

# Hydrogen Barrier Layer Against Silicon Oxidation during Atomic Layer Deposition of Al<sub>2</sub>O<sub>3</sub> and HfO<sub>2</sub>

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Growth at moderate temperatures, below ~100°C, is shown to prevent interfacial silicon oxidation during atomic layer deposition of high-permittivity (high-κ) gate dielectrics on hydrogen-terminated Si(100). Trimethylaluminum, employed for aluminum oxide growth, leaves the hydrogen layer completely intact. Tetrakis(ethylmethylamido)hafnium partially scavenges the hydrogen layer during hafnium oxide nucleation, resulting in an interface composed of H-terminated silicon atoms and Si–O–Hf bridges. In both cases, high-κ dielectrics are grown without formation of interfacial SiO<sub>2</sub>. Once grown at low temperatures, subnanometer Al<sub>2</sub>O<sub>3</sub> layers effectively prevent interfacial SiO<sub>2</sub> formation during subsequent growth at higher temperatures required for optimum high- κ quality. This two-step deposition scheme may thereby be useful for gate-stack scaling. © 2007 The Electrochemical Society. [DOI: 10.1149/1.2405839] All rights reserved.

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Metal oxides such as hafnium oxide, aluminum oxide, or hafnium aluminate are being seriously considered for Si-based microelectronics. Such materials, their alloys with silicon and/or nitrogen, and laminated stacks are expected to replace silicon oxynitride (SiON) soon as gate insulators in metal-oxide-semiconductor field effect transistor (MOSFET) technology.<sup>1-3</sup> Their distinctive features are higher permittivity (high- $\kappa$ ) than for SiON and sufficient band offsets and thermodynamic stability in contact with silicon.<sup>4</sup> By increasing gate-stack capacitance, the high- $\kappa$  materials increase device speed and/or reduce gate leakage.<sup>1</sup> High- $\kappa$  dielectrics should thereby help sustain the scaling of commercial silicon microprocessor technology, because the thickness of the traditional SiON gate insulator has been reduced close to its fundamental physical limit of ~1 nm where insulating properties disappear.<sup>5,6</sup>

For high-k dielectrics on Si to be competitive, however, good chemical and electrical quality of films and interfaces is essential. Minimum high- $\kappa$  layer thickness (~1 to 3 nm) and low gate leakage need to be achieved. Forming sufficiently continuous films with low surface roughness on essentially oxide-free Si has turned out to be a nontrivial task from a nucleation and growth chemistry perspective. In principle, conformal compound layers can be deposited with monolayer-level thickness control using a variant of chemical vapor deposition (CVD) known as atomic layer deposition (ALD).<sup>7,8</sup> This technique is based on alternating exposures of precursors with selfsaturating surface adsorption properties, e.g., a metal oxide can be grown from a metal containing molecule (M) and water vapor  $(H_2O)$  according to the sequence  $M-H_2O-M-H_2O-...$ . Popular precursor combinations include trimethylaluminum [TMA,  $Al(CH_3)_3$ ] and water for  $Al_2O_3$  growth<sup>8,9</sup> and hafnium tetrachloride (HfCl<sub>4</sub>) and water for HfO<sub>2</sub> growth.<sup>10</sup> The metal precursors are generally designed to react with OH groups, and ultrathin layers can indeed be grown in a linear fashion on hydrophilic  $SiO_2$  substrates.<sup>8,10</sup> However, such  $SiO_2$  nucleation layers partially compromise the benefit of high-k dielectrics by reducing the effective gate stack capacitance.

