Understanding the Mechanism of Electronic Defect Suppression Enabled by Nonidealities in Atomic Layer Deposition

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Supporting Information

ABSTRACT: Silicon germanium (SiGe) is a multifunctional material considered for quantum computing, neuromorphic devices, and CMOS transistors. However, implementation of SiGe in nanoscale electronic devices necessitates suppression of surface states dominating the electronic properties. The absence of a stable and passive surface oxide for SiGe results in the formation of charge traps at the SiGe-oxide interface induced by GeO_x. In an ideal ALD process in which oxide is grown layer by layer, the GeO_x formation should be prevented with selective surface oxidation (i.e., formation of an SiO_x interface) by controlling the oxidant dose in the first few ALD



cycles of the oxide deposition on SiGe. However, in a real ALD process, the interface evolves during the entire ALD oxide deposition due to diffusion of reactant species through the gate oxide. In this work, this diffusion process in nonideal ALD is investigated and exploited: the diffusion through the oxide during ALD is utilized to passivate the interfacial defects by employing ozone as a secondary oxidant. Periodic ozone exposure during gate oxide ALD on SiGe is shown to reduce the integrated trap density (D_{it}) across the band gap by nearly 1 order of magnitude in Al₂O₃ (<6 × 10¹⁰ cm⁻²) and in HfO₂ (<3.9 $\times 10^{11}$ cm⁻²) by forming a SiO_x-rich interface on SiGe. Depletion of Ge from the interfacial layer (IL) by enhancement of volatile GeO_x formation and consequent desorption from the SiGe with ozone insertion during the ALD growth process is confirmed by electron energy loss spectroscopy (STEM-EELS) and hypothesized to be the mechanism for reduction of the interfacial defects. In this work, the nanoscale mechanism for defect suppression at the SiGe-oxide interface is demonstrated, which is engineering of diffusion species in the ALD process due to facile diffusion of reactant species in nonideal ALD.

INTRODUCTION

Silicon germanium (SiGe) is a promising material system for novel electronic devices due to quantum confinement thanks to mature scaling technology. It is being investigated for (i) quantum computing due to its long spin coherence time, $^{2-4}$ (ii) neuromorphic devices due to threading dislocations allowing controlled filament formation for resistive switching,⁶ and (iii) channels in p-type metal oxide semiconductors (p-MOSs) for boosting transistor performance due to high carrier mobility.⁷ High transconductance in SiGe channels was reported by Hashemi et al. via replacement high-k/metal gate or interlayer oxides.^{10,11} While SiGe transistors with high-k dielectrics are being actively developed for commercial high-speed, low-power electronic devices; the practical integration of SiGe as a top surface channel in complementary metal oxide semiconductor (CMOS) transistors is hindered by poor interface formation between the gate oxide and SiGe primarily due to GeO_x

formation.^{12,13} Elimination of unstable GeO_x species may be possible with Si cap layers epitaxially grown on SiGe channels for planar devices; however, it may be problematic for gate-allaround devices or FinFETs due to space constraints and the limitation in Si ALDs, which may have low mobility due to defects.¹⁴ Previous studies on defect suppression at the gate oxide-SiGe interface have included pre-ALD passivation with nitrides^{15,16} and sulfur¹⁷ and post-ALD selective oxygen scavenging with physical vapor deposited (PVD) gettering metal gates.^{12,18} However, the interfaces are still degraded mainly by Ge outdiffusion¹³ during ALD at elevated temperatures. There are also processing challenges: for example, the gettering metal inducing a reduction in maximum capacitance by forming thicker gate oxides and PVD being incompatible with

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Figure 1. Schematic diagram of MOSCAP structure and photon energy dependent PES experiment geometry. A MOSCAP device with 5 nm HfO₂ gate oxide and Ni metal gates are displayed. X-ray photons from the synchrotron source are focused on the sample with a beam spot of $40 \times 40 \,\mu$ m on the HfO₂ surface between the Ni gate metals of the MOSCAP devices. Emission angle: the incident photon angle to the sample normal is 54.75°. The X-ray penetration depth is much deeper than the HfO₂ and SiGe layer thickness; however, the inelastic mean free path (λ) (IMFP) of the photoelectrons emitted by the elements is limited by the kinetic energy of the photoelectrons. By using X-ray energies of 150, 500, and 1000 eV, the MFP of photoelectrons is varied, and deeper composition profiles are obtained. Since the Si, Hf, and Ge binding energies are, the IMFPs of photoelectrons are close, which provides information from the same depth. It should be noted that photoelectrons can be scattered elastically with a longer mean free path, such as that of photoelectrons at ~1 keV in HfO₂ is ~6 nm;¹ therefore, SiGe—oxide interface probing is possible. A total of 65% of the spectrum intensity emanates within one λ of the top surface enhancing probing surface layer along with composition deeper into the oxide.

the nanoscale 3D devices employed.¹⁸ Another approach for defect reduction is selective oxygen scavenging at high temperature (>500 °C). As shown by Lee et al., this technique utilizes the differences in bond strength between SiO_2 (3.48 eV) vs GeO₂ (2.82 eV). The Ge–O bonds are broken selectively due to relative weakness in comparison to Si–O, which causes selective Si oxidation with GeO outdiffusion.¹⁹ However, the thermal budget may be a concern for this process. Therefore, new approaches are needed for the suppression of electronic defects in SiGe gate stacks.

Modification of semiconductor oxide interfaces during the ALD process using reactive oxygen species has been shown to be effective for reduction of charge traps via formation of GeO₂ (not GeO_x) interfaces on high-Ge-content Si substrates (>90%) by postoxidation through an Al₂O₃ barrier using oxygen plasma as studied by Zhang et al.,²⁰ or ozone exposure reported by Ando et al., in which very high mobility was observed.²¹ In these studies, instead of direct plasma oxygen or ozone dosing on the SiGe surface, the Al₂O₃ was deposited prior to plasma oxygen or ozone dosing. However, it is seen that the ratio of Si to Ge in the substrate can greatly change the chemistry of postoxidation through Al₂O₃ barriers. For instance, it was reported that, for pure Ge substrates, increasing the barrier Al_2O_3 thickness (1 to 1.5 nm) prior to postoxidation reduces the GeO_x IL thickness (from 1.2 to 0.23 nm) and unexpectedly increases D_{it} (~5×).²⁰ For SiGe substrates, it was shown that post-ALD oxidation on low-Ge-content SiGe (30-50%) forms a highly defective SiGeO_x interface, and the thickness of the IL decreases for higher Ge composition SiGe $(Si_{0.69}Ge_{0.31} \text{ to } Si_{0.5}Ge_{0.95})$ due to suppression of SiO_x in the IL.²¹ However, DFT and experimental studies have shown that formation of an SiO_x interface between SiGe and oxide results in an extremely low interfacial defect density on low Ge content SiGe.¹⁸

In the present study, comprehensive analysis of the effect of reactive oxidant exposure during ALD oxide deposition is studied with impedance measurements correlated with STEM- EELS and photon energy dependent PES analysis to elucidate the defect reduction mechanism with ozone insertion. The effect of ozone exposure during ALD oxide deposition on the SiGehigh-k oxide interface is investigated with a large set of MOSCAP samples, including gate oxides of Al₂O₃ only, HfO₂ only, and hetero Al₂O₃-HfO₂ structures by comparing ozone exposure directly on SiGe or with Al₂O₃ and HfO₂ barriers. In contrast to previous reports on high-Ge-content SiGe,^{20,21} using ozone during HfO2 gate oxide ALD on low Ge content SiGe $(Si_{0.7}Ge_{0.3})$ is found to decrease interface defects by reducing interfacial GeO_x. An ultralow D_{it} value of 0.32×10^{12} cm⁻²eV⁻ is observed with a very thin IL (<0.2 nm) on $Si_{0.7}Ge_{0.3}$ with ozone insertion into ALD Al₂O₃ gate oxides. STEM-EELS analysis shows significant interface defect reduction with SiO_xrich IL formation with ozone exposure into ALD Al₂O₃ or HfO₂ gate oxide on Si_{0.7}Ge_{0.3}. PES revealed enhanced Ge and Si diffusion through HfO_2 during ALD growth with ozone insertion consistent with a low-defect SiO_x-rich interface formed by selective surface oxidation. The mechanisms for defect suppression with ozone insertion into the ALD oxide were found to be different for Al₂O₃ and HfO₂. While ozone depletes Ge from the interface by forming GeO and enhances Ge outdiffusion depleting Ge from interface for both oxides, the ultralow D_{it} observed with ozone dosing during Al₂O₃ gate oxide ALD on SiGe is consistent with a second process occurring in which Al₂O₃ deposition selectively scavenges oxygen from the oxide/SiGe interface, thereby further reducing defect density.⁵ In this study, by correlating the two advance metrologies, STEM-EELS and energy-resolved PES, with multifrequency impedance spectroscopy, the mechanism for reduction of surface states during the ALD process is elucidated for the key new channel material in CMOS technology. However, a more general chemical insight is obtained. While ALD is idealized as a layer by layer growth process, this is incorrect, but the nonidealities can be utilized for defect reduction. It is rare that



