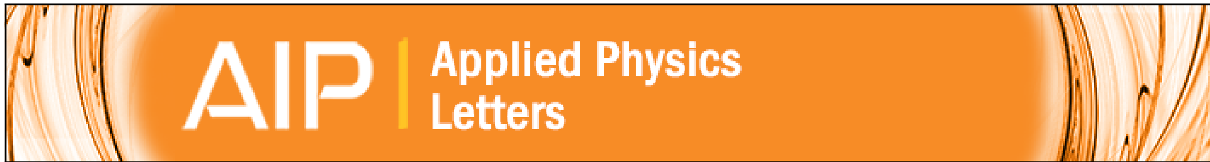

Hydrogen and deuterium incorporation and transport in hafnium-based dielectric films on silicon

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HTML ABSTRACT + LINKS

Hydrogen and deuterium incorporation and transport in hafnium-based dielectric films on silicon

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Hydrogen and deuterium incorporation into nitrided and non-nitrided hafnium silicate films on Si during thermal annealing in ^{1}H- and ^{2}H-containing atmospheres was investigated. ^{1}H profiling was accessed by means of nuclear resonant reaction profiling, whereas ^{2}H incorporation was quantified by nuclear reaction analysis. The effects of preannealing in different atmospheres and temperatures were determined, as well as the losses of ^{1}H and ^{2}H from these structures during postannealing in vacuum. The results reveal a rather uniform depth distribution of incorporated ^{1}H, in striking contrast with previous studies on hydrogen in silicon oxide and oxynitrides and hafnium oxide films on Si. These results are discussed in terms of the defects present in each one of the structures studied here. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1801682]

Intensive efforts have been made in recent years in order to retain SiO_2 or SiO_xN_y as the gate dielectric material in metal–oxide–semiconductor field-effect transistor (MOSFET) devices. However, the replacement of these materials with an alternative one holding a higher dielectric constant (high-*k* dielectrics) in advanced, ultralarge scale integration devices has enticed attention, owing to the exponential increase of the gate leakage current with decreasing gate dielectric film thickness.[1–9] Hydrogen incorporation mechanisms underlying the forming-gas sintering step responsible for passivation of the electrical activity near the dielectric/semiconductor interface has been little studied so far in high-*k* dielectrics.[10,11] Furthermore, deuterium (^{2}H) passivation of the SiO_2/Si or SiO_xN_y/Si interfaces was introduced[12] as a superior alternative to increase the stability of the H-electrically passivated dielectric /Si interface and thus reliability, deserving detailed study in high-*k* dielectrics.[13–18]

In this letter we present hydrogen and deuterium areal densities and concentration profiles in HfSiO, HfSiON, and HfSiN films on Si(001). The thermal stability of ^{1}H and ^{2}H as well as the effects of annealing previously to hydrogen or deuterium loading were also accessed by submitting the structures to annealing routines that simulate different steps of device manufacturing. We particularly examine the effect on the ^{1}H- and ^{2}H-incorporation dynamics of typical rapid thermal annealing at 1000 °C responsible for source and drain dopant activation, which also yields a densification of hafnium silicate gate dielectric films.[19]

The investigated thin films were all sputtered from a HfSi target in the following routes:

(i) reactive sputtering deposition of thick (50 nm), oxygen (nitrogen) defficient double oxide (nitride) films,[1] namely $(HfO_2)_x(SiO_2)_{1-x}$ and $(HfN)_x(Si_2N_3)_{1-x}$ with atomic ratio Si/Hf=1.3, hereafter called react-HfSiO and react-HfSiN.

(ii) thin HfSiO and HfSiON films (4 and 2 nm thick, respectively) produced by ultraviolet ozone oxidation[20] of HfSi and HfSiN films on Si (Si/Hf=1.7 ratio), with average stoichiometries $(HfO_2)_x(SiO_2)_{1-x}$ and $(HfNO)_x(SiNO)_{1-x}$, this last with O/N=3.5 atomic ratio, hereafter called UVOZ-HfSiO and UVOZ-HfSiON.

