Engineering High-k/SiGe Interface with ALD Oxide for Selective GeOₓ Reduction

Mahmut S. Kavrik, Peter Ercius, Joanna Cheung, Kechao Tang, Qingxiao Wang, Bernd Frubberger, Moon Kim, Yuan Taur, Paul C. McIntyre, and Andrew C. Kummel

ABSTRACT: Suppression of electronic defects induced by GeOₓ at the high-k gate oxide/SiGe interface is critical for implementation of high-mobility SiGe channels in complementary metal–oxide–semiconductor (CMOS) technology. Theoretical and experimental studies have shown that a low defect density interface can be formed with an SiOₓ-rich interlayer on SiGe. Experimental studies in the literature indicate a better interface formation with Al₂O₃ in contrast to HfO₂ on SiGe; however, the mechanism behind this is not well understood. In this study, the mechanism of forming a low defect density interface between Al₂O₃/SiGe is investigated using atomic layer deposited (ALD) Al₂O₃ insertion into or on top of ALD HfO₂ gate oxides. To elucidate the mechanism, correlations are made between the defect density determined by impedance measurements and the chemical and physical structures of the interface determined by high-resolution scanning transmission electron microscopy and electron energy loss spectroscopy. The compositional analysis reveals an SiOₓ rich interlayer for both Al₂O₃/SiGe and HfO₂/SiGe interfaces with the insertion of Al₂O₃ into or on top of the HfO₂ oxide. The data is consistent with the Al₂O₃ insertion inducing decomposition of the GeOₓ from the interface to form an electrically passive, SiOₓ-rich interface on SiGe. This mechanism shows that nanolaminate gate oxide chemistry cannot be interpreted as resulting from a simple layer-by-layer ideal ALD process, because the precursor or its reaction products can diffuse through the oxide during growth and react at the semiconductor interface. This result shows that in scaled CMOS, remote oxide ALD (oxide ALD on top of the gate oxide) can be used to suppress electronic defects at gate oxide semiconductor interfaces by oxygen scavenging.

KEYWORDS: SiGe CMOS, low-power electronics, high-mobility transistor, high-k dielectrics, Al₂O₃, HfO₂ interface trap charge, atomic layer deposition

INTRODUCTION

SiGe alloys are employed as stressor layers in mainstream complementary metal–oxide–semiconductor (CMOS) transistors and are being investigated as p-type field effect transistor (p-FET) channels due to their high mobility¹ and ease of integration into CMOS.² Thermally stable HfO₂ gate oxides with high dielectric constants reduce CMOS device power consumption.³⁴ SiGe p-FETs with high-k gate dielectrics, which have low defect interfaces, can provide better electrostatic control of the channel and higher drive current for low gate bias voltage. Conversely, a high density of interface defects between the high-k gate oxide and the SiGe channel degrades the device performance metrics, such as subthreshold slope, and reduces the on/off current ratio.⁵ The main challenge for implementing SiGe FETs is the binary atom termination (Si–Ge) of the surface which results in the formation of SiGeOₓ mixed oxides and dangling bonds on both Si and Ge atoms.⁶⁻⁷ GeOₓ and associated dangling bonds are the main sources of defects producing interface-trapped charge (Dₓ), whereas SiOₓ is a stable oxide that forms a nearly defect-free interface according to theoretical calculations.⁸

Previously, several techniques, such as nitride and sulfur passivation on Si₀.₇Ge₀.₃(001), were studied with Al₂O₃ gate oxides, and a reduction in the interface defect density via...
suppression of GeO formation was reported. However, similar low defect density interfaces could not be established with HfO gate oxide. This is because oxygen containing species, such as excess H2O, OH, and/or O, can diffuse through HfO during atomic layer deposition (ALD), forming GeO defects on the SiGe surface; in addition, the nature of HfO allows diffusion of Ge and GeO to the top surface of the oxide and TMA induced GeO decomposition. Recently, HfO/SiGe interfaces formed with Al2O3–HfO nanolaminates (NL) gate dielectric stacks were found to have a low interface state density, and it was hypothesized that the mechanism was reduction of GeO out-diffusion during ALD. Theoretical density functional theory (DFT) models of the amorphous HfO/SiGe (001) interface have shown that low defect interfaces may be formed even before hydrogen passivation with short anneals (<10 ps) when the interface is comprised solely of silicon monoxide (SiO). Experimental studies have shown a 10x reduction at the Al2O3/SiGe and HfO/SiGe interfaces via selective oxygen scavenging by using an oxygen scavenging, metallic Al gate; the selectivity is due to the difference in the formation enthalpy of GeO compared to SiO, facilitating transfer of oxygen from GeO to Al. However, this process induced thicker gate oxides and reduced the maximum capacitance density (Cmax) resulting from Al oxidation on top of ALD-grown gate oxide.