Figure 2. Multi frequency C-V graphs of SiGe MOSCAPs: (a) SiGe/45 cycles of HfO₂/Ni; (b) single 60 s ozone pulse prior to HfO₂ ALD (SiGe/60 s O₃ dose/45 cycles of HfO₂/Ni); (c) single 60 s ozone pulse after 10 HfO₂ ALD cycles (SiGe/10 HfO₂ /60 s O₃ /35 HfO₂/Ni); (d) single 60 s ozone pulse after 5 HfO₂ ALD cycles (SiGe/5 HfO₂ /60 s O₃ /40HfO₂/Ni); (e) nanolaminate with 5 s of ozone after each 5 HfO₂ ALD cycles (SiGe/5 Al₂O₃ /40HfO₂/Ni); (e) nanolaminate with 5 s of ozone after each 5 HfO₂ ALD cycles (SiGe/5 Al₂O₃ /45 HfO₂/Ni); (f) 5 s H₂O pulse after 5 cycles of HfO₂ oxide deposition (SiGe/5 HfO₂/5s H₂O/45 HfO₂/Ni); (g) bilayer device (SiGe/5 Al₂O₃ /45 HfO₂/Ni); (h) 60 s ozone pulse between Al₂O₃ and HfO₂ ALD cycles (SiGe/5 Al₂O₃ /60 s O₃ /45 HfO₂/Ni); (i) 60 s ozone pulse between Al₂O₃ and HfO₂ ALD cycles (SiGe/5 Al₂O₃ /Ni); (j) 5 s H₂O pulse after 5 cycles of HfO₂ oxide deposition (SiGe/5 Al₂O₃ /Ni); (j) 5 s H₂O pulse after 5 Al₂O₃ ALD cycles (SiGe/5 Al₂O₃ /Ni); (j) 5 s H₂O pulse after 5 Al₂O₃ ALD cycles (SiGe/5 Al₂O₃ /60 s O₃ /45 HfO₂/Ni); (h) os ozone pulse between Al₂O₃ device (SiGe/45 Al₂O₃ /Ni); (j) 5 s H₂O pulse after 5 Al₂O₃ ALD cycles (SiGe/5 Al₂O₃/60 s O₃/Al₂O₃/Ni); (k) control Al₂O₃ device (SiGe/60 s O₃ dose/45 cycles of Al₂O₃/Ni); (h) single 60 s ozone pulse prior to Al₂O₃ ALD (SiGe/60 s O₃ dose/45 cycles of Al₂O₃/Ni); (h) single 60 s ozone pulse prior to Al₂O₃ ALD (SiGe/60 s O₃ dose/45 cycles of HfO₂ althe D₄; increases when ozone is introduced prior to HfO₂ deposition in (b) and decreases when ozone is introduced after few cycles of HfO₂ deposition as seen in (c)– (e). Note that (a), (j) and (k) were previously reported results.⁵ Inset drawings illustrate the device structure along with the description above for a given graph. Except for the device in (m), all devices were treated with sulfur passivation prior to ALD oxide

nonidealities in semiconductor chemical processes actually improve the material quality.

METHODS

Interfacial defects at the gate oxide–SiGe interface were analyzed and quantified with multifrequency impedance spectroscopy on MOSCAPs fabricated on 8 nm thick p-type $Si_{0.7}Ge_{0.3}(100)$ epitaxially grown on p-type Si(100). Degreased SiGe substrates were cleaned with cyclic HF(aq) and sulfur passivated with $(NH_4)_2S(aq)$. HfO₂ (HfCl₄, 250 ms; H₂O, 250 ms) and Al₂O₃ (trimethyl aluminum (TMA, 500 ms); H₂O, 500 ms) gate oxides were grown at 300 °C in a Beneq TFS200 ALD reactor. After optimization of the ozone pulse length, ozone was introduced during oxide ALD in a single pulse (60 s with 100% power at a flow rate of 4 g/h (at 100 g/Nm³, 20 °C)) such as or intermittently (5 s each) (Figure 1e, "ozone nanolaminate - NL"). The gate metal and back contacts were formed with Ni thermal evaporation and Al

sputtering. Optimized forming gas annealing (5% H₂/95% N₂) was employed in 3 steps 300 °C-330 °C-350 °C for 10 min each; details of a very similar MOSCAP fabrication process can be found elsewhere.¹⁸ Electrical characterization of the MOSCAP devices was performed with a Keysight B1500 at 300 K by *I*–*V* and multifrequency *C*–*V* and *G*–*V* measurements from inversion at 2 V to accumulation at -2 V. Interface defect densities (D_{it}) at the oxide–SiGe interfaces were calculated with the full interface state model, fitting capacitance, and conductance graphs for each bias point.^{22,23} As previously documented, multiple devices on the same wafer were probed to define standard D_{it} error analysis and verify the repeatability. It is shown that the typical standard error is 3.9%; therefore, a relative D_{it} variation as low as 10% among different processing conditions can be reliably distinguished.⁵

The structures and the compositions of the MOSCAP devices and interfaces were studied using electron transparent specimens (<50 nm) prepared from device cross sections with a FEI Scios focused ion beam



Figure 3. Defect density distribution and leakage current comparison. (a) Interface defect density distribution of MOSCAPs across the band gap. (b) Leakage current density across the gate oxide for the devices. The full interface state model is used to extract the defect density across the band gap. In comparison to the 45 cycle HfO₂ control device with $4 \times 10^{12} \text{ eV}^{-1} \text{ cm}^{-2}$ (peak D_{it}), an ozone-pulsed bilayer device with 5 ALD cycles of HfO₂/60 s $O_3/40 \text{ ALD}$ cycles of HfO₂ has a value of $1.8 \times 10^{12} \text{ eV}^{-1} \text{ cm}^{-2}$. The defect density is significantly lower for Al₂O₃ control devices in comparison to control HfO₂ and decreases further with ozone insertion for $5 \text{ Al}_2O_3/60 \text{ s } O_3/40 \text{ ALD}$ cycles of Al₂O₃, which exhibits a value of $0.3 \times 10^{12} \text{ eV}^{-1} \text{ cm}^{-2}$. Inset values indicate total defect density across the band gap and show a more prominent decrease in trap density by ozone insertion. Devices with ozone have a lower leakage current in comparison to control devices, as indicated in the I-V graph on the right.

using Ga ions and low-energy Ar ions (<1 keV) for the last step to remove the Ga beam damage. A JEOL JEM-ARM300F transmission electron microscope equipped with double aberration correction was used in the scanning transmission electron microscope (STEM) mode at 200 keV for both imaging and compositional analysis. Oxidesemiconductor atomic structures were obtained by STEM high-angle annular dark field (HAADF) and bright field (BF) simultaneously. Similarly, the chemical composition of the devices was investigated simultaneously with both electron energy loss spectroscopy (EELS) and energy dispersive X-ray spectroscopy (EDS) using a Gatan GIF Quantum ER and JEOL dual large-angle silicon-drift EDS detectors. Dual EELS including zero loss and core loss spectra were collected to correct the energy drift and deconvolute plural scattering. A Gatan Digital Micrograph was used for the compositional analysis, and multiple linear least-squares (MLLS) fitting was performed after background subtraction.⁴

