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Thermochemical behavior of hydrogen in hafnium silicate films on Si

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HfSiO films on Si were sequentially annealed in vacuum, oxygen, hydrogen, or deuterium atmospheres followed by quantification of H and D by nuclear reaction analysis. The observed H(D) incorporation and desorption behaviors are discussed in terms of two H bonding states in the films. Si–H bonds are easier to break thermally and formation of these bonds can be suppressed by annealing in O_2 to fully oxidize Si atoms. O–H bonds are harder to break thermally. However, hydrogen atmospheres ease desorption of H in O–H species. The results indicate possible paths to achieve low H content in HfSiO gate dielectrics. © *2006 American Institute of Physics.*
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Materials with high dielectric constants (high-*k* materials) are being intensively investigated in order to find a replacement for SiO_2 as the gate dielectric material in Si-based metal-oxide-semiconductor field-effect transistors.[1,2] $(HfO_2)_{1-x}(SiO_2)_x$ mixed oxides,[3,4] alternatively called hafnium silicates (HfSiO for short), arose as promising gate dielectric materials because HfSiO films deposited on Si holding high dielectric constants while keeping appropriate thermal stability can be achieved. In addition, the presence of hydrogen in gate dielectrics constitutes a key feature, since H is known to critically influence device properties. Hydrogen at the dielectric/Si interface is necessary to passivate electrically active interfacial Si dangling bonds.[5,6] On the other hand, H in the bulk of gate dielectric films is a potential source of device instabilities[7,8] and therefore this bulklike H content must be minimized. Since Hf-based gate dielectrics commonly have H contents much higher than those found in thermally grown SiO_2,[9–11] understanding the nature of H incorporation and bonding in HfSiO films as well as developing possible ways to minimize H content is critical for achieving high quality and reliable HfSiO gate dielectrics.

We report here on quantitative investigation of hydrogen incorporation, bonding, and thermal stability in HfSiO films on Si sequentially annealed in vacuum, oxygen, hydrogen, or deuterium atmospheres. Hafnium silicates were deposited on Si(001) by metal-organic chemical vapor deposition run at 650 °C using $Hf[N(C_2H_5)_2]_4$ and $Si[N(CH_3)_2]_4$ precursors and O_2 as oxygen source. HfSiO films 4, 6, 8, 10, and 50 nm thick were produced with 30%, 60%, or 80% SiO_2 fraction. Channeled Rutherford backscattering spectrometry (not shown) failed to detect N residuals in the films, indicating N concentration below 5% (atomic). Samples were annealed in a Joule-effect heated furnace whose quartz tube was pumped down to a base pressure of 10^{-7} mbar. Each annealing was

performed for 30 min, either in vacuum or in a specific static gaseous atmosphere. Employed atmospheres were 1 mbar of O_2, 60 mbars of D_2 (H_2 95% enriched in the $^2H \equiv D$ isotope), or 600 mbars of forming gas (H_2:N_2, 10% H_2, so that H_2 partial pressure is also 60 mbars). Vacuum and O_2 annealings were performed at 800 °C, while forming gas and D_2 annealings were performed at 500 °C. The use of D_2 atmospheres is convenient because D_2 chemically mimics H_2 (forming gas) and also allows to distinguish atoms incorporated from the annealing atmosphere (D) from those previously existing in the films or incorporated from air (H).

Deuterium amounts incorporated into the 4, 6, 8, and 10 nm thick HfSiO films annealed in D_2 were determined by nuclear reaction analysis[12] employing 400 keV $^3He^+$ beams to induce the $D(^3He,p)^4He$ nuclear reaction. At this energy the cross section of the nuclear reaction is constant (within 3%) throughout the films[13] such that reaction yields are proportional to the total D amounts in the films. A sensitivity of approximately 10^{12} D cm^{-2} is achieved. Figure 1(a) shows incorporated D as a function of film thickness for samples containing 30% SiO_2. Incorporated D increases linearly with HfSiO film thickness, evidencing significant D incorporation in bulk regions of the films. This is in contrast to D incorporation in HfO_2/Si structures,[11] where D was seen incorpo-
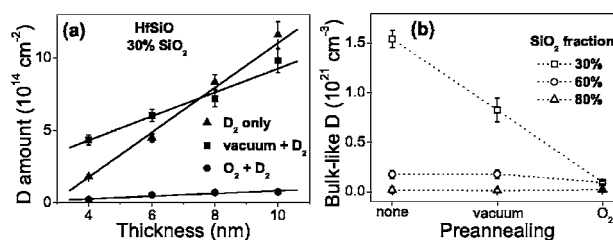

FIG. 1. (a) D amounts vs film thickness for the 30% SiO_2 HfSiO films after annealing in D_2 either with or without preannealing in vacuum or O_2. (b) Slopes derived by linear fitting of D amounts vs thickness data for the 30%, 60%, and 80% SiO_2 films.