In the present study, the formation of low interface defect density HfO/SiGe gate stacks using inorganic and organo-metallic ALD Al2O3 insertion in bilayers and nanolaminates of Al2O3 and HfO2 was investigated with scanning transmission electron microscopy (STEM)–electron energy loss spectroscopy (EELS) analysis. It is found that the insertion of the highly oxygen reactive trimethyl aluminum (TMA) ALD precursor for Al2O3 in HfO2 containing gate stacks reduces defects consistent with the remote selective oxygen scavenging from the interface. This new selective oxygen scavenging technique is most effective when Al2O3 layers are uniformly distributed across the HfO2 in a nanolaminate (NL) structure, but it also is effective when the Al2O3 ALD deposition occurs on top of the HfO2. In Al2O3 ALD, during each TMA half cycle, the TMA is dosed in excess; therefore, after the surface hydroxyl groups are eliminated, the TMA is available to reduce additional species either by diffusion through HfO or remotely at the growth surface. This is consistent with GeO out-diffusing to the top of HfO2 gate oxides and the remote oxide growth on top of HfO2. This hypothesis of the gate oxide acting as a H2O barrier to diffusion of GeO during ALD. This hypothesis of the gate oxide acting as a H2O barrier to diffusion of GeO during ALD. This hypothesis of the gate oxide acting as a H2O barrier to diffusion of GeO during ALD.
were fabricated with HfO2 and Al2O3 oxides onto Si0.7Ge0.3(100) rinses in acetone, isopropyl alcohol, and deionized (DI) H2O. Native epitaxially grown on p-type Si(100) (Applied Materials). Samples, and dried with N2. Subsequently, samples were transferred to the HF. The samples were dried in N2, passivated in an ammonium hydroxide (HF) solution and 1 min DI H2O, ending with 2% fluoric acid (HF) solution and 1 min DI H2O, ending with 2%

reduces the interface-trapped charge density by forming Si rich SiOx at the interface, consistent with the predictions of the DFT models. This is also consistent with the known ability of TMA to reduce low enthalpy of formation oxides on substrates at the start of ALD, a process known as ALD cleanup.18,19

Table 1. Comparison of $D_n$ Values Obtained with Conductance and Full Interface State Model

<table>
<thead>
<tr>
<th>MOSCAP devices in SiGe/Ni</th>
<th>$C_{eq}$ (μF cm$^{-2}$)</th>
<th>$V_m$ (V)</th>
<th>$D_n$ CM (cm$^{-2}$ eV$^{-1}$)</th>
<th>$D_n$ FISM (cm$^{-2}$ eV$^{-1}$)</th>
<th>standard errors of the mean</th>
<th>standard errors (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>45 HfO2</td>
<td>2.5</td>
<td>-0.02</td>
<td>3.57</td>
<td>3.74</td>
<td>0.266</td>
<td>7.1</td>
</tr>
<tr>
<td>5Al2O3/45 HfO2</td>
<td>1.96</td>
<td>-0.03</td>
<td>2.43</td>
<td>3.30</td>
<td>0.074</td>
<td>2.2</td>
</tr>
<tr>
<td>45 HfO2/5Al2O3</td>
<td>2.02</td>
<td>-0.01</td>
<td>2.35</td>
<td>3.15</td>
<td>0.10</td>
<td>3.1</td>
</tr>
<tr>
<td>5Al2O3/45 HfO2/5Al2O3</td>
<td>1.74</td>
<td>0.12</td>
<td>2.18</td>
<td>2.53</td>
<td>0.124</td>
<td>4.9</td>
</tr>
<tr>
<td>6 × (9HfO2/1Al2O3)</td>
<td>1.8</td>
<td>-0.05</td>
<td>2.02</td>
<td>2.22</td>
<td>0.05</td>
<td>2.2</td>
</tr>
</tbody>
</table>