Surface and depth compositional profiles across the gate oxide were investigated with energy-resolved photoelectron spectroscopy (PES) using a nondestructive soft X-ray probe equipped with a Scienta R400 analyzer at the MAESTRO beamline (micro ARPES end station) at the Lawrence Berkeley National Laboratory Advanced Light Source (ALS). Since the depth profiling with ion sputtering can alter the local oxide composition, especially in $\text{HfO}_2^{25,26}$ depth composition profiling was studied with photon-energy-dependent PES. Photon-energy-dependent PES was chosen instead of angle-dependent PES for depth profiling, since photon-energy-dependent PES can be done with a fixed experiment geometry and a small spot size; therefore, the composition of the oxide could be probed between the metal gates (Figure 1).^{27,28} Xray energy was varied among 150 eV, 500 eV, and 1 keV to benefit from differences in the inelastic mean free path (λ) (IMFP) of the photoelectrons. It should be noted that the mean free path for elastically scattered photoelectrons can be longer than the IMFP (e.g., the elastic mean free path for photoelectrons at ~ 1 keV in HfO₂ is ~ 6 nm¹). In addition, even for inelastically scattered electrons, only 65% of the intensity originates within one X-ray wavelength λ of the top surface. Therefore, photon-energy-dependent PES allowed probing the topmost layers due to the unique surface sensitivity obtained with lowenergy X-ray radiation as well as the oxide-SiGe interface probing with high-energy X-rays with elastic and inelastic electrons.

The incident photons and detection angles have a fixed relationship defined by the spectrometer. The incident photons were at an angle of 54.75° with respect to the sample normal, thereby positioning the electron spectrometer to measure at normal emission. The X-ray penetration depth is much deeper than the HfO₂ and SiGe layer thicknesses; therefore, the detection depth is mainly determined by the inelastic mean free path (λ) (IMFP) of the photoelectrons, which is a function of the kinetic energy of the photoelectrons; however, the effective distance through which the electrons travel through the sample is determined by the exit angle. Therefore, a normal detection angle was chosen, since this is the shortest path for photoelectrons to exit the substrate.

The soft X-ray photons were focused onto samples with a beam cross section of $40 \times 40 \,\mu\text{m}^2$ located on the HfO₂ surface between the Ni gate metals of the MOSCAP devices, as shown in Figure 1. Each sample was probed at 6 points with 10 scans averaged at each point. Compositions of the oxide at selected energy depth were obtained by monitoring Ge 3d, Hf 4f ,and Si 2p core level lines at a narrow energy scan. Since the focus of the experiments is Si and Ge composition in the HfO₂ and at the interface, the constant kinetic energy PES method²⁸ was employed by choosing the close ionization edges of Hf $4f_{7/2}$ (14.2 eV), Ge $3d_{5/2}$ (29.2 eV), and Si $2p_{3/2}$ (99.4 eV) to obtain similar kinetic energy photoelectrons and hence similar probing depths. To account for the change in photon flux as a function of X-ray energy, the Si and Ge signal intensities were normalized with respect to the Hf 4f_{5/2} signal. Details of the technique and experiment can be found in the Supporting Information. Data analysis, peak deconvolution, and multipeak fitting were performed with the IGOR Pro software (WaveMetrics, Inc., v.802). After Shirley background subtraction, PES peaks were fitted using Lorentzian-Gaussian type line shapes using the known binding energy positions. The Ge $3d_{5/2}$ peak at a binding energy of 29 eV and Hf $4f_{7/2}$ peak at 17.2 eV were used as references to correct the spectral shift due to charging effects.^{29,}

RESULTS

Multifrequency C-V measurements of the MOSCAP devices along with device structures are presented in Figure 2. Inset D_{it} values are the peak interface defect densities in the band gap obtained with a full interface state model. Control devices with 45 ALD cycles of HfO₂ in Figure 2a exhibit high accumulation capacitance ($C_{max} = 2.25 \ \mu F/cm^2$) along with high depletion capacitance, indicating a high density of interface traps ($D_{it} = 4 \times 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$) in comparison to all HfO₂ devices with ozone exposure during (not prior to) ALD. Ozone exposure of the SiGe surface for 60 s prior to HfO₂ deposition doubles the interface trap density to $8 \times 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$ with a negligible change in C_{max} as seen in Figure 2b. However, ozone insertion



Figure 4. STEM HAADF and BF images of MOSCAPs: (a, f) 45 cycles of Al_2O_3 ; (b, g) 5 cycles of $Al_2O_3/60$ s $O_3/40$ cycles of Al_2O_3 ; (c, h) control device of 45 cycles HfO₂; (d, i) bilayer device with 5 cycles of HfO₂/60 s $O_3/40$ cycles of HfO₂/Ni structure; (e, j) nanolaminate with 9(5HfO₂ + 5 s O_3) ALD cycles. In these images, the oxide structures and regions are defined according to *z* contrast. The interfacial layers between SiGe and oxide are indicated with black and white arrows on the corresponding STEM-HAADF and BF images. The control Al_2O_3 device had a 0.4 nm low *z* interface layer in comparison to <0.2 nm thick IL in the ozone– Al_2O_3 device. In comparison to the control device of HfO₂/SiGe (c, h), bilayer (d, i) and NL (e, j) devices show thicker interfaces, consistent with ozone forming a thicker oxide at the interface.

after 10 ALD cycles of HfO₂ decreases C_{max} to 2.0 μ F/cm² along with D_{it} to 2.25 × 10¹² cm⁻² eV⁻¹, as shown in Figure 2c. The 12% reduction in C_{max} is consistent with ozone forming a thicker interfacial layer, and the 45% decrease in D_{it} by changing the location of ozone exposure to 1 nm away from the SiGe surface is significant. This effect was more prominent when the ozone was introduced after 5 cycles of HfO₂ on SiGe, which induces a 55% reduction in D_{it} along with 20% decrease in C_{max} (Figure 2d). Furthermore, when ozone was evenly dispersed into HfO₂ by dosing after every 5 cycles, there was a 63% decrease in D_{it} to 1.5 $\times 10^{12}$ cm⁻² eV⁻¹ in comparison to the control sample, as shown in Figure 2e. This dispersion of ozone pulses across the HfO₂ reduces D_{it} by 17% in comparison to a single 60 s ozone pulse, as shown in Figure 2d. Instead of ozone, when water of an identical pulse length is dosed for 60 s after 5 cycles of HfO₂ as shown in Figure 2f, the interface deteriorates and D_{it} increases 15% in comparison to the control sample, indicating that even common reactant species diffuse through the gate oxide to the interface during ALD. The effect of ozone exposure during HfO₂ ALD is consistent with ozone dosing several nanometers from the SiGe still influencing interface trap density and, therefore, HfO₂ ALD being more complex than a true layer by layer process.

To elucidate the D_{it} reduction mechanism at the SiGe/HfO₂ interface by ozone exposure into HfO₂, several HfO₂-only and HfO₂-Al₂O₃ hetero gate oxides with ozone exposures are compared. A control Ni/45 cycles of HfO₂ + 5 cycles of Al₂O₃/ SiGe device with 1.75 μ F/cm² and $D_{it} = 3.3 \times 10^{12}$ cm⁻² eV⁻¹ is shown in Figure 2g. In comparison to the 45 ALD cycles of the HfO₂-only control device in Figure 2a, the control hetero oxide bilayer device exhibits a 18% decrease in D_{it} to 3.3 × 10¹² cm⁻² eV⁻¹ consistent with oxygen scavenging by the TMA precursor⁵ and a 23% decrease in C_{max} due to an increase in total oxide thickness along with the lower dielectric constant of Al₂O₃ in comparison to HfO₂. In comparison to the bilayer control sample in Figure 2g, the ozone-exposed bilayer device in Figure 2h exhibits only a 25% decrease in D_{it} with negligible change in C_{max} . It is hypothesized that ALD of the bottom Al₂O₃ layer induces GeO_x decomposition to Ge by oxygen scavenging; in addition, the bottom Al₂O₃ may reduce both O₃ and GeO_x diffusion, but this is likely to be a minor effect, since as shown below ozone is very effective in reducing D_{it} for Al₂O₃ gate oxides. In sum, the ozone dosing has a modest effect on bilayer HfO₂-Al₂O₃ oxides, consistent with the interfacial GeO_x already being at low concentration due to Al₂O₃ deposition,⁵ and this more modest effect of ozone on bilayer HfO₂-Al₂O₃ samples is consistent with both ozone and TMA dosing reducing interfacial GeO_x but using different chemical processes.

