HfO$_2$/Al$_2$O$_3$ Nanolaminate on Si$_{0.7}$Ge$_{0.3}$ (100) Surface by Thermal Atomic Layer Deposition

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To integrate Silicon-Germanium (SiGe) into future CMOS devices, it is essential to deposit very thin high-k dielectrics on SiGe surfaces with low density interfacial defects. In this study, Al$_2$O$_3$/HfO$_2$ nanolaminate (HfO$_2$ layers incorporated with Al$_2$O$_3$ monolayers) gate stacks were deposited by atomic layer deposition (ALD) using HfCl$_4$ and H$_2$O precursors. Electrical properties of the interfaces were quantified by capacitance-voltage (C–V) spectroscopy. Interfaces of nanolaminate stacks were found to have 2x smaller density of interface traps ($D_{it}$) than pure HfO$_2$ gate stacks. Cross sectional TEM with Energy-dispersive X-ray spectroscopy (EDS) showed that an SiO$_x$ rich interlayer was formed between the nanolaminate and the Si$_{0.7}$Ge$_{0.3}$(001) substrate. The SiO$_x$ interlayer contains almost no Ge indicating that the HfCl$_4$/TMA nanolaminate deposition reduced the GeO$_x$ in the interface. Furthermore, the SiGe surface was enriched in Ge from 30% to ~70% consistent with the HfCl$_4$/TMA nanolaminate process reducing and redepositing Ge on the SiGe surface.

INTRODUCTION

Silicon-Germanium (SiGe) alloys have shown a great promise as the channel material for fin field effect transistors (FinFETs) and nanowire field effect transistors (NW-FETs) due to tunability of their carrier mobilities and band gaps by variation in Ge content and tensile/compressive stresses (1),(2),(3),(4),(5),(6). In addition, SiGe alloys are expected to be more easily integrated into the existing Si CMOS fabrication technologies than III-V semiconductor or pure Ge due to rather facile growth of SiGe alloys on Si substrates (7), (8),(9),(10). However, to ensure full integration of SiGe into the future CMOS
technology, it is imperative to develop robust methods to deposit thin high-k dielectrics on SiGe surfaces with low leakage and high interface quality \((11),(12),(13),(14),(15)\).

One of the challenges in realizing low-defect interfaces between high-k dielectrics and SiGe is to control the Ge reactions during the oxide deposition and post deposition annealing steps \((16),(17),(18),(19)\). The presence of Ge at the high-k/SiGe interface could lead to Ge sub-oxide \((\text{GeO}_x)\) formation which can readily diffuse within the high-k oxides \((20)\). In addition, since GeO and GeO\(_2\) are volatile and unstable in the presence of Ge, they can pose reliability issues for devices \((21)\). Therefore, it is essential to chemically passivate the interfaces to minimize Ge concentration at the high-k/SiGe interfaces.

Various approaches have been tested for limiting the Ge–O bond formation at the interface including sulfur passivation \((18)\) and plasma nitridation \((22)\). However, these approaches were only successful for pure Al\(_2\)O\(_3\) or Al\(_2\)O\(_3\)/HfO\(_2\) bilayers with a 1-2 nm thick Al\(_2\)O\(_3\) interfacial layer. Additionally, Al\(_2\)O\(_3\)/HfO\(_2\)/Al\(_2\)O\(_3\) tri-layers (or sandwich) have been deposited on strained p-SiGe by ALD at 300°C, where a 0.7nm thick layer of mixed Al\(_2\)O\(_3\)-SiO\(_x\) was observed at the interface \((23)\). In that report, Al\(_2\)O\(_3\) was employed as a spacer between HfO\(_2\) and SiGe to prevent interfacial reactions (i.e. Ge out-diffusion) during the routine post deposition annealing of the devices. However, despite low gate leakage as a function of gate bias, the C-V curves showed high fixed and interface trap charges as well as false inversion \((23)\).

In this report, electrical characteristics of the nanolaminates and laminates/SiGe interfaces were compared by capacitance-voltage (C-V) and current-voltage (I-V) spectroscopy measurements on MOS capacitors (MOSCAPs). Al\(_2\)O\(_3\)-HfO\(_2\) nanolaminates were prepared by periodic incorporation of Al\(_2\)O\(_3\) monolayers in between HfO\(_2\) multilayers from HfCl\(_4\) based ALD. For comparison, Al\(_2\)O\(_3\)-HfO\(_2\) laminates were prepared by deposition of single monolayers or multilayer of Al\(_2\)O\(_3\) on the bottom and the top of the HfO\(_2\). The nanolaminate gate oxides enabled formation of low-defect oxide/SiGe interfaces. High resolution TEM-EDS (transmission electron microscopy-energy dispersive x-ray spectroscopy) shows that the nanolaminates form a nearly pure SiO\(_x\) interlayer between the oxide and SiGe substrate.