In an attempt to obtain atomically sharp Si/high-κ interfaces, oxide-free, H-terminated Si (H/Si) substrates have been utilized. Such H/Si(100) can be prepared quickly and reproducibly by a hydrofluoric acid (HF) wet etch ("HF-last") followed by rinsing in ultrapure deionized water.<sup>11</sup> H/Si is remarkably resistant to oxidation in laboratory air and even in O<sub>2</sub>- or H<sub>2</sub>O-containing environments at temperatures as high as 300°C.<sup>12,13</sup> Recently, H/Si reactiv-

ity with respect to O<sub>2</sub>, H<sub>2</sub>O, NH<sub>3</sub>, and high-κ precursors has been reviewed comprehensively.<sup>9</sup> While low surface reactivity may be advantageous in terms of oxidation resistance, it also causes poor nucleation characteristics of many ALD-grown high-κ films, resulting in nonlinear growth kinetics and the formation of discontinuous and electrically leaky gate stacks. Indeed, this is the case for the HfCl<sub>4</sub>/water<sup>10,14,15</sup> and Al(CH<sub>3</sub>)<sub>3</sub>/water<sup>9,14,16</sup> processes at 300°C. More importantly, interfacial SiO<sub>2</sub> is formed during growth, partially defeating the purpose of starting with an O-free substrate.<sup>9,14,15</sup> Nucleation can be enhanced, and more linear growth achieved, when employing in situ activation of the H/Si surface by a very reactive oxygen precursor such as O<sub>3</sub>. However, this results in even more interfacial SiO<sub>2</sub>.<sup>17,18</sup>

In the present work, we demonstrate an approach to minimize interfacial SiO<sub>2</sub> formation on H/Si(100). This approach is based on ALD growth at reduced temperatures, e.g., 50–100°C, exploiting the remarkable kinetic stability of H/Si against oxidation.<sup>9</sup> We use in situ transmission Fourier transform infrared (FTIR) absorption spectroscopy to study the early stages of the ALD process and the nature of the Al<sub>2</sub>O<sub>3</sub>/Si and HfO<sub>2</sub>/Si interfaces. For Al<sub>2</sub>O<sub>3</sub> growth, we examine the TMA/water system. Because the incorporation of impurities can be substantial at low growth temperatures, <sup>19</sup> we also discuss a two-step low/high temperature growth scheme that allows for minimum impurity concentration while ensuring minimum interfacial layer thickness. For HfO<sub>2</sub> growth, we use tetrakis(ethylmethylamido)hafnium [TEMAH, Hf(NC<sub>2</sub>H<sub>5</sub>CH<sub>3</sub>)<sub>4</sub>] and water. TEMAH has been shown to be particularly suitable for the formation of impurity-free, conformal, and smooth films at deposition temperatures as low as 50°C.<sup>20</sup>

## Experimental

The substrates are double-side polished, float-zone grown, and lightly doped ( $\rho \sim 10 \ \Omega \ cm$ ) Si(100) wafers. Hydrogen termination is achieved by HF etching (~20%, 1 min) after RCA cleaning.<sup>11</sup> The H-terminated silicon samples are immediately loaded into home-built, nitrogen-purged ALD reactor chambers<sup>9,21,22</sup> connected to Fourier transform infrared (FTIR) spectrometers for in situ surface analysis. The infrared transparent KBr windows of the ALD cells are protected from contamination by shutters or gate valves during precursor exposures. High- $\kappa$  dielectric growth is performed by alternating metal precursor and water pulses delivered in N<sub>2</sub> carrier gas, with N<sub>2</sub> purge between precursor pulses. Metal precursors are TMA (exposure per pulse: ~5 × 10<sup>7</sup> langmuir) for Al<sub>2</sub>O<sub>3</sub> growth and TEMAH (exposure per pulse: ~3 × 10<sup>4</sup> langmuir) for HfO<sub>2</sub> growth. Isotopically marked water (D<sub>2</sub>O) is employed as oxy-

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Figure 1. (Color online) In situ transmission infrared spectra of H-terminated Si(100) (a) before and (b)–(f) after the specified number of TMA and water exposures at 50°C, (g) after subsequent inert anneal to 300°C, and (h) after a final water exposure at 300°C. The reference surface for oxide phonon and C–H stretch regions was H-terminated Si (because no independent reference surface is available for spectrum (a) from H-terminated Si, the ideal spectrum is indicated with a dotted line) and for Si–H stretching region was SiO<sub>2</sub>/Si.