To study the decrease in trap density at the Al₂O₃/SiGe interface by ozone insertion, a set of samples with only Al₂O₃ gate oxide with and without ozone insertion was fabricated (Figure 2k-o). The control 45 cycles of Al_2O_3 devices have a $C_{\rm max}$ value of 1.12 μ F/cm² and $D_{\rm it}$ value of 1.26 × 10¹² cm⁻² eV⁻¹, as shown in Figure 2k. In comparison to control HfO₂ in Figure 2a and control hetero Al₂O₃-HfO₂ devices in Figure 2f, Al₂O₃-only devices exhibit 70% and 60% lower interface trap density, respectively, consistent with oxygen scavenging by TMA exposure during Al₂O₃ growth.⁵ For ozone insertion into Al₂O₃ after 5 ALD cycles of Al₂O₃ on SiGe as shown in Figure 2l, the depletion capacitance almost disappears, consistent with a 75% decrease in $D_{\rm it}$ to 0.32×10^{12} cm⁻² eV⁻¹ along with a small decrease in accumulation capacitance in comparison to the control device in Figure 2k. Conversely, when SiGe is exposed to ozone prior to Al_2O_3 growth, D_{it} increases significantly without (Figure 2m) and with sulfur treatment (Figure 2n) prior to Al_2O_3 growth. The sulfur-passivated surface showed a lower D_{it} value, consistent with sulfur reducing $\text{GeO}_{x^*}^{17}$ The 75% decrease

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Figure 5. STEM-EELS compositional analysis of MOSCAP devices: (a) 45 cycles of HfO₂ control device; (b) 45 cycles of Al₂O₃ control device; (c) bilayer device with 5 ALD cycles of HfO₂/60 s O₃/40 ALD cycles of HfO₂ structure; (d) nanolaminate device with 9(SHfO₂ + 5 s O₃) ALD cycles. The EELS experiment was performed at 200 keV. Inset drawings illustrate the corresponding device structure. The graphs above the EELS data indicate the intensity of the STEM-HAADF and -BF images. Note that the STEM images are not taken simultaneously with EELS due to experimental constraints. Correlations are made between the EELS sampled area and STEM imaged area in scale to define the regions of the oxide. The compositions of the elements average areas of ~6 × 0.2 nm parallel to the sample surface. The blue shaded areas correspond to the interlayer thickness and boundaries defined with the half-peak values of the O and Hf signals. A comparison of the blue shaded areas of (a) vs (c) and (d) indicates that the SiGe–HfO₂ interface layer is increased by ozone insertion. Black and pink arrows denote Si and Ge compositions in the IL. In comparison to control HfO₂, the Al₂O₃ control device in (b) shows diminished Ge in the IL. The control HfO₂ device shows a Ge tail at the interface (a) which is diminished for the ozone-dosed devices in (c) and (d). Unlike the NL ozone device in (d), the bilayer ozone device in (c) shows Ge accumulation close to the SiGe.

in D_{it} for ozone dosing into $Al_2O_3/SiGe$ devices is consistent with both ozone and TMA dosing reducing interfacial GeO_x but using different yet complementary chemical processes. The TMA reduces GeO_x by gettering the oxygen from the SiGeO_x interface to form Al_2O_3 throughout the entire ALD process,⁵ and it is hypothesized that the ozone promotes GeO_x outdiffusion and eventually sublimation to form a Si-rich interface. Therefore, two distinct processes take place when ozone is inserted during Al_2O_3 ALD: (1) D_{it} reduction with ozone and (2) oxygen scavenging with remote oxide (TMA) gettering. To confirm the importance of remote gettering and its synergy with ozone dosing for even HfO₂-based gate oxides, a top Al_2O_3 layer was grown on HfO₂ (Figure 2i) as well as a traditional Al gettering gate (Figure 2j). In comparison to an ozone-dosed HfO₂-Al₂O₃/SiGe bilayer device (Figure 2h), the ozone-dosed Al₂O₃-HfO₂-Al₂O₃/SiGe trilayer device (Figure 2i) exhibits a 44% decrease in $D_{\rm it}$. This is consistent with remote oxygen scavenging by Al₂O₃ ALD grown on top of HfO₂, which is shown to be an effective method for IL modification for $D_{\rm it}$ reduction even 4 nm from SiGe surface.⁵

In the second remote scavenging example, a remote gettering gate Al metal is employed which is separated from the gate oxide with a thin Ni layer, as shown in Figure 2j. This sample was also exposed to additional intentional water exposure after 5 cycles of



Figure 6. STEM-EELS compositional analysis of nanolaminate with $9(5HfO_2 + 5 \text{ s } O_3)$ ALD cycles MOSCAP. (a) Raw EELS data obtained at 200 keV from $9(5HfO_2 + 5 \text{ s } O_3)$ NL sample are shown in a 3D semilog graph with the energy axis indicating the electron energy loss and corresponding intensity. The axis labeled with distance indicates the location of the electron beam on the sample. 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 the energy loss averaged from areas of 5×0.2 nm parallel to the sample surface. The peaks appearing on the graphs correspond to the Si K edge (1839 eV), Ge L edge (1217 eV), Hf M edge (1662 eV), O K edge (532 eV), and Ni L edge (885 eV). The black arrow indicates SiO_x interface formation between SiGe and HfO₂. Orange and green arrows indicate the Si and Ge compositions on the SiGe surface. The Ge signal decays earlier than Si as it approaches the HfO₂ layer. (b-d) To increase the visibility of the peaks, 2D graphs of raw EELS data with 1000–2350 keV energy loss range are presented in graph along with data for the control and bilayer sample. After background subtraction, offsets are introduced between each curve to improve visibility. In comparison to the control device, bilayer and NL devices show a Si peak even Ge signal decays, as seen from spectrum lines labeled 6 and 7.

 HfO_2 to deteriorate and increase interface defects. In comparison to the control sample in Figure 2f, the device with remote Al gettering gate exhibits a 60% decrease in $D_{\rm it}$ with a negligible decrease in $C_{\rm max}$. The data are consistent with the

remote gettering by Al metal or a top surface Al_2O_3 ALD layer reducing D_{it} by a mechanism which is independent of the D_{it} reduction by ozone or increase by H_2O insertion during gate oxide ALD.



Figure 7. PES compositional analysis of MOSCAP devices. The schematic drawing above the graphs constructed with STEM and EELS-EDS data illustrates the structure and the composition of the samples studied with PES. Distributions of the Si and Ge elements are shown across the 45 cycles of the HfO₂ control device (black), the bilayer device with 5 ALD cycles of HfO₂/60 s O₃/40 ALD cycles of HfO₂ structure (red), and the nanolaminate with 9(5HfO₂ + 5 s O₃) ALD cycles (blue). The Si 2p, Ge 3d, and Hf 4f signals are probed with soft X-rays at 150 eV (λ 7 Å), 500 eV (λ 17 Å), and 1000 eV (λ 26 Å). The Ge and Si peaks are normalized with respect to Hf 4f spectra for each energy to obtain relative intensity. Metallic Ge⁰ at 29 eV and Si⁰ (2p_{3/2}) at 99.4 eV are seen for all the devices at 1000 eV consistent with probing the SiGe bulk. The broad peaks at binding energies of 32.6 and 103.1 eV are defined as GeO₂ and SiO₂. Ge²⁺ at 31 eV and Si²⁺ at 101.3 eV are indicated with black lines. For all of the devices, the 150 eV GeO_x shows similar signal intensity for a given energy, indicating Ge outdiffusion from SiGe layer through the HfO₂. Conversely, the variation in Si⁴⁺ signal among the samples is pronounced. The greater Si⁴⁺ at the surface for both samples with ozone treatment is consistent with the O₃ inducing Si as well as Ge diffusion. The Ge⁴⁺/Ge⁰ ratio increases with ozone dose, indicating reduced GeO_x formation at the SiGe surface.