METHODS

Metal–oxide–semiconductor (MOS) capacitor (MOSCAP) devices were fabricated with HfO2 and Al2O3 oxides onto Si0.7Ge0.3(100) epitaxially grown on p-type Si(100) (Applied Materials). Samples were degreased by sonication in methanol for 1 min followed by 10 s rinses in acetone, isopropyl alcohol, and deionized (DI) H2O. Native oxides were removed by cycling 2.5 times through 1 min 2% hydrofluoric acid (HF) solution and 1 min DI H2O ending with 2% HF. The samples were dried in N2, passivated in an ammonium sulfide solution (25% (NH4)2S) for 15 min, rinsed with water for 30 s, and dried with N2. Subsequently, samples were transferred to the atomic layer deposition (ALD) chamber, and oxide structures were grown by using a Beneq TFS200 cross flow reactor at 275 °C using tetrakis dimethyl amino hafnium (TDMAH), HfCl4 and TMA metal precursors and water as an oxidant. Each HfO2 cycle consisted of 1 s of a TDMAH or HfCl4 pulse and a 500 ms of H2O pulse, each Al2O3 cycle consisted of a 1 s TMA pulse and a 500 ms H2O pulse. Ar was used as a carrier gas for all processes, and 6 s purges were employed between each pulse. A set of samples were fabricated in bilayer, trilayer, and nanolaminate (NL) structures formed by Al2O3 and HfO2 in a gate stack for MOSCAPs, as shown in Figure S1 and the insets of Figure 1. Nickel gates (50 nm thick, 150 μm diameter) were deposited with a shadow mask onto the oxide surface using a Denton 502A thermal evaporator in vacuum <2 x 10−6. Al back contacts were deposited by sputtering after native oxide removal with Ar plasma at 100 W, 5 mTorr in a Denton Discovery 635 sputtering system. Samples were annealed using an optimized recipe for 30 min total (10 min at 300 °C, 10 min at 330 °C, and 10 min at 350 °C) in forming gas (5% H2, 95% N2) in a Ulvac MILA-3000 Minilamp annealer at 3 s/m at 1 atm. MOSCAP characterization at 300 K was performed with Keysight B1500. Multifrequency capacitance–voltage (C–V) and conductance–voltage (G–V) measurements were obtained from 2 kHz to 1 MHz with 30 mV alternating current signal superimposed on a direct current gate bias varied from 2 to −2 V. For the structural and compositional analyses, transmission electron microscopy (TEM) specimens (~50 nm) were prepared from MOSCAP devices using a FEI-Scios Ga focus ion beam. STEM/TEM analyses on high-field (BF) along with TEM images were obtained. Compositional analysis was performed with electron energy loss spectroscopy (EELS) both at 80 and 200 keV with a JEOL ARM 200CF equipped with a Gatan Quantum EELS spectrometer.

RESULTS AND DISCUSSION

Electrical characterizations of the MOSCAP devices with various gate oxide structures after forming gas annealing (FGA) are shown in Figure 1. The C–V analyses for 45 cycles (~4.5 nm) of HfO2 control sample with a $C_{max}$ of 2.5 μF cm$^{-2}$ and corresponding G–V characterization are presented in Figure 1a,f; a peak defect density of ($D_n$) 3.74 × 10$^{12}$ eV$^{-1}$ cm$^{-2}$ (see Figure 2) is obtained. The full interface state model20,21 is used to calculate the energy distribution of the $D_n$ by fitting multifrequency C–V and G–V curves for each bias point from inversion (2 V) to accumulation (−1 V). The result peak $D_n$ values from the full interface state model are