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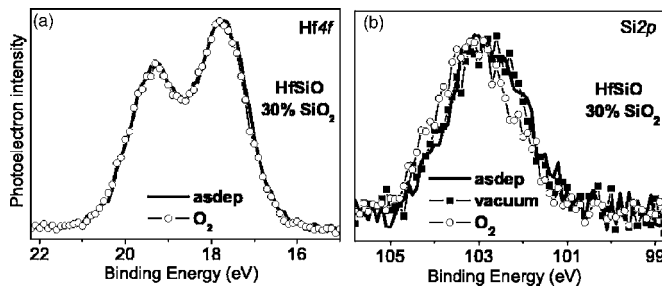
FIG. 2. X-ray photoelectron spectroscopy spectra in the (a) Hf 4f and (b) Si 2p regions taken from as-deposited and 800 °C-annealed films.
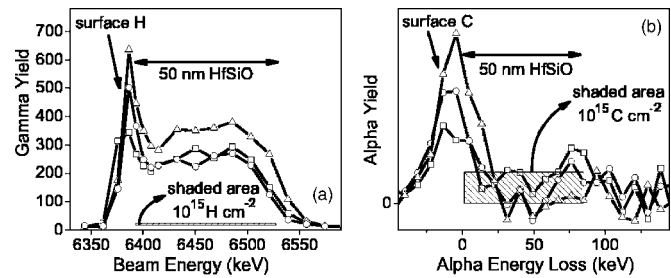

FIG. 3. H and C depth sensitive signals from 30%, 60%, and 80% (squares, circles, and triangles, respectively) SiO$_2$ as-deposited HfSiO films. (a) Excitation curves of the ^{1}H(^{15}N, $\alpha\gamma$)^{12}C nuclear reaction. (b) Alpha spectra of the ^{12}C(α, α)^{12}C elastic nuclear reaction taken from the same samples from (a). Shaded areas corresponding to 10^{15} H cm^{-2} or 10^{15} C cm^{-2} are shown for comparison purposes.

rated mainly in near-surface regions of the HfO$_2$ films, as well as in contrast to SiO$_2$/Si structures, where D incorporates mainly in the SiO$_2$/Si interfacial region.[12]

The slopes derived from the linear fitting of the experimental data on D amounts versus HfSiO thickness, expressing the concentration of bulklike D (in units of at. cm^{-3}), are shown in Fig. 1(b) for 30%, 60%, and 80% SiO$_2$ films annealed in D$_2$, either with or without preannealing in vacuum or O$_2$. For samples annealed in D$_2$, either with or without vacuum preannealing, one observes an increase of the concentration of bulklike D with decreasing SiO$_2$ fraction. On the other hand, for D$_2$ annealing performed after preannealing in O$_2$, there is essentially no dependence of incorporated D on the SiO$_2$ fraction. Moreover, the 30% SiO$_2$ silicate shows a marked decrease in D incorporation when preannealing was performed prior to D$_2$ exposure, the decrease being more pronounced when preannealing was performed in O$_2$.

The effects of preannealing on film chemistry were accessed by analyzing 10 nm thick HfSiO films by x-ray photoelectron spectroscopy. Mg Kα x-ray source and 30° photoelectron takeoff angle (relative to sample normal) were employed. Figure 2(a) shows Hf 4f photoelectron regions of the as-deposited and O$_2$-annealed 30% SiO$_2$ films. One observes that the Hf 4f peaks do not shift after annealing in O$_2$, indicating no change in the Hf oxidation state. On the other hand, the Si 2p signal shifts 0.3 eV towards higher binding energies after O$_2$ annealing [Fig. 2(b)]. Oxidation of Si substrate cannot be responsible for this shift since the analyzed 10 nm films are thick enough to attenuate signal coming from the HfSiO/Si interface, as evidenced by the absence of Si substrate signal at 99.6 eV. The Si 2p signal shift evidences that a significant fraction of the Si atoms in the 30% SiO$_2$ silicate film were in suboxidized states, which were converted into fully oxidized Si during O$_2$ annealing.