gen precursor to ensure clear spectral separation of hydroxyl groups on the sample from those present in the infrared optical setup. This is expected to leave growth chemistry unaffected. Growth temperatures are 50°C for Al<sub>2</sub>O<sub>3</sub> and 100°C for HfO<sub>2</sub>, chosen to be as low as possible while ensuring (Al<sub>2</sub>O<sub>3</sub>) good temperature control in the experimental setup used and (HfO<sub>2</sub>) consistency with previous studies. Postdeposition annealing via resistive heating is performed in situ under purified N<sub>2</sub> gas purge (oxygen impurities <10<sup>-6</sup> ppm). During infrared (IR) analysis, the sample is kept at a constant temperature of 50°C (Al<sub>2</sub>O<sub>3</sub> experiments) or 60°C (HfO<sub>2</sub> experiments) to minimize artifacts due to bulk Si phonon absorption. The IR beam is incident at 70° from the surface normal (approximately the Brewster angle).

## **Results and Discussion**

We start by briefly reviewing the structure and infrared spectrum of the starting surface, i.e., wet-chemically H-terminated Si(100). Its infrared spectrum (Fig. 1a) exhibits a structured Si–H stretching band, reflecting the fact that the H/Si(100) surface is atomically rough on the double-layer scale, with several types of hydride termination: mono-(~2085 cm<sup>-1</sup>), di-(~2110 cm<sup>-1</sup>), and trihydride (~2135 cm<sup>-1</sup>) species.<sup>23</sup> A very small concentration of chemical defects (oxygen in Si–H surface backbonds) is evidenced by a signal at ~2250 cm<sup>-1.24</sup> We have previously shown that H/Si is chemically stable during water vapor exposure at temperatures as high as  $300^{\circ}C.^{9,12}$  In the following, we therefore concentrate on dielectric growth initiated by metal precursor pulses.

Aluminum oxide growth.— First, we discuss low-temperature Al<sub>2</sub>O<sub>3</sub> growth. The first TMA exposure at 50°C (Fig. 1b) causes the rise of modes due to Al–CH<sub>3</sub> bonding (–CH<sub>3</sub> umbrella mode at  $\sim$ 1220 cm<sup>-1</sup> and C–H stretching mode at  $\sim$ 2940 cm<sup>-1</sup>).<sup>25-27</sup> A Si–CH<sub>3</sub> minority species ( $\sim$ 1270 cm<sup>-1</sup>) is formed as well,<sup>28,29</sup> indicating some transfer of methyl groups to Si substrate defect sites.<sup>12</sup> Low-frequency features (800–900 cm<sup>-1</sup>) are likely due to Al–O bonding,<sup>30</sup> indicating partial oxidation of the Al by O-containing trace impurities in the precursor gas stream.<sup>31</sup> How-



**Figure 2.** Si-H stretch mode intensity as a function of the number of  $Al_2O_3$  and  $HfO_2$  ALD cycles performed at the specified temperatures (H-terminated Si = 1). Data for  $Al_2O_3$  grown at 300°C was extracted from spectra in Ref. 12.

ever, attack of the Si surface is insignificant. The H/Si signal intensity originating from O-free surface sites ( $\sim 2085-2135 \text{ cm}^{-1}$ ) is undiminished (Fig. 1b and 2) and essentially full H coverage is therefore maintained (a minor increase in Si–H stretch intensity is believed to be due to changes in the dielectric environment, but such effect is small). A slight broadening indicates perturbation of the H–Si vibrational modes by interaction with the partially oxidized Al(CH<sub>3</sub>)<sub>x</sub> film physisorbed on top of the H/Si layer. We note that the small H–Si feature at  $\sim 2250 \text{ cm}^{-1}$ , originating from minority defect sites with oxygen in Si–H surface backbonds, is suppressed by TMA exposure, indicating that TMA may chemisorb at such sites.