Interface defect distributions across the band gap for selected devices calculated with the full interface state model are shown in Figure 3a. Ozone insertion into HfO_2 -only and Al_2O_3 -only samples reduce interface trap charges almost uniformly across the band gap; the integrated D_{it} across the band gap exhibits 65% and 82% decreases, respectively. In addition, ozone insertion into the devices reduces the leakage current consistent with thicker IL formation with ozone dosing as shown in Figure 3b. An Al_2O_3 sample (Figure 2l) had exceptionally low D_{it} because two complementary mechanisms of D_{it} reduction are active: (1) D_{it} reduction with ozone exposure and (2) D_{it} decrease with remote oxygen scavenging via TMA pulsing during Al_2O_3 ALD. In contrast, for the HfO₂-only device exposed to ozone in Figure 2, there is only a single D_{it} reduction mechanism.

The interlayer and oxide thicknesses of the selected devices were determined from STEM-HAADF and STEM-BF recorded simultaneously from the MOSCAP device structure in Si $\langle 110 \rangle$ projection, as shown in Figure 4. The control Al₂O₃ device in Figure 4a,f had a darker (HAADF)/brighter (BF) IL region of 0.4 nm along with a 4.9 nm gate oxide thickness, indicated with black and white arrows in the images. Furthermore, these assignments have been confirmed by compositional analysis. Insertion of ozone into Al₂O₃ forms an IL of similar thickness

~0.2 nm and increases the gate oxide thickness to 5.5 nm, as shown in Figure 4b,g. In contrast, insertion of ozone into HfO₂ increases the IL thickness from 0.9 to 1.1 nm and increases the gate oxide thickness from 4.2 to 4.4 nm as shown in Figure 2c,h vs Figure 2d,i, respectively. Both results are consistent with the decrease in C_{ox} with ozone insertion into Al₂O₃ (Figure 2k vs Figure 2l) and into HfO₂ (Figure 2a vs Figure 2d); however, the mechanism of D_{it} reduction necessitates the compositional analysis to elucidate the differences in ozone-induced reduction/growth with Al₂O₃ vs HfO₂.

STEM-EELS compositional analysis of the selected devices along with associated structures are shown in Figure 5. STEM-HAADF and BF intensity profiles correlated with EELS analysis are also shown. Note that these STEM images are a representation of similar areas where EELS analyses were performed but were not taken simultaneously with EELS due to experimental restraints. A multiple linear least-squares (MLLS) fitting²⁴ is employed to resolve Al, Hf, and Si edges and spectroscopic overlay issues. The IL regions are shaded blue and are located between the half-maximum of oxygen and the halfmaximum of Hf. For the Al₂O₃ sample, since there is electron beam induced damage seen in the middle of the oxide, the halfmaximum of the Al is defined by extrapolation of the maximum peak point for the Al signal, which is estimated to be 75 a.u. The blue IL boundaries are confirmed by correlating the EELS with the corresponding STEM HAADF-BF contrast intensity profiles. The Si–Ge composition in IL is denoted with black and pink arrows, respectively; the arrows point to the Si and Ge intensity in the middle of the interlayer. As shown in the control HfO₂ device in Figure 5a, the Hf and O signals have offsets indicating the presence of a thick $Si_xGe_xO_x$ IL; the black and pink arrows show high Ge composition in this IL. In contrast, the control Al₂O₃ device in Figure 5b has a thinner interlayer, as documented by the Al and O signals decaying in similar positions. The Al₂O₃ IL has a small Ge signal (pink), indicating Si rich IL formation. Note that the EELS data indicate a significant Al component in the Al₂O₃/SiGe interlayer, indicating that the IL may be AlSiO_x.

The ozone bilayer HfO_2 device shown in Figure 5c has a larger offset between the Hf and O signals with diminished Ge signal in IL (pink arrow) in comparison to the control device in Figure 5a, consistent with a thicker Si-rich IL region. This ozone bilayer HfO₂ IL has a region which is Hf poor; therefore, it is divided with a dashed line to distinguish regions of $Si_rHf_rO_r$ and $Si_x Ge_x O_x$. In addition, the Si peak beyond the half-maximum of oxygen extends further into the gate oxide for the ozone bilayer HfO_2 (3 nm from the right edge of the blue region) in comparison to control HfO_2 (1.5 nm from the right edge of the blue region), consistent with ozone enhancing Si diffusion into HfO₂; the ozone-enhanced diffusion of Si is also confirmed by PES data below. Finally, for an ozone bilayer (Figure 5c), a slightly increased Ge peak near the SiGe surface is observed, consistent with Ge pile-up in the SiGe layer. $^{31-33}$ When ozone is dispersed into HfO₂ as shown in Figure 5d, the Hf–O offset was increased, consistent with $Si_xGe_xO_x$ and $Si_xHf_xO_x$ formation. Similar to the bilayer ozone in Figure 5c, the Si signal in the ozone nanolaminate (Figure 5d) extended further into HfO₂ (3.8 nm from the right edge of the blue region), consistent with ozone enhancing Si diffusion into HfO₂ mostly in the IL region. Therefore, the ozone insertion into HfO₂ increases the IL thickness along with increasing the SiO_x concentration in the IL and perhaps in HfO_2 , whereas ozone decreases the IL thickness and does not change the Si diffusion into the gate oxide for Al_2O_3 , which is consistent with Al_2O_3 being a better diffusion barrier to both GeO_x and SiO_x than HfO₂.

For a better illustration of the Si and Ge distributions, raw EELS data for HfO_2 with dispersed ozone (NL device) is shown in a 3D semilog graph in Figure 6a. The elemental profiles of the oxide can be seen from the peaks arising after element-specific edges due to electron energy loss: for example, Hf M edges at 1662 eV and the O K edge at 532 eV. The black arrow indicates the SiGe/HfO₂ interface region. Tracing the Si and Ge signal from SiGe into the HfO₂ region, Ge decay (green arrow) is observed earlier than the Si decay (orange arrow), consistent with a SiO_x-rich IL formation.

A side by side comparison of interface regions for HfO_2 devices with raw EELS data after proper background subtraction is shown in Figure 6b–d. Each color-coded and numbered graphical line is an EELS spectrum at a given location on the sample with the corresponding beam spot size indicated on the top right corner of the graphs (note that 5 nm regions parallel to the SiGe surface are averaged). By tracing the Si K edge at 1839 eV and Ge L edges at 1217 eV from SiGe into HfO₂, it is seen at spectrum number 5 that Si and Ge signals decay simultaneously for the control HfO₂ device. In contrast, an earlier Ge decay is seen in both the bilayer and NL device at spectrum 5. The only

Si peak observed at spectrum line 6 for bilayer and NL devices indicates SiO_x IL formation. The data are consistent with the ozone increasing the Si content of the IL for both the bilayer and NL devices.

It is hypothesized that ozone increases the Si content of the IL by depletion of Ge through oxidation of Ge at the interface, which diffuses to the surface of the oxides and then sublimates. To prove the Ge and Si diffusion hypothesis, PES was employed after full gate oxide deposition since PES has better compositional sensitivity especially for the topmost surface of the sample with low photon energy (see the Supporting Information). PES compositional analysis of MOSCAP devices are shown in Figure 7 for Ge (left) and Si (right). The schematic drawings above the graphs are constructed from the STEM-EELS data, illustrating the structure and the composition of the samples studied with PES. Metallic Ge 0 at 29 eV and Si $^0\left(p_{3/2}\right)$ peaks with spin–orbit splitting at 99.4 eV are seen for all of the devices at 1000 eV, which indicates that the probing depth extends into the SiGe bulk. Broad peaks at 32.6 and 103.1 eV are defined as GeO₂³ and SiO₂, respectively.²⁹ Additional analysis and controls are provided in the Supporting Information. It should be noted that, in these graphs, the Si and Ge intensities should not be directly compared to each other because the relative sensitivity the measurement system to the two different elements is not well characterized.