**EXPERIMENTAL DETAILS**

A 12nm thick p-type Si\(_{0.7}\)Ge\(_{0.3}\)(100) with doping level of 2x10\(^{18}\) cm\(^{-3}\) (Applied Materials) was grown epitaxial on p-type Si(100) by molecular beam epitaxy (MBE). Prior to ALD, SiGe native oxides were removed by cyclic HF clean using 2% HF solution and DI water at 25°C, ending with HF dip \((24)\). For surface passivation, HF-treated samples were immersed in 25% \((\text{NH}_4)_2\)S solution at 25°C for 15 min followed by 30 s of DI H\(_2\)O rinse. After surface clean, the samples were transferred to the ALD chamber with less than 2 min of air exposure. HfO\(_2\) ALD was performed at 300 °C in a commercial continuous cross-flow reactor (Beneq TFS-200) with Ar as the carrier gas. The chamber base pressure during the ALD process was about 1.7 torr. HfO\(_2\) was deposited by consecutive cycles of 500 ms of HfCl\(_4\) and 500 ms of H\(_2\)O. After each HfCl\(_4\) and H\(_2\)O pulse, a 6 s long Ar purge was employed. For Al\(_2\)O\(_3\) deposition in the cross-flow reactor, 20 cycles of 45 ms TMA pre-pulses were followed by consecutive cycles of 200 ms of TMA and 50 ms of H\(_2\)O. Similar to the HfO\(_2\) recipe, after each TMA and H\(_2\)O
pulse, a 6s Ar purge was employed. Al₂O₃ – HfO₂ nanolaminate structures were prepared by applying the above-mentioned HfO₂ and Al₂O₃ recipes in two different orders: i) 4 x [9 cycles of HfO₂ + 1 cycle of Al₂O₃]. ii) 12 x [3 cycles of HfO₂ + 1 cycle of Al₂O₃]. Note for the nanolaminates, no TMA prepulsing was employed for each Al₂O₃ cycle. After ALD, 50 nm thick Ni gates were deposited by thermal evaporation. 100nm thick Al back gate electrode deposition was followed by DC magnetron sputtering on the back sides of the SiGe substrates. After completion of fabrication, MOSCAPs were annealed in forming gas (5% H₂, 95% N₂) at 300 °C for 15 min.

Capacitance-Voltage (C-V) spectroscopy of the MOSCAPs was performed using an Agilent B-1500 semiconductor analyzer, with AC modulation amplitude of 30 mV, and with a gate bias range of -2 to 2 V, at multiple frequencies from 2 KHz to 1 MHz. Current-voltage (I-V) spectroscopy measurements was also carried out in the bias range from -2V to 2V. Gate leakage vs. gate bias was measured in the same bias range.