We suggest that annealing in D$_2$ forms Si–D bonds in these suboxidized Si atoms. Hence, when Si atoms become fully oxidized these D incorporation sites are eliminated, resulting in the observed decrease in D incorporation after preannealing in O$_2$ (Fig. 1). For the 60% and 80% SiO$_2$ films, shifts in Hf 4f and Si 2p signals (not shown) by O$_2$ annealing were below our experimental uncertainty (0.1 eV). These absences of significant shifts in the Si 2p spectra as well as the absences of significant changes in D incorporation after O$_2$ preannealing [Fig. 1(b)] are both related to the absence of significant concentration of suboxidized Si in these SiO$_2$-richer HfSiO films.

Hydrogen depth profiling in the 50 nm thick HfSiO films was accomplished using the ^{1}H(^{15}N, $\alpha\gamma$)^{12}C nuclear reaction near the resonance at 6.385 MeV.[14] By progressively in-

creasing the ^{15}N beam energy above the resonance energy the presence of H is sampled at progressively deeper layers in the films. Resulting excitation curves [Fig. 3(a)] show a surface peak at the resonance energy, corresponding to H at sample surface due to exposure to air, whereas signals at higher energies correspond to H inside the 50 nm HfSiO films. By integrating signals corresponding to H inside the films and comparing with that from a polystyrene standard one derives total H amounts inside the 50 nm HfSiO films to be (30, 28, and 44) ×10^{15} H cm^{-2} for the 30%, 60%, and 80% SiO$_2$ films, respectively. These H amounts correspond to average H concentrations of (6.0, 5.8, and 8.8) ×10^{21} H cm^{-3}, respectively.

In order to investigate whether part of the H inside the films could be in the form of C–H bonds remaining from deposition precursors, we employed the elastic ^{12}C(α, α)^{12}C nuclear reaction[15] and compared with a SiC wafer standard to quantify C in the HfSiO films. By analyzing the alpha spectra one could separate signal from C at sample surface (due to air exposure) from C inside the 50 nm films [Fig. 3(b)]. C amounts inside the as-deposited HfSiO/Si structures are at or below 10^{15} cm^{-2}, which is at least 20 times lower than the determined H amounts even when uncertainties in H and C amounts are taken into account. This implies C–H bond breaking during deposition and formation of new bonds between H and the other elements present in the films. Hf–H and Si–H bonds are both related to a local oxygen deficiency, since these bonds are replacing, respectively, Hf–O and Si–O bonds which are the only expected bonds in a stoichiometric, defect-free hafnium silicate. Therefore, both Hf–H and Si–H bonds tend to be removed by O$_2$ annealing. Since, differently from Si, we could never detect O$_2$-induced changes in Hf oxidation state (Fig. 2), we suggest that Hf–H bonds are a minor contribution to the H content in the HfSiO films.