The subsequent water pulse (Fig. 1c) fully oxidizes the Al and causes the loss of most (though not all) Al-bonded methyl groups, as expected for a good ALD growth. Infrared signals originating from H/Si (Fig. 2) and from Si-bonded methyl groups remain undiminished. Also, there is no evidence of H bonded to oxidized Si atoms  $(O_n$ -Si-H, 2130–2300 cm<sup>-1</sup>)<sup>24</sup> or of SiO<sub>2</sub> phonon signals (ca. 1000–1200 cm<sup>-1</sup>).<sup>32</sup> Based on phonon intensity calibration using SiO<sub>2</sub> films of known thickness,<sup>12,21</sup> we find that the amount of SiO<sub>2</sub> is substantially below a total average thickness of 1 Å. This shows that the water pulse leaves both the hydrogen layer and the Sibonded methyl groups fully intact, and Si oxidation is small.

These characteristics of surface reactivity at 50°C are in marked contrast to what was previously observed during precursor exposures at 300°C, otherwise employing identical exposure conditions.<sup>9,12,14</sup> At 300°C, the first TMA pulse and (more so) the subsequent water pulse scavenge H from the surface, causing a H loss of 60% during the first ALD cycle (Fig. 2), and a 1.2 Å thick interfacial SiO<sub>2</sub> film is formed, catalyzed by surface Al. In contrast, at 50°C the Al<sub>2</sub>O<sub>3</sub> is formed on top of a nearly unaffected H layer, and interfacial SiO<sub>2</sub> formation does not occur. This shows that hydrogen provides a barrier layer against silicon oxidation when exposed to Al<sub>2</sub>O<sub>3</sub> ALD precursors at moderate temperatures.

The remarkable stability of the H layer at 50°C becomes even more evident when following  $Al_2O_3$  growth during subsequent ALD cycles. A second TMA exposure (Fig. 1d) again deposits  $Al-(CH_3)_x$ species on the surface. These are subsequently oxidized by the second water pulse (Fig. 1e), leaving the H–Si signal intensity unaffected (Fig. 2), without the appearance of any distinct SiO<sub>2</sub> phonon mode or incorporation of oxygen in backbonds (O<sub>x</sub>Si–H). Even after 8.5 ALD cycles (Fig. 1f), the interface remains oxide-free. In-



Figure 3. (Color online) In situ transmission infrared spectra of H-terminated Si(100) (a) before and (b)–(e) after the specified number of TEMAH and water exposures at 100°C and (f) after subsequent inert anneal to 300°C. The reference surface for oxide phonon and C–H stretch regions was H-terminated Si and for Si–H stretching region was SiO<sub>2</sub>/Si.

deed, the integrated intensity of the H–Si signal is not diminished during  $Al_2O_3$  growth at 50°C, as shown in Fig. 2. At 50°C, thick  $Al_2O_3$  films can thus be grown on H/Si while leaving the protective H layer intact. In contrast,  $Al_2O_3$  growth at 300°C results in nearcomplete H removal after 2 ALD cycles (Fig. 2) and formation of 4 Å interfacial SiO<sub>2</sub> underneath thick  $Al_2O_3$  films.<sup>12</sup>

*Hafnium oxide growth.*— With the TEMAH and water precursors,  $HfO_2$  dielectric constant and insulating properties are essentially independent of temperature between 200 and 300°C.<sup>33</sup> Given that impurity-free films grow even at deposition temperatures as low as 50°C,<sup>20</sup> we expect gate dielectrics formed at 100°C to still exhibit comparable electrical quality. Also, growth is nearly linear on H/Si, indicating that near-continuous films are formed.<sup>22,33</sup> This is in contrast to films formed by HfCl<sub>4</sub> and water, which require growth temperatures around 300°C for acceptable electrical quality.<sup>34</sup> and suffer from islanding on H/Si.<sup>10,14,15</sup> Besides high film quality and good nucleation at low temperatures, the TEMAH-water process also exhibits relatively low interfacial oxide formation on H/Si; even at the fairly high temperature of 250°C, no more than 5 Å of interfacial SiO<sub>2</sub> are formed.<sup>33</sup> At 100°C, an even sharper high-κ/Si interface may be expected.