Hydrogen concentrations versus depth were determined by nuclear resonant reaction profiling (NRP) using the $^1H(^{15}N,\alpha\gamma)^{12}C$ nuclear reaction near the resonance at 6.385 MeV,[14] while deuterium areal densities were determined by NRA using the $^2H(^3He,p)^4He$ nuclear reaction[13] at 700 keV. Samples were annealed in a Joule-effect heated furnace or by rapid thermal annealing, in vacuum ($p \sim 10^{-7}$ mbar, vacuum annealing), in 50 mbar of N_2 (N_2 annealing), or in 50 mbar of O_2 (O_2 annealing). ^{1}H and ^{2}H loadings were carried, respectively, in 500 mbar of forming-gas (90% N_2:10% H_2) (FG annealing) or 50 mbar of ^{2}H (^{2}H annealing) for 30 min at 500 °C.

Figure 1 shows the excitation curves of the $^1H(^{15}N,\alpha\gamma)^{12}C$ nuclear reaction near the resonance at 6.385 MeV for the 50-nm-thick react-HfSiO (top) and react-HfSiN (bottom) structures. Since the NRP analyses were performed *ex situ*, there is a strong peak at the energy corresponding to the sample surface, see Fig. 1(inset), owing to H incorporation in this region as a consequence of exposure to air. Furthermore, the H concentration levels in the bulk of the as-deposited films (solid lines) are very low, as expected for sputter-deposited films in the present conditions. After FG annealing (open circles) hydrogen is found uniformly distributed from the surface down to the interface in both HfSiO and HfSiN films on Si, in contrast with previous results for SiO_2 as well as for HfO_2 films, where a peak is observed in

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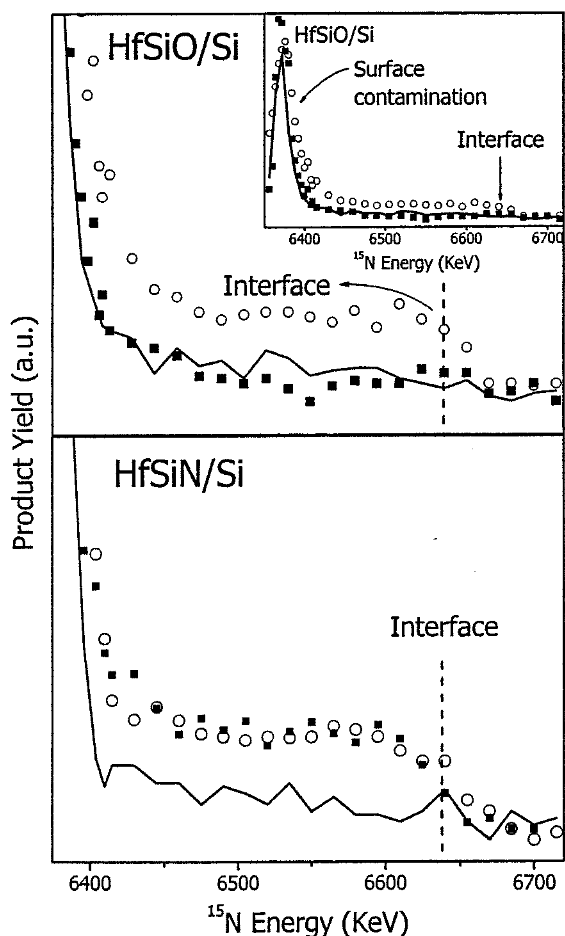

FIG. 1. Excitation curves of the $^{1}H(^{15}N,\alpha\gamma)^{12}C$ nuclear reaction around the resonance at 6.385 MeV from the 50-nm-thick react-HfSiO/Si (top) and react-HfSiN/Si (bottom) structures: as-prepared samples (solid lines); annealed in 500 mbar of forming-gas—90% N_2, 10% H_2—for 30 min at 500 °C (open circles); and annealing in forming-gas followed by vacuum-annealing for 30 min at 500 °C (closed squares). The inset shows the complete excitation curves, including the contributions from the surface contamination layer.