RESULTS AND DISCUSSION

The effects of the Al₂O₃/HfO₂ nanolaminate on the electrical properties of HfO₂/SiGe interfaces were determined by variable frequency C-V spectroscopy. Figure 1a-1c displays the C–V results measured from 2 KHz to 1 MHz for HfO₂/SiGe and Al₂O₃/HfO₂ nanolaminate MOSCAPs. Densities of interface traps (D_it) were calculated using the conductance method (25). Figure 1a displays the C-V characteristics of a MOSCAP with 50 cycles of HfO₂ deposited using HfCl₄ and H₂O as the precursors. As shown in Fig 1b and 1c, use of nanolaminate structures resulted in 29% (Nanolaminate with 12 cycles of 3:1) and 39% (Nanolaminate with 5 cycles of 9:1 HfO₂: Al₂O₃) reduction in the density of interface traps relative to the pure HfO₂, at the expense of less than 0.2 µF/cm² drop in the accumulation capacitance. Note these nanolaminates have no direct Al₂O₃ deposition on the SiGe interface but instead have only HfO₂ deposition on SiGe. This improvement of D_it is hypothesized to be due to incorporated Al₂O₃ as a Ge diffusion barrier, a H₂O diffusion barrier or Ni gate metal protection layer; however, as shown by Kavrik et al, it is possible that the TMA may diffuse to the interface during deposition (26). To better quantify the effect of TMA dosing, the values of Cox/Dit were compared; the unit of this approximate metric was defined as μF × eV × 10^-12. For the 9:1 and 3:1 HfO₂: Al₂O₃ nanolaminates, the Cox/Dit values were increased by 17% and 48% respectively compared to the pure HfO₂ device. Figure 1d-1F displays the I-V spectroscopy of the pure HfO₂/SiGe and Al₂O₃/HfO₂ nanolaminate MOSCAPs. Compared to 50 cycles of HfO₂, nanolaminate samples resulted in more than 3 orders of magnitude lower leakage current which is consistent with less Ge diffusion into the nanolaminate or less diffusion of Ni during gate metallization.
Figure 1. Capacitance – voltage characteristics for high-k/SiGe MOSCAPs with HfCl₄ precursor: (a) 50 cycles of pure HfO₂ ALD (b) Nanolaminate with 12 cycles of 3:1 HfO₂:Al₂O₃; (c) Nanolaminate with 5 cycles of 9:1 HfO₂:Al₂O₃. Dıt values in eV⁻¹.cm⁻² were calculated by the conductance method. Current – voltage spectroscopy for high-k/SiGe MOSCAPs with HfCl₄ precursor: (d) 50 cycles of pure HfO₂ ALD (e) Nanolaminate with 12 cycles of 3:1 HfO₂:Al₂O₃; (f) Nanolaminate with 5 cycles of 9:1 HfO₂:Al₂O₃.

In addition to being incorporated into the nanolaminate structure, Al₂O₃ can be used as an interlayer or a cap. The Al₂O₃ interlayer is hypothesized to prevent Ge out-diffusion by forming a Si-O-Al interface, while Al₂O₃ cap layer is used to protect top surface of the oxide from damage induced by the gate electrode deposition process (this includes ambient oxidation prior to gate metal deposition and Ni diffusion during gate metal deposition) (18). For thin HfO₂ layers, the chemistry of the Al₂O₃ cap may be more complicated since TMA might diffuse through the nanolaminate to the interface as shown by Kavrik et al. (26). Al₂O₃ directly deposited on SiGe may reduce native GeOx to Ge (27). Figure 2 displays the C-V characteristics of HfO₂/SiGe MOSCAPs with Al₂O₃ cap/interlayer. To determine the effect of the cap/interlayer layers, 3 different structures were studied: i) bilayer with Al₂O₃ interlayer: 1 or 5 cycles Al₂O₃ followed by 49 or 45 cycles of HfO₂ (Fig. 2a and 2d); ii) bilayer with Al₂O₃ cap layer: 49 or 45 cycles of HfO₂ followed by 1 or 5 cycles Al₂O₃ (Fig. 2b and 2e); iii) Al₂O₃/HfO₂/Al₂O₃ trilayer: 1 or 5 cycles Al₂O₃ followed by 48 or 40 cycles of HfO₂ and 1 or 5 cycles Al₂O₃ (Fig. 2c and 2f).

A thicker Al₂O₃ layer both as a cap and interlayer resulted in lower Dıt. The trilayer structure with 5 cycles of Al₂O₃ has Dıt levels even below the nanolaminates but with reduced Cmax compared to the nanolaminate; the EOT of the trilayer structure with 5 cycles of Al₂O₃ estimated by curve fitting of CV is about 1.9 nm. Compared to the pure
HfO$_2$/SiGe (Fig 1a), adding a single monolayer of Al$_2$O$_3$ either on top (Fig 2a), on the bottom (Fig 2b), or both on the top and bottom (Fig 2c) had no significant effect on the $D_{it}$. However, adding 5 cycles of Al$_2$O$_3$ either on the bottom (Fig 2d), on the top (Fig 2e) or both on the top and bottom caused a significant drop in $D_{it}$, but also $C_{ox}/D_{it}$ values were also improved by adding 5 layers of Al$_2$O$_3$ either on the bottom of HfO$_2$ to the top of HfO$_2$ consistent with Al$_2$O$_3$ acting either as a diffusion barrier or for GeOx reduction.