An initial TEMAH exposure of H/Si(100) causes a decrease of Si–H vibrational intensity by  $\sim$  10% (Fig. 3a and b, and Fig. 2). The TEMAH thus clearly reacts with H/Si at moderate temperatures and at much lower exposures than is the case for TMA (TEMAH exposure = 0.06% of TMA exposure in the present study, and Al<sub>2</sub>O<sub>3</sub> islanding occurs when using such low TMA exposures).<sup>16</sup> It is this reaction that gives rise to the near-linear growth behavior reported previously.<sup>22</sup> Upon subsequent  $D_2O$  exposure (Fig. 3c), no additional loss of surface hydride occurs. Additional precursor cycles cause gradual H loss during TEMAH exposure (Fig. 3d and 2). However, half of the surface hydrogen remains in place after 20-30 TEMAH/D<sub>2</sub>O exposure cycles (Fig. 3e and 2). The absorption band of Si-H stretch mode also red-shifts and becomes broader, suggesting a chemical interaction in the immediate vicinity of Si–H species induced by Hf-containing structures.<sup>35</sup> The observation of C–H symmetric and asymmetric stretch modes in the spectra region of 2800–3000  $\text{cm}^{-1}$  (Fig. 3) is due to organic ligands remaining inside and on top of the growing film,<sup>36</sup> especially after TEMAH exposure.



**Figure 4.** (a) I–V and (b) high-frequency C–V characteristics of Hg/HfO<sub>2</sub>/H/p-Si(100) MOS capacitors measured with a Hg probe (10 kHz, area  $7.3 \times 10^{-4}$  cm<sup>2</sup>). The HfO<sub>2</sub> was deposited using 20 ALD cycles of TEMAH and water exposures at 100°C, resulting in an effective HfO<sub>2</sub> thickness of ~18.7 Å as determined by Rutherford backscattering spectrometry.

In addition, the in situ infrared characterization of HfO<sub>2</sub> growth reveals that no interfacial SiO<sub>2</sub> (<0.5 Å) is formed between the high- $\kappa$  layer and silicon substrate at moderate deposition temperatures. Instead of features attributed to SiO<sub>2</sub>, a feature at ~1000 cm<sup>-1</sup> indicates that the interfacial structure is likely Si–O–Hf (Fig. 3).<sup>37</sup> The amount of interfacial Si–O–Hf saturates after ~10 ALD cycles.<sup>22</sup> Because half of the initial Si–H is still present, we infer that the Si–O–Hf species involve approximately half of the surface Si atoms.

As interfacial Si–H likely reduces the areal density of interfacial covalent bonds, poor  $HfO_2$ –Si adhesion could be suspected. A simple Scotch tape test, i.e., the application and subsequent removal of adhesive tape, coupled with Rutherford backscattering spectrometry (RBS) measurements of surface composition before and after the test, did not provide evidence for facile  $HfO_2$  delamination.<sup>38</sup>

To assess the electrical quality of these unconventional HfO<sub>2</sub>/H/Si stacks, we have recorded current-voltage (I-V) and high-frequency capacitance-voltage (C-V) characteristics of Hg/HfO<sub>2</sub>/H/p-Si MOS capacitors using a mercury probe (Fig. 4). Gate leakage (Fig. 4a) at moderate gate voltages ( $\sim 10^{-5} \text{ A/cm}^2$ ) is more than seven orders of magnitude lower than what is acceptable for high-performance MOSFET applications (100 A/cm<sup>2</sup> and more<sup>39</sup>), proving that continuous HfO<sub>2</sub> layers are formed. The C-V characteristics (Fig. 4b) show that interface state density  $(D_{it})$  and the extent of charge trapping are low (we refrain from a quantitative evaluation of the C–V data, because accurate gate-stack-capacitance measurements may be hampered by frequency-dependent artifacts when employing the mercury probe technique). Low  $D_{it}$  without a forming gas anneal is possibly due to the large areal density of residual interfacial H, passivating any dangling bonds. We conclude that good-quality HfO<sub>2</sub> layers can be grown on H/Si using a lowtemperature ALD process.