^{1}H(^{15}N, $\alpha\gamma$)^{12}C excitation curves before and after annealing at 800 °C either in vacuum or in O$_2$ are shown in Fig. 4. One observes that the fraction of H lost during annealing depends on the SiO$_2$ fraction of the HfSiO films, the higher the SiO$_2$ fraction, the lower the H loss. Previous study in SiO$_2$ (Ref. 16) indicated that 800 °C annealing for 30 min completely desorbs H from Si–H bonds while promoting little desorption of H from O–H bonds. This desorption behavior reflects O–H bonds being stronger than Si–H bonds (typical bond energies are 5.1 and 3.9 eV, determined from reference data on the removal of one H atom from water and silane molecules, respectively). Hence, we attribute H loss
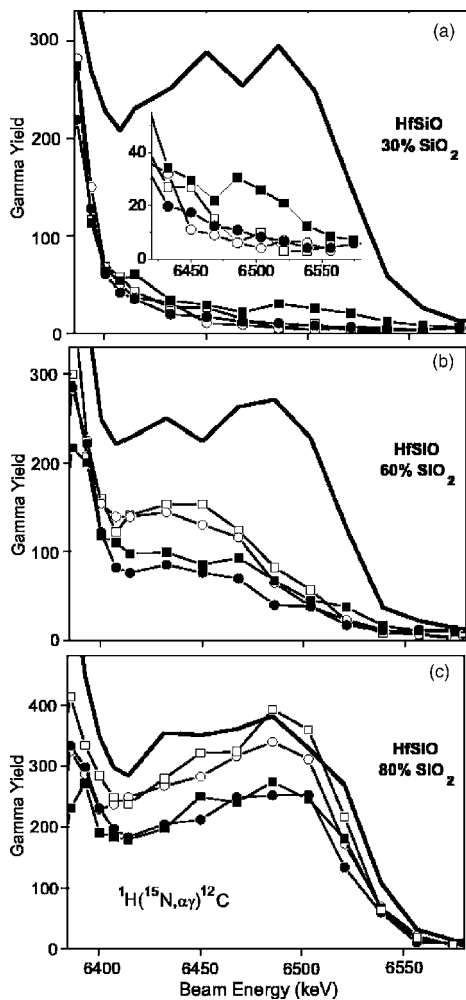
FIG. 4. Excitation curves of the $^1H(^{15}N,\alpha\gamma)^{12}C$ nuclear reaction for as-deposited (solid lines) and annealed 50 nm HfSiO films. Annealing was performed in vacuum (squares) or O_2 (circles) either followed by H_2 annealing (solid symbols) or not (empty symbols). The horizontal scale is chosen so as to show only signal coming from H inside the HfSiO films.

during this 800 °C annealing to be mainly due to breakage of Si–H bonds.

Moreover, the observed H losses (Fig. 4) were higher in the corresponding silicates where higher D incorporation was observed [see Fig. 1(b)], which can be justified by the fact that H loss and D incorporation are both related mainly to the dissociation and formation of Si–H(D) bonds. One can speculate that the existence of more Si–H bonds in films with lower SiO_2 fraction (and, therefore, less Si atoms), which is counterintuitive, is so because lower SiO_2 fraction (or, alternatively, higher HfO_2 fraction) would lead to increasing tendency of O deficiencies to move towards Si atoms. Such tendency was observed in phase-separated HfO_2/SiO_2,[17,18] where O deficiencies tend to move towards the SiO_2 side of HfO_2/SiO_2 interfaces. Nevertheless, this tendency of increasing Si–H for decreasing SiO_2 concentrations cannot be extrapolated to bulk HfO_2, where there are no Si atoms and, not surprisingly, no D incorporation was observed.[11]

Incorporation of H by annealing 30% SiO_2 samples in H_2 (forming gas) after either vacuum or O_2 preannealing [Fig. 4(a)] is consistent with D incorporation after the same preannealing (Fig. 1). However, for the higher SiO_2 silicates

one also observes H *loss* by annealing in H_2. It is interesting to note that H desorbed by annealing in H_2 at 500 °C could not be previously desorbed in vacuum or O_2 at 800 °C, indicating that the H_2 atmosphere eases the desorption process. We suggest that this H desorbed with the help of the H_2 atmosphere is in the form of O–H groups. This assignment is consistent with the observed resistance for thermal desorption (in vacuum) of H in the form of O–H groups inside SiO_2.[16] Moreover, differently from Si–H bonds which are related to a local O deficiency, O–H bonds are related to a local Si or Hf deficiency, or, alternatively, O excess. This reasoning relating O–H bonding to local O excess helps in understanding the observed role of the reducing H_2 atmosphere on H desorption. We speculate that the desorption reaction taking place is $H_2 + 2OH \rightarrow 2H_2O$. The H_2O products desorb, resulting in no remaining H in sites where there was an O–H group.

In summary, the H content in hafnium silicate films on Si was investigated by nuclear reaction analysis as a function of the postdeposition annealing to which the HfSiO films were exposed to. Based on the response of the H content to the annealing atmospheres we described two different H bonding states with different thermal behaviors. Si–H bonds form on suboxidized Si atoms and H in these bonds can be desorbed by an 800 °C, 30 min anneal. These H binding sites are eliminated after fully oxidation of Si atoms by annealing in O_2, leading to lower H incorporation after O_2 preannealing. On the other hand, H in O–H bonds are more resistant to thermal desorption, probably reflecting stronger bonding. Nevertheless, by employing a H_2 atmosphere, desorption of H in O–H groups is eased. These results indicate that by appropriately managing postdeposition annealing atmospheres HfSiO films with low H content can be achieved.

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