![Graph](C:\Users\<username>\Documents\Graph.png)
compared with the $D_n$ values from the conductance method (CM)\textsuperscript{22} and shown to be in agreement, as documented in Table 1. Figure 1b,c shows the $C-V$ for five cycles of Al\textsubscript{2}O\textsubscript{3} insertion below and above 45 cycles of HfO\textsubscript{2}. As expected, Al\textsubscript{2}O\textsubscript{3} insertion decreases $C_{\text{max}}$ in both cases due to an increase in total oxide thickness and the lower dielectric constant of Al\textsubscript{2}O\textsubscript{3} in comparison to HfO\textsubscript{2}. However, the magnitude of the dispersive, depletion capacitance $D_n$ feature also decreases, as shown in Figure 1b,c. Al\textsubscript{2}O\textsubscript{3} insertion below or above HfO\textsubscript{2} has a nearly identical effect on an interface defect density corresponding to peak $D_n$ values of 3.30 × 10\textsuperscript{12} eV\textsuperscript{−1} cm\textsuperscript{−2} and 3.15 × 10\textsuperscript{12} eV\textsuperscript{−1} cm\textsuperscript{−2}. Note that full $D_n$ distributions as a function of the thickness are shown below confirming the trends. Because interface trap response involves defects at the semiconductor oxide interface, a change in $D_n$ resulting from the addition of five ALD cycles of Al\textsubscript{2}O\textsubscript{3} on top of a 4.5 nm thick HfO\textsubscript{2} layer is unexpected. Moreover, as shown in Figure 1d, Al\textsubscript{2}O\textsubscript{3} insertion both above and below HfO\textsubscript{2} in an Al\textsubscript{2}O\textsubscript{3}/HfO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} trilayer structure further decreases the interface-trapped charge density by 10% to 2.53 × 10\textsuperscript{12} eV\textsuperscript{−1} cm\textsuperscript{−2}. Furthermore, as shown in Figure 1e, when Al\textsubscript{2}O\textsubscript{3} layers dispersed across the HfO\textsubscript{2} in the nanolaminate structure (NL), the $D_n$ decreases further down to 2.22 × 10\textsuperscript{12} eV\textsuperscript{−1} cm\textsuperscript{−2}, 12% lower than the trilayer with a small increase in $C_{\text{max}}$. The $C_{\text{max}}$ reduction due to an increase in total oxide thickness is expected, but $D_n$ reduction with more Al\textsubscript{2}O\textsubscript{3} incorporation remote from the interface is not.

To better document the effects of bottom versus top Al\textsubscript{2}O\textsubscript{3}, samples were grown with 10 cycles of Al\textsubscript{2}O\textsubscript{3} inserted either below the HfO\textsubscript{2} or above the HfO\textsubscript{2}. This caused very large decreases in $D_n$, as shown in Figure 2. Again, the deposition of Al\textsubscript{2}O\textsubscript{3} on top of the HfO\textsubscript{2} induced a 57% decrease in the peak $D_n$ as well as a 54% decrease in the integrated $D_n$, whereas the Al\textsubscript{2}O\textsubscript{3} inserted below the HfO\textsubscript{2} only induced a 40% decrease in the peak $D_n$ as well as a 40% decrease in the integrated $D_n$. The integrated $D_n$ is obtained by the summation of the defect densities across the band gap in Figure 4; this is equivalent to the integration of the areas under the $D_n$ curves; these integrated $D_n$ are a measure of the total defects induced in the band gaps. Curves provide total defects induced in the band gap.

For the five cycles of Al\textsubscript{2}O\textsubscript{3} insertion, although absolute defect density quantification is challenging, small decreases in the magnitude of the interface trap-related depletion capacitance feature while maintaining an essentially constant $C_{\text{max}}$ suggest a lower defect density at the interface oxide/semiconductor interface for the nanolaminate structure compared to the trilayer sample or the bilayer samples. For each processing condition, 5–10 devices were studied. The two to three devices with the most consistent $C-V$ were chosen for further analysis. Therefore, although absolute $D_n$ calculations are accurate only within 30%; even 10% changes in $D_n$ decay with Al\textsubscript{2}O\textsubscript{3} insertion are reliable as confirmed via the fabrication of multiple sample sets, as shown in Figure S8. The $D_n$ standard errors of the mean (in cm\textsuperscript{−2} eV\textsuperscript{−1} and percentage)
change for $V$ however, when there is frequency dependence, the highest
in this comparison. The insertion of $\text{Al}_2\text{O}_3$ ALD layers, MOSCAP devices with only
less precisely determined in part because the uncertainty in $C_{\text{ox}}$
is about 10% which can translate into 10–20% uncertainly in absolute
1.0 $\mu$Cm. There is a superlinear decrease in $C_{\text{ox}}$ for 40 cycles consistent with nearly linear growth. Because the
for samples were calculated, as shown in Table 1. The typical
standard error is 3.9%, and changes in $D_{\text{it}}$ of 10% are significant
in this comparison. The $D_{\text{se}}$ standard error analysis has shown that changes in $D_{\text{it}}$ of 10% can reliably be determined. Error
bars are not given for each data point since the absolute $D_{\text{it}}$ is
less precisely determined in part because the uncertainty in $C_{\text{ox}}$
is about 10% which can translate into 10–20% uncertainly in absolute
$D_{\text{it}}$. Additional details for standard error analysis are shown in Table 1. As shown in Table 1, there is no significant
change for $V_{\text{fb}}$ as a function of processing conditions. In addition, there is a very little dependence of $V_{\text{fb}}$ on frequency;
however, when there is frequency dependence, the highest
frequency $C$–$V$ is employed to access $V_{\text{fb}}$ since it is least
affected by traps.