**Figure 2.** MOSCAP Capacitance – voltage characteristics for bilayer and trilayer oxides on deposited SiGe using HfCl$_4$ precursor: (a) Bilayer with 1 cycle of Al$_2$O$_3$ followed by 49 cycles of HfO$_2$; (b) Bilayer with 49 cycles of HfO$_2$ followed by 1 cycle of Al$_2$O$_3$; (c) Trilayer with 1 cycle of Al$_2$O$_3$ followed by 49 cycles of HfO$_2$ and 1 cycle of Al$_2$O$_3$; (d) Bilayer with 5 cycle of Al$_2$O$_3$ followed by 45 cycles of HfO$_2$; (e) Bilayer with 45 cycles of HfO$_2$ followed by 5 cycles of Al$_2$O$_3$; (f) Trilayer with 5 cycle of Al$_2$O$_3$ followed by 40 cycles of HfO$_2$ and 5 cycle of Al$_2$O$_3$. All samples were passivated by wet sulfur clean prior to ALD. $D_{it}$ values in eV$^{-1}$cm$^2$ were calculated by conductance method.

Effect of Al$_2$O$_3$ cap and interlayer on the nanolaminate structures was also evaluated by adding 5 cycles of Al$_2$O$_3$ to the top or bottom of 9:1 and 3:1 HfO$_2$ : Al$_2$O$_3$ structures. Figure 3 shows the C-V characteristics of nanolaminates with and without Al$_2$O$_3$ caps/interlayers. For the 9:1 HfO$_2$ : Al$_2$O$_3$ nanolaminate (Fig. 3a), addition of 5 cycles of Al$_2$O$_3$ either as an interlayer (Fig. 3b) or a cap (Fig 3c) resulted in lower $D_{it}$ levels and lower $C_{ox}$. Comparing the $C_{ox}/D_{it}$ values of the 9:1 HfO$_2$ : Al$_2$O$_3$ nanolaminates ($C_{ox}/D_{it} = 0.89$ (Fig 3a)) with 5 cycles Al$_2$O$_3$ interlayers or caps, both the Al$_2$O$_3$ interlayer and cap showed an improvement ($C_{ox}/D_{it} = 0.94$ (Fig. 3b) and 0.98 (Fig. 3c)). The data is consistent with the Al$_2$O$_3$ in the nanolaminite lowering Dit by reducing diffusion of H$_2$O (from the ALD process) through the gate oxide or reduction of GeOx at the interface; since the Al$_2$O$_3$ at the interface is most efficient in reducing the Dit, the GeOx reduction by TMA probably plays a role in the Dit reduction.
The role of Al₂O₃ acting as a diffusion barrier or TMA acting as a reducing agent instead of Al₂O₃ directly passivating SiGe is consistent with the study on the 3:1 HfO₂ : Al₂O₃ nanolaminate. For the 3:1 HfO₂ : Al₂O₃ nanolaminate (Fig 3d), addition of 5 cycles of Al₂O₃ as a capping layer (Fig 3f) only modestly changed the Dᵢₜ and the Cₒₓ/Dᵢₜ value only slightly increased (Cₒₓ/Dᵢₜ = 0.70 (fig 3d) vs 0.72 (fig3f)). However, the device with 5 cycles of Al₂O₃ interlayer (Fig 3e) had a very low Dᵢₜ of 1.43 x 10¹² eV⁻¹.cm², which is remarkably low for nanolaminate structures with EOT of less than 2nm. Furthermore, the Cₒₓ/Dᵢₜ value of the device (Cₒₓ/Dᵢₜ = 1.12 (Fig 3e) was increased by nearly 60% compared to the nanolaminate only device (Cₒₓ/Dᵢₜ = 0.70 (Fig 3d)).

**Figure 3. MOSCAPs Capacitance – voltage characteristics for Nanolaminate with Al₂O₃ Caps and Interlayers with HfCl₄ precursor:**

(a) Nanolaminate with 5 cycles of 9:1 HfO₂:Al₂O₃; (b) 5 cycles of Al₂O₃ interlayer followed by nanolaminate with 5 cycles of 9:1 HfO₂:Al₂O₃ followed by (IL); (c) Nanolaminate with 5 cycles of 9:1 HfO₂:Al₂O₃ followed by 5 cycles of Al₂O₃ cap; (d) Nanolaminate with 12 cycles of 3:1 HfO₂:Al₂O₃; (e) 5 cycles of Al₂O₃ interlayer followed by nanolaminate with 12 cycles of 3:1 HfO₂:Al₂O₃ plus 5 cycles of Al₂O₃ interlayer (IL); (f) Nanolaminate with 12 cycles of 3:1 HfO₂:Al₂O₃ followed by 5 cycles of Al₂O₃ cap. Dᵢₜ values in eV⁻¹.cm² were calculated by conductance method.