Thermal stability and two-step deposition process.— We have seen that nearly interfacial SiO<sub>2</sub>-free Al<sub>2</sub>O<sub>3</sub> layers can be grown on H/Si at moderate temperatures. This may be expected to result in superior capacitance (electrical thickness) scaling compared to conventional growth at the more typical growth temperature of  $\sim 300^{\circ}$ C. However, when grown at moderate temperatures, the quality of the Al<sub>2</sub>O<sub>3</sub> itself is inferior, as indicated by a lower density.<sup>41</sup> For example, the infrared spectra in Fig. 1c and e demonstrate a higher degree of CH<sub>x</sub> incorporation, consistent with an increased amount of hydrogen detected in low-temperature grown films.<sup>19,41</sup> Such hydrocarbon species can be removed by higher temperature



**Figure 5.** In situ transmission infrared spectra for  $Al_2O_3$  films on H-terminated Si(100) formed during 8–12 ALD cycles, employing (bottom) conventional constant temperature growth at 300°C and (top) a two step 50°C/300°C scheme. Reference surface was H-terminated Si.

processing. We therefore propose that good-quality Al<sub>2</sub>O<sub>3</sub> films with reduced interfacial SiO<sub>2</sub> thickness can be fabricated using a two-step deposition process: (*i*) Initial growth at moderate temperatures (<100°C) of a very thin Al<sub>2</sub>O<sub>3</sub> film (e.g., ~10 Å) to avoid interfacial SiO<sub>2</sub> formation while achieving film uniformity, followed by (*ii*) higher temperature (~300°C) growth to reduce carbon impurities and obtain a good-quality gate dielectric, until the desired total film thickness is reached. With this process, the thin Al<sub>2</sub>O<sub>3</sub> film initially formed acts as a diffusion barrier, preventing O from accessing the Si substrate during growth at 300°C. In the following, we examine the relevant process steps individually with infrared spectroscopy.

Starting with the 50°C-grown film discussed in a previous section (Fig. 1f), the sample is first annealed to 300°C in the inert N<sub>2</sub> carrier gas (Fig. 1g). The methyl groups partially decompose, while the feature due to interfacial H/Si decreases in intensity to about 60% of the H/Si(100) intensity (Fig. 2). A water pulse at 300°C (Fig. 1h) decomposes all methyl groups, leading to higher quality Al<sub>2</sub>O<sub>3</sub> such as that formed at this conventional Al<sub>2</sub>O<sub>3</sub> growth temperature. Still, the Si-H stretch band retains 40% of its original intensity (Fig. 2), demonstrating that interfacial H is still present in appreciable quantities after the oxidizing anneal. In line with this finding, despite some overlap with the Al<sub>2</sub>O<sub>3</sub> phonon tail, no significant longitudinal-optical phonon mode of SiO<sub>2</sub> ( $\sim 1200 \text{ cm}^{-1}$ ) emerges, demonstrating that interfacial SiO<sub>2</sub> formation is prevented. During the next growth cycle at 300°C (Fig. 2 and 3), the hydrogen layer still exhibits  $\sim 40\%$  of the initial coverage and continues to act as a barrier layer against interfacial Si oxidation.

Figure 5 shows Al<sub>2</sub>O<sub>3</sub> phonon spectra for 8–12 cycle Al<sub>2</sub>O<sub>3</sub> films grown conventionally at 300°C (Fig. 5, bottom) and via the two-step process proposed herein (Fig. 5, top). Estimated thicknesses, based on published data for Al<sub>2</sub>O<sub>3</sub> thickness increase per ALD cycle (~1.2 Å/cycle at 50°C; ~0.95 Å/cycle at 300°C),<sup>9,41</sup> are 8 and 11 Å Al<sub>2</sub>O<sub>3</sub> for the 300°C films and 12 Å Al<sub>2</sub>O<sub>3</sub> for the 50/300°C film. The infrared spectra show that amorphous Al<sub>2</sub>O<sub>3</sub> is grown in both cases, identified by a characteristic longitudinal-optical phonon mode at ~950 cm<sup>-1</sup>. Furthermore, they prove that interfacial SiO<sub>2</sub> formation is greatly reduced by initial low-temperature growth ( $\leq 1.5$  vs 4 Å SiO<sub>2</sub>).<sup>9,12</sup>