To investigate the mechanism of $D_{\text{it}}$ reduction due to the
insertion of $\text{Al}_2\text{O}_3$ ALD layers, MOSCAP devices with only
$\text{Al}_2\text{O}_3$ gate oxides of varying thickness were prepared, as shown in
Figure 3. As expected, $C$–$V$ and $G$–$V$ measurements from
$\text{Al}_2\text{O}_3$ devices after FGA as a function of deposition cycles or
oxide thickness show a decrease in $C_{\text{max}}$ from 1.3 $\mu$F cm$^{-2}$ to
1.0 $\mu$F cm$^{-2}$ by increasing the oxide thickness. The depletion
capacitance $D_{\text{se}}$ feature also decreases in amplitude. Once the
ALD-grown oxide thickness increases above a critical value, there is a superlinear decrease in $D_{\text{se}}$. For an increase of 25% in the
number ALD cycles (40–50 cycles), the $D_{\text{it}}$ decreases by
>4X from $2.93 \times 10^{12}$ to $0.67 \times 10^{12}$ eV$^{-1}$ cm$^{-2}$. The lower $D_{\text{it}}$
from increasing the number of ALD cycle from 40 to 50 is not the result of a sudden increase in the oxide thickness due to an
ALD onset delay. The $C_{\text{max}}$ for 50 cycles is just 25% lower than
for 40 cycles consistent with nearly linear growth. Because the
$D_{\text{it}}$ originates from defects at the interface with the semi-
conductor, $D_{\text{it}}$ reduction by growing additional $\text{Al}_2\text{O}_3$ layers is
consistent with the chemical modification of the interface by
exposure to the TMA-based ALD environment. The $C$–$V$
curves obtained from MOS capacitors containing $\text{Al}_2\text{O}_3$ before
FGA shown in Figure S4 exhibit a similar trend. It is noted that
for Si interfaces, $\text{Al}_2\text{O}_3$ ALD is reported to reduce defects by a
post deposition hydrogen passivation mechanism. However,
for SiGe, the most important dangling bonds are on Ge which
are not readily passivated by hydrogen as shown by the lowest
$D_{\text{it}}$ devices being ones which eliminate interfacial GeO
post deposition hydrogen passivation mechanism. However,
for SiGe, the most important dangling bonds are on Ge which
are not readily passivated by hydrogen as shown by the lowest
$D_{\text{it}}$ devices being ones which eliminate interfacial GeO
using a gettering gate. This is also consistent with previous reports of
extremely low $D_{\text{it}}$ for HfO$_2$/SiGe by the deposition of Al
getting metal on top of HfO$_2$ in which the FGA was performed after Al deposition.\textsuperscript{16}

The suppression of the interface defects with the $\text{Al}_2\text{O}_3$
insertion into gate oxide influences is not limited to a single
energy but is distributed across the band gap as shown in the
$D_{\text{it}}$ energy distributions extracted from measured $C$–$V$ and
conductance–voltage ($G$–$V$) data using the full interface state
model,\textsuperscript{20} as shown in Figure 4. Note that interface defect
distribution across the band gap for all of the devices in this
work is summarized in Figure 4 side by side for a better
comparison. In addition, the insertion of 1, 3, 5, and 10
monolayers of $\text{Al}_2\text{O}_3$ below HfO$_2$ (Figure S2) and on top of
HfO$_2$ (Figure S3) was studied via $C$–$V$ and $G$–$V$ and indicates
similar trends. Trapped charge energy distributions of the
corresponding capacitors shown in Figure 4a,b are consistent
with Figure 1 and show a decrease of $D_{\text{it}}$ with the incorporation of $\text{Al}_2\text{O}_3$ ALD layers but below and above

Figure 4. Interface defect density distributions across the band gap for MOSCAP devices calculated with the full interface state model. Interface
defects at SiGe–oxide interface decrease by the insertion of $\text{Al}_2\text{O}_3$ layers before HfO$_2$ (a) and after HfO$_2$ (b) gate oxide. (c) Comparison of the
interface defects variation at the SiGe
×10$^{11}$ eV$^{-1}$ cm$^{-2}$ and integrated defects across the
band gap are as low as $0.19 \times 10^{11}$ eV$^{-1}$ cm$^{-2}$.

