelvin). The line in Fig. 4 stands for D

loss proportional to $T^{0.5}$ and moderate agreement is achieved within data precision. For the interaction of H_2 with zirconia, it has been proposed that H incorporates by dissociating the H_2 molecule and making Zr–H and O–H bonds at adjacent Zr and O surface sites.¹⁷ We speculate whether spontaneous recombination of these two H atoms would be the rate-limiting step of the desorption path from HfO_2 surface.

In summary, we annealed $\text{HfO}_2/\text{SiO}_2/\text{Si}$ structures in D_2 at temperatures between 400 and 600°C and incorporated D amounts were determined by NRA. We found that D from the D_2 annealing atmosphere incorporates in amounts below 10^{13} cm^{-2} inside HfO_2 films, although much higher spurious H was found therein probably coming from impurities adsorbed from air (e.g., H_2O) or deposition residuals (CH_x groups from MOCVD precursors). This high spurious H content is under investigation. In addition, D amounts in the SiO_2 interlayer region ($\sim 10^{13} \text{ cm}^{-2}$) and near the HfO_2 film surfaces (up to $2.2 \times 10^{14} \text{ cm}^{-2}$) were also determined. The reaction of D_2 with HfO_2 surface region allows speculating for possible generation of monoatomic D during D_2 annealing. This new specie (monoatomic D) may introduce alternative reaction paths for the passivation of Si dangling bonds at HfO_2/Si interfaces. H amounts, depth distribution, and bonding type are critical information for the investigation of H-related instabilities in HfO_2 gate dielectric films.

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