For all of the devices, the 150 eV X-ray energy probed GeO_x shows similar signal intensities for a given energy, indicating Ge outdiffusion from the SiGe layer through the HfO₂. Conversely, the variation in the Si⁴⁺ signal intensity among the samples is pronounced. The SiO₂ signal is strongest at 150 eV, consistent with ozone-induced Si outdiffusion to the surface or the near-surface region as the oxide is growing.^{35,36} This is consistent with EELS, which shows enhancement of Si outdiffusion with ozone pulsing. It should be noted that in PES in Figure 7 the amount of Ge²⁺ is low in comparison with Ge⁴⁺, consistent with the difference in the heats of formation between GeO₂ ($\Delta H^{\circ} = -580.0 \text{ kJ/mol}$) and GeO ($\Delta H^{\circ} = -261.9 \text{ kJ/mol}$); the greater thermodynamic stability of GeO₂ in comparison to GeO is consistent with Ge⁴⁺ dominating the XPS spectra after full device fabrication.

The diminished Si and Ge composition near the oxide top surface in EELS data may seem to be inconsistent with PES data; however, as explained in the Supporting Information in detail, this is a result of the difference in sensitivity and nature of the techniques. It should be emphasized that in the PES spectrum the intensity of elements results from the integrated signal from material normal to the SiGe surface, while in EELS the integrated signal is generated from material parallel to the SiGe surface. It is noted that, at 1000 eV photon energy, Si⁰ is a significant fraction of the Si spectrum in comparison the fraction of Ge⁰ in the Ge spectrum. Since this effect is only seen at 1000 eV, it must originate from Si and Ge at the oxide/SiGe interface. Beam-induced decomposition is unlikely, since GeO_x is less thermodynamically stable than SiO_r . However, the relative escape probabilities (elastic plus inelastic) of the photoelectrons from Si $2p_{3/2}$ and Ge $3d_{5/2}$ are unknown and likely to differ (see the Supporting Information) and, therefore, this region is best studied with STEM-EELS, since it gives true composition vs depth. However, the PES data documents the presence of GeO_x and SiO_x on the top surface of the gate oxides or incorporated into the top of the oxide as a germinate or silicate, confirming the ozone-induced diffusion of GeO_x and SiO_x during ALD.

Article



Figure 8. Schematic drawing of the interface defect reduction mechanism with ozone insertion into oxide during the ALD process. The interface defect reduction mechanism on SiGe with ozone dosing is explained in four steps: (a) ozone diffuses into the gate oxide; (b) ozone dissociates and oxygen bonds to interfacial Si and Ge atoms to form SiGeO_x; (c) GeO outdiffuses into the gate oxide; (d) GeO desorbs from the surface and leaves an SiO_x-rich interface behind.

DISCUSSION AND CONCLUSION

The kinetics of Ge diffusion into gate oxides and GeO desorption from the oxide surface are well-documented.^{31,37-39} Kita et al. and others report the formation of volatile GeO due to oxidation of Ge at the interface of SiGe (or Ge) which diffuses through the gate oxide and desorbs from the surface as GeO.^{38,40,41} Unlike SiO desorption from surfaces at high temperature (standard sublimation temperature \sim 780 °C), sublimation of GeO occurs at low temperature (standard sublimation temperature ~400 °C).^{41,42} GeO, formation can induce significant Ge consumption from the interface.^{40,43} In addition, it has been shown that high-pressure oxygen can suppress GeO desorption by forming relatively stable GeO₂ at the oxide-Ge interface, which is a common mechanism for the high-quality IL on Ge substrates;^{20,21,44} therefore, GeO desorption can be enhanced at low oxidant pressure due to transformation from GeO₂ into volatile GeO in an oxygendeficient environment.^{38,41} The standard Gibbs free energy of Si oxidation is higher than that for Ge, but for very reactive oxidants, such as atomic O from O₃ dissociation, this difference may be less important. In sum, the Ge outdiffusion into the gate oxide and GeO desorption from the system can be controlled by tuning temperature, oxidant type, and oxidant concentration.

It is hypothesized that interface defect reduction by ozone insertion into the HfO2 gate is primarily induced by enhancement of GeO formation, followed by GeO diffusion through the gate oxide and sublimation of GeO from the gate oxide surface, as illustrated in Figure 8. Ozone from each ozone pulse can diffuse to the SiGe oxide interface and form mobile GeO. This process can deplete Ge from the SiGe top layer and form the Sirich IL shown in STEM-EELS. The nature of the Ge diffusion process especially through a thin oxide layer is not known. Studies on oxygen vacancy formation and diffusion in HfO₂ suggest that Ge diffusion would be oxygen vacancy dependent, but a DFT study is needed to understand the true mechanism.^{45,46} GeO desorption from a GeO₂ surface (on a Ge substrate) has been shown using thermal desorption spectroscopy (TDS) by Kita et al.; since an ALD process precludes TDS experiments, the results of Kita et al. are for the proposed mechanism. This process is Ge selective due to the difference in activation energy for GeO desorption and diffusion and the propensity of SiO_x to form a silicate instead of desorb from gate oxides.^{42,47,48} Preferential SiO_x formation because of the difference in oxidation kinetics of Si versus Ge might also play a role. However, ozone is very active oxidant and each

dosing introduces excess of it which is enough to oxidize Ge along with Si on SiGe. Hence, although the kinetics of oxidation difference may play a role in these experiments, it cannot be the mechanism for the observed results. Reports of the effect of oxygen plasma on Ge and SiGe oxidation^{18,36} suggest that the oxygen radicals (O atoms) can diffuse through the oxide and form GeO₂ at the oxide–SiGe or –Ge interface, lowering defect density. However, plasma oxygen is not preferred, since ion or electron bombardment can induce fixed oxide charge traps and may be a concern for device reliability. Conversely, oxygen molecules (O₂) do not induce any damage but are not as reactive as ozone or oxygen radicals; therefore, interface defect reduction is not expected with molecular oxygen exposure during the ALD process.

 Al_2O_3 only gate oxide growth with ozone insertion on SiGe is very effective for D_{it} reduction because there are two complementary mechanisms active in reducing D_{it} : (1) ozone selectively depletes Ge from the SiGe surface, leaving an Si-rich interface, while (2) the Al_2O_3 deposition process itself reduces D_{itt} driven by the highly oxygen reactive Al₂O₃ precursor TMA and the differences in formation enthalpies of GeO_x and SiO_x. The defect reduction occurs by excess TMA diffusing into the oxide and reducing interface defects via oxygen scavenging.⁵ Therefore, Al₂O₃ ALD selectively scavenges oxygen from Ge, which reduces the IL thickness and forms an ultralow defect density $(D_{it} = 3.2 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1})$ Al₂O₃-SiGe interface. Ozone insertion into bilayer HfO2-Al2O3-SiGe is not as effective as ozone insertion into only HfO₂-SiGe devices; this is consistent with the Al₂O₃ in the bilayer already partially decreasing the interfacial GeO_r and reducing the Ge outdiffusion, since it is a good diffusion barrier.³² The TMA diffusion through the gate oxide during ALD is nominally a nonideality in the ALD mechanism but produces devices with the lowest D_{it} .

For HfO₂, the most effective D_{it} reduction with ozone is found when ozone is dispersed into the HfO₂ gate oxide in a nanolaminate structure, consistent with the ozone oxidant continuing to generate interfacial GeO_x and its sublimation during the entire ALD process, thus providing a continuous removal of Ge from the interface. While ALD is usually modeled as a layer by layer process, for gate oxide deposition, the data are more consistent with processes in which the interface continuously evolves during ALD and thus requires a continuous defect reduction or postdeposition defect reduction process. This continuous defect reduction can be implemented by using an Al₂O₃-HfO₂ nanolaminate to getter oxygen from GeO_x continuously during ALD,⁵ oby using an ozone–HfO₂ nanolaminate to continuously deplete Ge from the IL by GeO sublimation during ALD, or by using a gettering gate to scavenge oxygen from GeO_x after ALD;¹⁸ however, in all cases these processes depend on facile diffusion of oxidants during or after ALD through the gate oxide. Correlations between experimental results suggest that the ALD process itself modifies the oxide– channel interface during the entire ALD process. In essence, the nonideality of the ALD process (even for the Al₂O₃–HfO₂ nanolaminate) is critical for the suppression of electronic defects.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.9b06640.

Information about the energy-resolved photoelectron spectroscopy (PES) setup and PES spectra for Si, Ge, Hf, O at various energies (PDF)

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Notes

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REFERENCES

(1) Powell, C. J.; Jablonski, A. Dependence of calculated electron effective attenuation lengths on transport mean free paths obtained from two atomic potentials. *Surf. Interface Anal.* **2006**, 38 (10), 1348–1356.