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HfO2 layers. Inset $D_i$ values in Figure 4c,d denote the integrated defect density across the band gap and are in good agreement with the behavior observed for the peak $D_i$. As shown in Figures 2 and 4, the shapes of the $D_i$ distributions for HfO2/SiGe and Al2O3/SiGe are similar (not identical), but the $D_i$ values vary more than $2 \times$; this is consistent with the source of $D_i$ being similar for both oxides (for example GeOx) but present in greater concentration for HfO2/SiGe than Al2O3/SiGe.

In Al2O3 ALD, during each TMA half cycle, the TMA is dosed in excess; therefore, after the surface hydroxyl groups are eliminated, the TMA is available to reduce additional species. However, during each H2O half cycle, the H2O is present in excess at the end of the pulse, and some H2O or H2O-derived species may diffuse through thin Al2O3 gate stacks. Also, although the Al2O3 is a better diffusion barrier in comparison to the HfO2, it has been reported previously that GeOx can diffuse through thin Al2O3 gate stacks. The Al2O3–SiGe interface is known to include GeOx species which are the source of interface defects. It is hypothesized that above a critical thickness, the Al2O3 becomes a good barrier to H2O; therefore, excess TMA exposure during ALD can scavenge oxygen from GeOx species and convert it into Ge which might be redeposited on SiGe without the formation of new GeOx from the water pulses. This mechanism is consistent with decreasing $D_i$ by insertion of Al2O3 into HfO2-containing gate dielectric stacks or deposition of Al2O3 on top of HfO2 gate dielectrics. However, as noted earlier, Al2O3 is a more effective diffusion barrier in comparison to HfO2 for oxygen containing species; consequently, the $D_i$ suppression with HfO2 dielectrics is not expected to be as great as with Al2O3 dielectrics of similar thickness. This suggests that the number of Al2O3 layers incorporated into oxide is mainly responsible for the interface defect density reduction observed in these experiments. Similar to $6 \times (9\text{HfO}_2 + 1\text{Al}_2\text{O}_3)$ NL gate dielectric structure, gate oxide without an oxidant during Al2O3 ALD is performed by only TMA dosing and $D_i$ reduction along with $C_{\text{max}}$ observed indicating Al2O3 layer formation by oxygen scavenging. It is noted that for HfO2-based gate stacks with incorporated Al2O3 layers, the TMA may diffuse to the interface to directly reduce the GeOx to Ge since HfO2 is a poor diffusion barrier; however, the mechanism likely co-exists with the remote scavenging mechanism.

Figure 5 shows STEM high-angle annular dark-field (HAADF), bright field (BF), and TEM images of the HfO2–SiGe bilayer, the Al2O3–HfO2/SiGe bilayer, and Al2O3–HfO2 Nanolaminate MOSCAPs. In these images, oxide structures and regions are defined according to z contrast. The interfacial layer between SiGe and oxide indicated with black and white arrows on corresponding STEM-HAADF, STEM-BF, and TEM image. Note in (b), the interlayer consists of both SiGeOx and Al2O3 so it appears thicker than the control device in (a). In comparison to control device of HfO2–SiGe, bilayer (c) and NL (d) show thinner interface consistent with remote Al2O3 insertion reducing IL.
and is employed to indicate the SiGe surface. Black and green arrows denote Si and Ge compositions of the SiGe surface. It should be noted that the determination of interface location in STEM-EELS is subject to interpretation especially due to the surface roughness. However, even with the surface roughness, the IL should be within few angstroms of the dashed lines, and this metric was confirmed by determining the location of the Si/SiGe interface since these layers are epitaxially grown. Any uncertainty in the exact location of the interface will not impact the trends in the elemental composition across the IL.