near-interface regions. Thus, the H-trapping sites, either dangling bonds, stoichiometry faults, or other chemically active defects are rather uniformly distributed in the react-HfSiO and react-HfSiN films, whereas they are strongly concentrated in the near-interface regions in SiO_2 or HfO_2 films on Si.[21,22]

The incorporation and stability of ^2H in the same react-HfSiO and react-HfSiN films on Si were accessed by annealing in $^2H_2$ instead of forming gas. The ^2H areal densities as determined by the $^2H(^3He,p)^4He$ nuclear reaction are shown in Fig. 2. Besides corroborating the effects observed in Fig. 1, Fig. 2 reveals that ^2H incorporates in substantially higher amounts into react-HfSiN than into the react-HfSiO.

Figure 3 shows the excitation curves of the $^{1}H(^{15}N,\alpha\gamma)^{12}C$ nuclear reaction from react-HfSiO/Si and react-HfSiN/Si structures first annealed in N_2 at 500 °C and then H loaded (triangles). One notices a reduction in the level of H incorporation into both react-HfSiO and react-HfSiN with respect to the non-preanneled samples. Thus, a fraction of H-trapping defects in both structures are removed during N_2 annealing, while keeping their corresponding depth distributions unchanged.

The much thinner UVOZ-HfSiO (4 nm) and UVOZ-HfSiON(2 nm) films on Si, were also annealed in $^2H_2$ atmo-

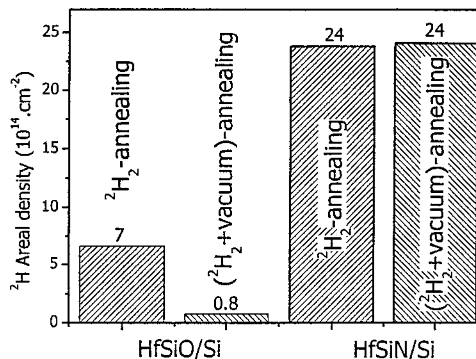

FIG. 2. Deuterium areal densities incorporated into the 50-nm-thick react-HfSiO/Si and react-HfSiN/Si structures after the indicated annealing sequences, as determined by nuclear reaction analysis using the $^2H(^3He,p)^4He$ nuclear reaction at 700 keV. D_2-loading at 450 °C for 30 min; vacuum-annealing at 500 °C for 30 min. The errors in the ^2H areal densities are 10%.

sphere. Table I shows the ^2H areal densities as determined by NRA using the $^2H(^3He,p)^4He$ nuclear reaction, obtained after submitting the films to different annealing routes prior to ^2H loading. Preannealing in N_2 or in O_2 reduced the ^2H incorporation in UVOZ-HfSiO whereas in UVOZ-HfSiON, ^2H incorporation is only reduced by O_2 preannealing. Table I reveals that there is a one order of magnitude larger reduction in the amount of incorporated ^2H in both UVOZ-HfSiO and UVOZ-HfSiON structures when submitted to rapid thermal preannealing at 1000 °C in N_2 or N_2 followed by O_2, as compared to those preannealed at 400–500 °C. These data indicate a strong reduction in defect density in these dielectric films, which may be correlated to the previously observed[19] densification of hafnium silicate films on Si at high temperatures. The N content, as measured by NRA