The fact that high-quality HfO<sub>2</sub> can be formed at temperatures as

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low as ~100°C, as indicated by a low concentration of hydrocarbons (Fig. 3e) and other impurities,<sup>20</sup> makes a similar two-step process for HfO<sub>2</sub> less important. However, the passivating effect of interfacial hydrogen is also operative during thermal processing of HfO<sub>2</sub>. For instance, much of the interfacial H remains in place during inert gas anneal to 300°C (Fig. 3f), and interfacial SiO<sub>2</sub> formation (with hydroxyl groups from the HfO<sub>2</sub> film as oxygen source),<sup>22</sup> accordingly is insignificant, in line with the Al<sub>2</sub>O<sub>3</sub> results.

Finally, we note that anneals up to ~1000°C are required for transistor fabrication. Such anneals can result in significant interfacial rearrangements. For example, for HfO<sub>2</sub> layers grown at 100°C, interfacial H desorbs and ~7 Å SiO<sub>2</sub> form during inert 700°C anneals, indicating that excess oxygen in the HfO<sub>2</sub> film (for example, in the form of hydroxyl groups) can react with the depassivated Si substrate.<sup>22</sup> However, gate electrodes are present during device anneals, many of which tend to getter diffusing oxygen.<sup>42</sup> In this case, sharp Si/high- $\kappa$  interfaces can be preserved during high-temperature processing.

# Conclusions

Utilizing the TMA/water ALD process at 50°C,  $Al_2O_3$  films can be grown on H/Si(100) while leaving the H termination intact; the H layer acts as a barrier that prevents interfacial Si oxidation. Only a few covalent bonds are formed at the  $Al_2O_3$ –H/Si interface. In most locations, the  $Al_2O_3$  film can therefore likely be regarded as physisorbed on the H/Si substrate. The exact nature of interfacial bonding and  $Al_2O_3$  film adhesion are important objects of future study. By contrast,  $Al_2O_3$  growth at 300°C results in near-complete H removal and formation of 4 Å interfacial SiO<sub>2</sub>.<sup>9,12</sup>

HfO<sub>2</sub> growth from TEMAH and water at 100°C results in partial H removal from the H/Si(100) substrate by the metal precursor, with formation of Si-O-Hf bridges; however, interfacial Si oxidation is prevented as well. Such HfO2/H/Si stacks exhibit good electrical quality, with low gate leakage and interface state density. Even after inert anneal at 300°C, significant H passivation remains in place both for  $Al_2O_3$  (~60% of a monolayer) and for HfO<sub>2</sub> (~35%), and SiO<sub>2</sub> formation is minimal. High-quality  $Al_2O_3$  films with drastically reduced interfacial SiO<sub>2</sub> thickness (from 4 to  $\leq$  1.5 Å SiO<sub>2</sub>) can be fabricated using a two-step deposition process. First, a sharp Si-Al<sub>2</sub>O<sub>3</sub> interface is ensured via initial growth at moderate temperature, then high-quality Al<sub>2</sub>O<sub>3</sub> growth is performed at 300°C. The thin Al<sub>2</sub>O<sub>3</sub> film initially formed acts as a diffusion barrier, impeding O from accessing to the Si substrate during growth at 300°C. We conclude that H termination of Si can be maintained during ALD (and likely also CVD) growth of oxides utilizing water as the O precursor if low to moderate temperatures (e.g., no higher than 100°C) are maintained during formation of an initial closed metal oxide film.

It may seem surprising that  $SiO_2$  formation does not occur during  $HfO_2$  growth, despite partial removal of interfacial hydrogen during the first TEMAH exposure. We propose that this may be related to details of interface structure near Si–O–Hf bridging arrangements thus formed. The bulky metal precursor itself clearly is not able to scavenge all surface H, due to steric hindrance. Therefore, residual H-passivated sites may surround each site reacted with TEMAH. Our results suggest that, given such a local bonding arrangement, there is no facile pathway for H<sub>2</sub>O molecules or O atoms/ions to move directly into the Si subsurface layer. Molecular dynamic calculations will be required to estimate the activation barrier and probability of O insertion near such depassivated sites.

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