Figure 6. STEM-EELS compositional analysis of MOSCAP devices. EELS experiment performed at 80 and 200 keV as indicated. The inset drawings illustrate corresponding gate stack structure along with the ALD chemistry above it. The compositions of the elements are averages area of ∼6 × 0.2 nm² parallel to the sample surface. The red dashed line intercepts the half peak values of the O signals and indicates the SiGe–HfO₂ interface. Black and green arrows denote Si and Ge compositions on the SiGe surfaces, respectively. The blue arrow indicates the Al composition in the oxide. Al₂O₃–HfO₂ interdiffusion is seen for bilayer samples regardless of the initial structure and confirmed with the raw data analysis in the figure and Figure S5. This interdiffusion is prominent for EELS analysis at 80 keV. In comparison to (a) and (b), devices in (c)–(f) show lower Ge/Si ratio at the intersection with red dashed lines indicate the Si rich interface formation with Al₂O₃ incorporation into HfO₂. Ni interdiffusion is seen in devices (a) and (b) and Al₂O₃ insertion into HfO₂ impedes the Ni diffusion as seen in (c)–(f).
oxide which indicates the suppression of Ge out-diffusion with Al₂O₃ incorporation. Figure 6a,b shows 200 keV EELS analysis of the same structures fabricated with hafnium tetrachloride at 300 °C and tetradimethylamido hafnium(IV) ALD precursors at 275 °C; no significant differences were observed as seen in Figure 6a,b consistent with interface defects obtained with multifrequency C−V analysis. Both the HfCl₄ and TDMAH gate stacks have a nearly identical elemental distribution across the device and have a Ge tail extending about 2 nm into the HfO₂ layer in contrast to the capacitors in Figure 6c−f which show a diminished or zero Ge tail. This may be attributed to the Al₂O₃ layer impeding Ge out-diffusion. It is surprising that Al₂O₃ reduces Ge out-diffusion even when Al₂O₃ is deposited onto HfO₂ (Figure 6c−f). This may be the result of TMA reaction products (either AlOₓ or AlCₓH_y) diffusion into HfO₂ reaching IL.

Further documentation that even remote Al₂O₃ ALD can control the GeOₓ in the interlayer is observed in the composition of the interlayers. For all of the gate stacks with Al₂O₃, the amount of Ge and the ratios of Si to Ge at the interface (between full max and 1/2 height of the oxygen peak) are greater than the control HfO₂/SiGe (Figure 6a); the exact comparison of the interfacial Si/Ge ratio between the samples with Al₂O₃ (Figure 6b−f) is challenging since the ratio can vary with slight adjustment of the nominal interface position. All of the samples have an interlayer above the SiGe as shown by the gap between the Hf and O edges; however, the Si signal falls off most steeply for Si on the nanolaminate samples (Figures S5−S7) consistent with these samples having the most abrupt interface.

STEM-EELS at both 80 and 200 keV is employed to investigate the AlOₓ distribution in the ALD HfO₂ layer, while controlling beam induced Al damage due to high energy electrons. For the HfO₂/Al₂O₃/SiGe structures (Figure 6c,d), the 200 keV spectrum shows a complete diffusion of the Al, whereas the 80 keV spectrum shows only a small retention of Al at the interfaces likely due to the limited signal to noise of the 80 keV spectra; the data is consistent AlOₓ diffusing during the HfO₂ deposition. For the Al₂O₃/HfO₂/SiGe structures (Figure 6e,f), the 200 keV spectrum shows two Al peaks, one above and one below HfO₂, whereas the 80 keV spectrum shows a just small retention of AlOₓ above the HfO₂.

Figure 7. STEM-EELS compositional analysis of Ni/Al₂O₃/HfO₂/SiGe MOSCAP device. Raw EELS data taken at 200 keV from the sample in Figure 6e is shown in a 3D semilog graph (a) with the energy axis indicating the electron energy loss and corresponding intensity in arbitrary units. The peaks appear on the graphs corresponds to Si K edge (1839 eV), Ge L edge (1217 eV), Hf M edge (1662 eV), O K edge (532 eV), Al K edge (1560 eV), Ni L edge (885 eV). The colored consecutive black and light blue lines indicate electron energy loss for the given location on samples and two colors chosen to enhance the image contrast. Each data line projects energy loss averaged from areas of 5 × 0.2 nm² parallel to the sample surface. The peaks appear on the graphs corresponds to Si K edge (1839 eV), Ge L edge (1217 eV), Hf M edge (1662 eV), O K edge (532 eV), Al K edge (1560 eV), Ni L edge (885 eV). The blue arrow indicates the SiGe interface formation between SiGe and HfO₂. Pink and red arrows indicate the Ge and Si compositions on SiGe surface. The Ge signal decays earlier than Si as it approaches the HfO₂ layer. Black arrows denote Al composition across the oxide. Al₂O₃ insertion onto HfO₂ in bilayer structure forms intermixing by Al diffusion. To increase the visibility of Al peak and interdiffusion, semilog two-dimensional graph of raw EELS data with 1−2 K energy loss range is presented in graph (b) (SiGe/HfO₂ interface region) and (c) (HfO₂/Ni interface region). Two graphs prepared with offsets introduced between each curve to improve the visibility.
layer, consistent with the limited signal to noise of the 80 keV spectra. Overall both are consistent with the diffusion of TMA or its reaction products into the HfO2 when the Al2O3 ALD is performed after HfO2 ALD. The nanolaminate gate stack (Figure 1e) composition studied with 80 keV EELS shows dispersed Al (Figure S5).