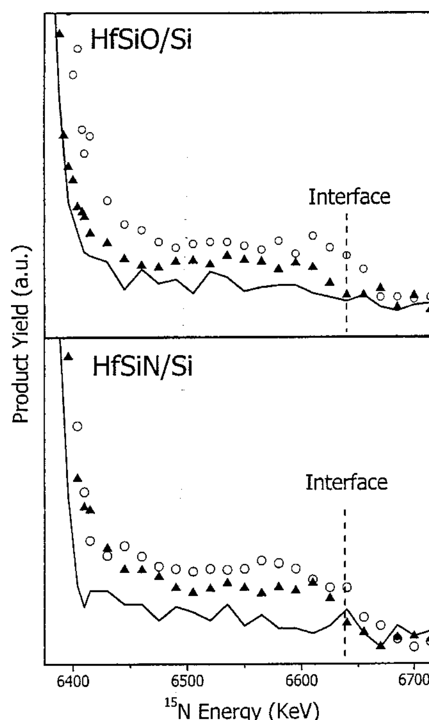

FIG. 3. Excitation curves of the $^{1}H(^{15}N,\alpha\gamma)^{12}C$ nuclear reaction around the resonance at 6.385 MeV from the 50-nm-thick react-HfSiO/Si and react-HfSiN/Si structures. The solid lines stand for the as-prepared samples, open circles for the forming-gas annealed samples, and triangles for the N_2 preannealed samples followed by forming-gas annealing.

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TABLE I. ^2H areal densities, as determined by nuclear reaction analysis using the $^2H(^3He,p)^4He$ nuclear reaction at 700 keV, for the 4 nm UVZO-HfSiO/Si and 2 nm UVZO-HfSiON/Si structures after the indicated annealing sequences, performed from left to right. $^2H_2$-loading and 450 °C preannealing were for 30 min, whereas 1000 °C rapid thermal preannealing were for 10 s. The precision in the ^2H areal densities is 10%.

Annealing sequences			^2H areal density (10^{14} cm^{-2})	
N_2 °C	O_2 °C	$^2H_2$ °C	HfSiO/Si 4 nm	HfSiON/Si 2 nm
⋯	⋯	500	8.6	3.5
450	⋯	500	4.9	4.1
⋯	450	500	5.7	1.4
450	450	500	2.2	0.8
1000	⋯	500	0.4	0.3
1000	1000	500	0.4	0.25

(not shown), decreases significantly during annealing in O_2 at 1000 °C.

The ^2H loading in as-prepared react- and UVOZ-samples cannot be directly compared for different reasons, including the following: (i) The very large difference in thickness of the two groups of samples, (ii) the differences in relative oxygen and nitrogen content and defect structures in the two groups, resulting from the two different preparation routes, and (iii) the thickness differences within the UVOZ-HfSiO and HfSiON group of samples, which may require a normalization to equal thicknesses. When normalized to equal thicknesses, the incorporated amounts of ^2H in non-preanneled UVOZ-HfSiO and UVOZ-HfSiONare rather similar.

In summary, hydrogen and deuterium were seen to incorporate in nitrided and non-nitrided hafnium silicate films on Si to amounts that exceed by one order of magnitude those found in silicon oxide and oxynitride films. This is a consequence of the more rigid metal silicate (nitrided or not) structures of the present work in which, compared to silicon oxide(oxynitride), a growth defect is less likely to be healed during annealing as this would require significant rearrangement of a number of neighboring bonds.[23–25] Preannealing in different atmospheres at moderate temperatures (400–500 °C) was able to strongly reduce the areal densities of incorporated hydrogen(deuterium), although their profiles remained unaltered. Different incorporated amounts for different preannealing atmospheres revealed the different nature of the H-trapping defects in nitrided and non-nitrided silicates, namely mainly structural defects in hafnium silicate and mainly stoichiometric ones in nitrided hafnium silicates. Three additional facts are also certainly influencing the incorporation of H in react- and UVOZ-samples, namely the different O–H and N–H bond strength, oxygen incorporation (stoichiometry completion), and N loss during annealing, owing mainly to N–O exchange.[21] Annealing at temperatures as high as 1000 °C implied an even larger reduction in defect density and N losses, and therefore in hydrogen(deuterium) incorporation. The bond rearrangements underlying this effect also explain the observed film densification during annealing at high temperatures.

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