(2) Maune, B. M.; Borselli, M. G.; Huang, B.; Ladd, T. D.; Deelman, P. W.; Holabird, K. S.; Kiselev, A. A.; Alvarado-Rodriguez, I.; Ross, R. S.; Schmitz, A. E.; Sokolich, M.; Watson, C. A.; Gyure, M. F.; Hunter, A. T. Coherent singlet-triplet oscillations in a silicon-based double quantum dot. *Nature* **2012**, *481*, 344.

(3) Xiao, M.; House, M. G.; Jiang, H. W. Measurement of the Spin Relaxation Time of Single Electrons in a Silicon Metal-Oxide-Semiconductor-Based Quantum Dot. *Phys. Rev. Lett.* **2010**, *104* (9), 096801.

(4) Coppersmith, S. N.; Lagally, M. G.; Celler, G.; Friesen, M.; McGuire, L. M.; Slinker, K. A.; Goswami, S.; Savage, D. E.; Roberts, M. M.; Klein, L. J.; Eriksson, M. A. In SiGe: Materials and Devices for Quantum Computing?, 2006 International SiGe Technology and Device Meeting, 15–17 May 2006; 2006; pp 1–1.

(5) Kavrik, M. S.; Ercius, P.; Cheung, J.; Tang, K.; Wang, Q.; Fruhberger, B.; Kim, M.; Taur, Y.; McIntyre, P. C.; Kummel, A. C. Engineering High-k/SiGe Interface with ALD Oxide for Selective GeOx Reduction. *ACS Appl. Mater. Interfaces* **2019**, *11* (16), 15111–15121.

(6) Choi, S.; Tan, S. H.; Li, Z.; Kim, Y.; Choi, C.; Chen, P.-Y.; Yeon, H.; Yu, S.; Kim, J. SiGe epitaxial memory for neuromorphic computing with reproducible high performance based on engineered dislocations. *Nat. Mater.* **2018**, *17* (4), 335–340.

(7) Lu, D. Silicon Germanium FinFET Device Physics, Process Integration and Modeling Considerations. *ECS Trans.* **2014**, *64* (6), 337–345.

(8) Höck, G.; Kohn, E.; Rosenblad, C.; Känel, H. v.; Herzog, H.-J.; König, U. High hole mobility in Si0.17Ge0.83 channel metal–oxide– semiconductor field-effect transistors grown by plasma-enhanced chemical vapor deposition. *Appl. Phys. Lett.* **2000**, *76* (26), 3920–3922. (9) Ismail, K.; Chu, J. O.; Meyerson, B. S. High hole mobility in SiGe

alloys for device applications. Appl. Phys. Lett. 1994, 64 (23), 3124-3126.

(10) Hashemi, P.; Kam-Leung, L.; Ando, T.; Balakrishnan, K.; Ott, J. A.; Koswatta, S.; Engelmann, S. U.; Dae-Gyu, P.; Narayanan, V.; Mo, R. T.; Leobandung, E. In Demonstration of record SiGe transconductance and short-channel current drive in High-Ge-Content SiGe PMOS FinFETs with improved junction and scaled EOT, 2016 IEEE Symposium on VLSI Technology, 14–16 June 2016; 2016; pp 1–2.

(11) Hashemi, P.; Ando, T.; Balakrishnan, K.; Cartier, E.; Lofaro, M.; Ott, J. A.; Bruley, J.; Lee, K.; Koswatta, S.; Dawes, S.; Rozen, J.; Pyzyna, A.; Chan, K.; Engelmann, S. U.; Park, D.; Narayanan, V.; Mo, R. T.; Leobandung, E. In Replacement high-K/metal-gate High-Ge-content strained SiGe FinFETs with high hole mobility and excellent SS and reliability at aggressive EOT \sim 7Å and scaled dimensions down to sub-4nm fin widths, 2016 IEEE Symposium on VLSI Technology, 14–16 June 2016; 2016; pp 1–2.

(12) Zhang, L.; Guo, Y.; Hassan, V. V.; Tang, K.; Foad, M. A.; Woicik, J. C.; Pianetta, P.; Robertson, J.; McIntyre, P. C. Interface Engineering for Atomic Layer Deposited Alumina Gate Dielectric on SiGe Substrates. *ACS Appl. Mater. Interfaces* **2016**, *8* (29), 19110–19118.

(13) LeGoues, F. K.; Rosenberg, R.; Nguyen, T.; Himpsel, F.; Meyerson, B. S. Oxidation studies of SiGe. J. Appl. Phys. **1989**, 65 (4), 1724–1728.

(14) Mitard, J.; Witters, L.; Bardon, M. G.; Christie, P.; Franco, J.; Mercha, A.; Magnone, P.; Alioto, M.; Crupi, F.; Ragnarsson, L.; Hikavyy, A.; Vincent, B.; Chiarella, T.; Loo, R.; Tseng, J.; Yamaguchi, S.; Takeoka, S.; Wang, W.; Absil, P.; Hoffmann, T. In High-mobility 0.85nm-EOT SiGe pFETs: Delivering high performance at scaled VDD, 2010 International Electron Devices Meeting, 6–8 Dec 2010; 2010; pp 10.6.1–10.6.4.

(15) Sardashti, K.; Hu, K.-T.; Tang, K.; Madisetti, S.; McIntyre, P.; Oktyabrsky, S.; Siddiqui, S.; Sahu, B.; Yoshida, N.; Kachian, J.; Dong, L.; Fruhberger, B.; Kummel, A. C. Nitride passivation of the interface between high-k dielectrics and SiGe. *Appl. Phys. Lett.* **2016**, *108* (1), 011604.

(16) Huang, J.; Wu, N.; Zhang, Q.; Zhu, C.; Li, M. F.; Tay, A. A. O.; Cheng, Z.-Y.; Leitz, C. W.; Lochtefeld, A. Surface NH3 anneal on strained Si0.5Ge0.5 for metal-oxide-semiconductor applications with HfO2 as gate dielectric. *Appl. Phys. Lett.* **2006**, 88 (14), 143506.

(17) Sardashti, K.; Hu, K.-T.; Tang, K.; Park, S.; Kim, H.; Madisetti, S.; McIntyre, P.; Oktyabrsky, S.; Siddiqui, S.; Sahu, B.; Yoshida, N.; Kachian, J.; Kummel, A. Sulfur Passivation for the Formation of Si-Terminated Al2O3/SiGe(001) Interfaces. *Appl. Surf. Sci.* **2016**, *366*, 455–463.

(18) Kavrik, M. S.; Thomson, E.; Chagarov, E.; Tang, K.; Ueda, S. T.; Hou, V.; Aoki, T.; Kim, M.; Fruhberger, B.; Taur, Y.; McIntyre, P. C.; Kummel, A. C. Ultralow Defect Density at Sub-0.5 nm HfO2/SiGe Interfaces via Selective Oxygen Scavenging. *ACS Appl. Mater. Interfaces* **2018**, *10* (36), 30794–30802.

(19) Lee, C. H.; Kim, H.; Jamison, P.; Southwick, R. G.; Mochizuki, S.; Watanabe, K.; Bao, R.; Galatage, R.; Guillaumet, S.; Ando, T.; Pandey, R.; Konar, A.; Lherron, B.; Fronheiser, J.; Siddiqui, S.; Jagannathan, H.;

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Paruchuri, V. In Selective GeOx-scavenging from interfacial layer on Si1–xGexchannel for high mobility Si/Si1–xGexCMOS application, 2016 IEEE Symposium on VLSI Technology, 14–16 June 2016; 2016; pp 1–2.

(20) Zhang, R.; Iwasaki, T.; Taoka, N.; Takenaka, M.; Takagi, S. In High mobility Ge pMOSFETs with ~ 1nm thin EOT using Al2O3/ GeOx/Ge gate stacks fabricated by plasma post oxidation, 2011 Symposium on VLSI Technology - Digest of Technical Papers, 14–16 June 2011; 2011; pp 56–57.