This unexpected interdiffusion of Al2O3 is also shown with EELS raw data in the three-dimensional (3D) semilog graph in Figures 7 (Ni/Al2O3/HfO2/SiGe) and S6 (Ni/HfO2/Al2O3/Ni). The oxide compositional profile can be seen from the electron energy loss peaks starting after element specific edges; for example, the Si K edge is at 1839 eV (orange arrow) and the Ge L edges at 1217 eV (pink arrow). The blue arrow indicates the SiGe/HfO2 interface region. It is seen that the Ge peak decays earlier than the Si peak as a function of distance from the SiGe surface consistent with a SiOx-rich region at the interface. The black arrow indicates energy loss due to Al (K edge 1560 eV) across the oxide. The peak intensity is significantly lower in comparison to other elements; however, it can be seen in several regions in the HfO2 and reaches a maximum close to the HfO2/Ni interface since it is deposited on HfO2 as shown in 3D data and the region of interest in Figure 7a,b. However, the Al peak can also be seen close to SiGe/HfO2 interface, almost 4 nm away where it was

Figure 8. Comparison of Ni/Al2O3/SiGe/Si and Al/HfO2/SiGe/Si MOSCAPs. Note that the Al is a gettering gate metal. High-resolution STEM-HAADF and BF images at 80 keV of devices with (a, b) Ni/Al2O3 and (c, d) Al/HfO2 gate oxides; both have 50 ALD cycles. Nearly abrupt interfaces are observed in both bright field and dark-field imaging for both devices. (e, f) C–V graphs of Al/HfO2 and Ni/Al2O3 devices with very low depletion capacitance are shown, insets denote integrated $D_i$ values across the band gap extracted with the full interface state model. EELS elemental composition of Ni/Al2O3/SiGe/Si is shown in (g). The regions of Al2O3 gate oxide defined with z contrast in (a) and (b) and are in good agreement with the EELS spectra in (g). The red dashed line intercepts the half peak values of the O, Si, and Ge signals and delineates the SiGe–HfO2 interface. Black and green arrows denote Si and Ge composition on SiGe surface; a Si rich interface observed. The blue and red arrows indicate the electron beam damaged (80 keV) region of Al2O3. A similar effect also observed for samples studied at 2000 keV. Ni gate metal overlaying with Al indicating Ni and Al intermix. Note at the SiGe interface, the Al and O profiles are nearly identical consistent with a near zero SiGeOx interlayer.
Novel gate oxide structures were investigated which suppress electronic defects at high-k/SiGe interfaces by employing an oxygen scavenging ALD precursor, TMA. The approach utilizes the difference in the heat of formation of SiO2 and GeO2 achieving lower interface trap densities at the high-k/SiGe interface with just a modest reduction of C_{max}. Although metallic Al remains more effective at oxygen scavenging, it induces a much larger C_{max} reduction, demonstrating the benefit of TMA remote oxygen scavenging. The data is consistent with the insertion of Al2O3 into the HfO2 gate oxide, removing a GeO2 component of the interlayer between the channel and the deposited gate dielectric, and suggests that effective oxygen scavenging can be achieved with TMA during ALD. This TMA-based oxygen scavenging technique is most effective when the Al2O3 layers are uniformly distributed across the HfO2 in a nanolaminate structure, but it also is effective when the Al2O3 ALD deposition occurs on top of the HfO2. To achieve the effect, during each TMA half cycle of Al2O3 ALD, TMA is dosed in excess to provide sufficient TMA for the reduction of additional chemical species after the surface hydroxyl groups are eliminated. In the present study, for the first time, the mechanism for the low defect interface formation with Al2O3 in contrast to HfO2 is explained with the experimental data. In contrast to previous reports, in which the good diffusion barrier properties of Al2O3 are considered to be the source of D_{it} improvement, the mechanism for interface defect reduction with Al2O3 in the present work is shown to be selective oxygen scavenging by diffusion of TMA reaction products in HfO2. Furthermore, direct and remote oxygen scavenging using ALD Al2O3 deposited on HfO2 gate oxide 4 nm away from SiGe surface is demonstrated. By deposition of Al2O3 and etching back with atomic layer etching, it is likely that low D_{it} can be obtained in high aspect ratio structure such as on fins which is not possible with Al deposition for gettering gates.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b22362.

Variation of interface defect density on samples as well as the comparison of interface defect calculation methods used in the article and the EELS analysis for few devices (PDF)

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**Notes**

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