Cross sectional scanning TEM with energy-dispersive x-ray spectroscopy (STEM-EDX) was performed (Fig. 4a-d) on a 5 cycles of 9:1 HfO₂: Al₂O₃ nanolaminate sample to determine the thickness of the interlayer between nanolaminate and SiGe. The TEM clearly shows an ~0.8nm thick interlayer of low atomic number between the AlHfOₓ and the SiGe (Fig 4a) meaning the nanolaminate does not directly bond to SiGe. EDS composition analysis (Fig. 4b and 4c) of the sub 1 nm interlayer shows that it consists of SiO₂ and contains almost no Ge nor Hf. The interlayer could be formed during the ALD or FGA process. Figure 4d is an EDX lines can across the interface of 9:1 Hf:Al.
nanolaminate after FGA. The oxygen signal (green line) in the SiGe region was attributed to the thin substrate having surface oxidation when it was exposed to the air between FIB cross sectioning and TEM analysis. The 5 nm thick nanolaminate layer consisting of HfAlOx was formed on SiOx. The annealing process which creates the pure SiO$_2$ layer also induces Ge enrichment of the SiGe substrate surface (blue arrow in Fig 4d). The Ge/Si atomic weight percent ratio next to the interlayer is 2 times greater than in the bulk SiGe. The data is consistent that in the presence of the NL, the annealing of SiGeOx results in formation of a SiO$_2$ interlayer and reabsorption of Ge into the SiGe substrate: Si$_x$Ge$_y$O$_z$ $\rightarrow$ SiO$_2$ + Ge. This is consistent with an ALD cleanup process in which TMA reduces GeO$_x$ to Ge and the Al$_2$O$_3$ in the nanolaminate reduces Ge and GeO$_x$ diffusion, so Ge is concentrated on the SiGe substrate (28), (29).

Figure 4: STEM-EDX of 5 cycles of 9:1 HfO$_2$: Al$_2$O$_3$ nanolaminate
(a) STEM-EDX characterization of $\sim$10% Al$_2$O$_3$ and $\sim$90% HfO$_2$/ Si$_{0.7}$Ge$_{0.3}$(001). Blue box shows a region of interlayer for EDX analysis revealing a Ge-free SiOx interlayer. The orange box is a control region in the SiGe. (b) The EDX spectra of the interlayer is in blue while the spectra on the SiGe control region is in orange. Note the absence of Ge in the interlayer. (c) EDX analysis of SiOx layer region (blue box). Note that the oxide composition is SiO$_2$. (d) EDX line scan across the interface of 9:1 Hf:Al nanolaminate.
CONCLUSION

Al$_2$O$_3$/HfO$_2$ nanolaminate by thermal ALD has been applied to Si$_{0.7}$Ge$_{0.3}$(100) surface at 300 °C. Compared to pure HfO$_2$, use of the nanolaminate structures effectively reduced the density of interface traps more than 30% at the expense of a small drop in the accumulation capacitance. In addition, at least 3 orders of magnitude lower leakage currents were achieved compared to pure HfO$_2$ layer. Effects of Al$_2$O$_3$ layer as an interlayer and a capping layer were also studied. Comparison of deposition of Al$_2$O$_3$ between HfO$_2$ and SiGe (interlayer) vs on top of HfO$_2$ (cap) shows the lower D$_{it}$ was achieved when the Al$_2$O$_3$ is in the interlayer instead of the capping layer. The data is consistent with Al$_2$O$_3$ acting as a diffusion barrier to Ge diffusion for the substrate or TMA clean-up effect reducing Ge oxides. While the nanolaminate do not have a distinct Al$_2$O$_3$ layer, the data is consistent with the incorporation of Al into HfO$_2$ improving the diffusion barrier properties thereby lowering the D$_{it}$. Cross sectional scanning TEM showed formation of SiO$_x$ interlayer between the AlHfO$_x$ and the SiGe. EDX spectra of the interlayer revealed that the SiO$_x$ layer contains almost no Ge showing the nanolaminate effectively prevents interfacial GeO$_x$ formation.

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