(21) Ando, T.; Hashemi, P.; Bruley, J.; Rozen, J.; Ogawa, Y.; Koswatta, S.; Chan, K. K.; Cartier, E. A.; Mo, R.; Narayanan, V. High Mobility High-Ge-Content SiGe PMOSFETs Using Al2O3/HfO2 Stacks with In-Situ O3 Treatment. *IEEE Electron Device Lett.* **2017**, *38* (3), 303–305.

(22) Chen, H.-P.; Yuan, Y.; Yu, B.; Chang, C.-S.; Wann, C.; Taur, Y. Re-examination of the Extraction of MOS Interface-State Density by C–V Stretchout and Conductance Methods. *Semicond. Sci. Technol.* **2013**, *28* (8), 085008.

(23) Chen, H. P.; Yuan, Y.; Yu, B.; Ahn, J.; McIntyre, P. C.; Asbeck, P. M.; Rodwell, M. J. W.; Taur, Y. Interface-State Modeling of Al2O3 InGaAs MOS From Depletion to Inversion. *IEEE Trans. Electron Devices* **2012**, *59* (9), 2383–2389.

(24) Leapman, R. D.; Swyt, C. R. Separation of Overlapping Core Edges in Electron Energy Loss Spectra by Multiple-Least-Squares Fitting. *Ultramicroscopy* **1988**, *26* (4), 393–403.

(25) Satake, T.; Yamamoto, M.; Natio, S.; Mabuchi, M.; Kaneda, A.; Kurahashi, M.; Hashino, T. Auger electron, electron energy loss, secondary electron emission and secondary ion mass spectroscopic studies on the oxidation of hafnium at room temperature. *J. Chem. Soc., Faraday Trans.* **1993**, 89 (19), 3611–3618.

(26) Iacona, F.; Kelly, R.; Marletta, G. X-ray photoelectron spectroscopy study of bombardment-induced compositional changes in ZrO2, SiO2, and ZrSiO4. *J. Vac. Sci. Technol., A* **1999**, *17* (5), 2771–2778.

(27) Merzlikin, S. V.; Tolkachev, N. N.; Strunskus, T.; Witte, G.; Glogowski, T.; Wöll, C.; Grünert, W. Resolving the depth coordinate in photoelectron spectroscopy – Comparison of excitation energy variation vs. angular-resolved XPS for the analysis of a self-assembled monolayer model system. *Surf. Sci.* **2008**, *602* (3), 755–767.

(28) Girard-Lauriault, P.-L.; Gross, T.; Lippitz, A.; Unger, W. E. S. Chemical and Elemental Depth Profiling of Very Thin Organic Layers by Constant Kinetic Energy XPS: A New Synchrotron XPS Analysis Strategy. *Anal. Chem.* **2012**, *84* (14), 5984–5991.

(29) Schmeisser, D.; Schnell, R. D.; Bogen, A.; Himpsel, F. J.; Rieger, D.; Landgren, G.; Morar, J. F. Surface oxidation states of germanium. *Surf. Sci.* **1986**, *172* (2), 455–465.

(30) Morant, C.; Galán, L.; Sanz, J. M. An XPS study of the initial stages of oxidation of hafnium. *Surf. Interface Anal.* **1990**, *16* (1–12), 304–308.

(31) Lu, N.; Bai, W.; Ramirez, A.; Mouli, C.; Ritenour, A.; Lee, M. L.; Antoniadis, D.; Kwong, D. L. Ge Diffusion in Ge Metal Oxide Semiconductor with Chemical Vapor Deposition HfO2 Dielectric. *Appl. Phys. Lett.* **2005**, *87* (5), 051922.

(32) Ogawa, S.; Asahara, R.; Minoura, Y.; Sako, H.; Kawasaki, N.; Yamada, I.; Miyamoto, T.; Hosoi, T.; Shimura, T.; Watanabe, H. Insights into Thermal Diffusion of Germanium and Oxygen Atoms in HfO2/GeO2/Ge Gate Stacks and Their Suppressed Reaction with Atomically thin AlOx Interlayers. J. Appl. Phys. **2015**, 118 (23), 235704.

(33) Long, E.; Galeckas, A.; Kuznetsov, A. Y. Ge concentrations in pile-up layers of sub-100-nm SiGe films for nano-structuring by thermal oxidation. J. Vac. Sci. Technol., B: Nanotechnol. Microelectron.: Mater., Process., Meas., Phenom. 2012, 30 (4), 041212.

(34) Prabhakaran, K.; Ogino, T. Oxidation of Ge(100) and Ge(111) surfaces: an UPS and XPS study. *Surf. Sci.* **1995**, *325* (3), 263–271.

(35) Prabhakaran, K.; Ogino, T.; Scimeca, T.; Watanabe, Y.; Oshima, M. Bonding partner change reaction in oxidation of Ge on Si(001): Observation of two step formation of SiO2. *Appl. Phys. Lett.* **1994**, *64* (14), 1839–1841.

(36) Prabhakaran, K.; Nishioka, T.; Sumitomo, K.; Kobayashi, Y.; Ogino, T. In situ oxidation of a thin layer of Ge on Si(001): Observation of GeO to SiO2 transition. *Appl. Phys. Lett.* **1993**, *62* (8), 864–866.

(37) Hosoi, T.; Hideshima, I.; Tanaka, R.; Minoura, Y.; Yoshigoe, A.; Teraoka, Y.; Shimura, T.; Watanabe, H. Ge diffusion and bonding state change in metal/high-k/Ge gate stacks and its impact on electrical properties. *Microelectron. Eng.* **2013**, *109*, 137–141.

(38) Kita, K.; Wang, S. K.; Yoshida, M.; Lee, C. H.; Nagashio, K.; Nishimura, T.; Toriumi, A. In Comprehensive study of GeO2 oxidation, GeO desorption and GeO2 metal interaction -understanding of Ge processing kinetics for perfect interface control, 2009 IEEE International Electron Devices Meeting (IEDM), 7–9 Dec 2009; 2009; pp 1–4.

(39) Oniki, Y.; Koumo, H.; Iwazaki, Y.; Ueno, T. Evaluation of GeO desorption behavior in the metal/GeO2/Ge structure and its improvement of the electrical characteristics. *J. Appl. Phys.* **2010**, *107* (12), 124113.

(40) Oh, J.; Campbell, J. C. Thermal desorption of Ge native oxides and the loss of Ge from the surface. *J. Electron. Mater.* **2004**, *33* (4), 364–367.

(41) Hansen, D. A.; Hudson, J. B. The adsorption kinetics of molecular oxygen and the desorption kinetics of GeO on Ge(100). *Surf. Sci.* **1993**, *292* (1), 17–32.

(42) Prabhakaran, K.; Maeda, F.; Watanabe, Y.; Ogino, T. Distinctly different thermal decomposition pathways of ultrathin oxide layer on Ge and Si surfaces. *Appl. Phys. Lett.* **2000**, *76* (16), 2244–2246.

(43) Wang, S. K.; Kita, K.; Lee, C. H.; Tabata, T.; Nishimura, T.; Nagashio, K.; Toriumi, A. Desorption kinetics of GeO from GeO2/Ge structure. *J. Appl. Phys.* **2010**, *108* (5), 054104.

(44) Mukhopadhyay, M.; Ray, S. K.; Maiti, C. K.; Nayak, D. K.; Shiraki, Y. Electrical properties of oxides grown on strained SiGe layer at low temperatures in a microwave oxygen plasma. *Appl. Phys. Lett.* **1994**, 65 (7), 895–897.

(45) Ferrari, S.; Fanciulli, M. Diffusion Reaction of Oxygen in HfO2/ SiO2/Si Stacks. J. Phys. Chem. B 2006, 110 (30), 14905–14910.

(46) Hu, Y.; Wang, C.; Dong, H.; Wallace, R. M.; Cho, K.; Wang, W.-H.; Wang, W. Origin of Indium Diffusion in High-k Oxide HfO2. *ACS Appl. Mater. Interfaces* **2016**, *8* (11), 7595–7600.

(47) NIST *NIST Chemistry WebBook;* National Institute of Standards and Technology: 2017; SRD 69.

(48) Uematsu, M. Self-diffusion and impurity diffusion in silicon dioxide. J. Phase Equilib. Diffus. 2005, 26 (5), 547–554.