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To cite this article: Laura Zurauskaite *et al* 2020 *ECS Trans.* **98** 387

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Si-passivated Ge Gate Stacks with Low Interface State and Oxide Trap Densities Using Thulium Silicate

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Ultra-thin epitaxially grown Si layers have been used for Ge surface passivation in CMOS devices utilizing standard silicon SiO₂/HfO₂ gate stack. In this work, we propose a high-k TmSiO interfacial layer, which has shown excellent performance on Si, instead of the chemical SiO₂. We successfully transfer a TmSiO/Tm₂O₃/HfO₂ gate stack from silicon to Si-passivated Ge devices, yielding interface state density of $3 \cdot 10^{11} \text{ eV}^{-1} \text{ cm}^{-2}$, which is comparable to GeO_x passivation. Moreover, Si-capped Ge gates with TmSiO interfacial layer achieve significant improvement in oxide trap density compared to GeO_x passivation, exhibiting a potential for superior reliability. We further investigate the robustness of Si layer growth process and show that small ($\pm 3^\circ \text{C}$) variations of growth temperature can be detrimental to the interface state density of the gate stacks.

Introduction

Germanium is considered as one of the options for future CMOS technology nodes due to its high intrinsic electron and hole mobilities. Ge surface passivation with a thin silicon layer (Si-cap) has been shown to be efficient for pFETs in terms of interface state density (D_{it}) and reliability because of a sufficient valence band offset between Ge and Si-cap, which confines the holes in the Ge layer. Strained Ge pFinFETs outperforming Si pFinFETs by four times higher mobility have been demonstrated using Si-cap process (1). Interfacial defects can be further passivated with a high-pressure anneal in H₂ resulting in increased mobility in both pFETs (2) and nFETs (3). Moreover, negative (and positive) bias temperature instability reliability is improved when using Si-cap compared to GeO_x passivation because of the energy decoupling between the holes (electrons) and traps in the gate oxide by introducing a dipole at SiO₂/high-k interface (2), (3). However, Si-cap process poses gate stack scalability issues because in order to achieve sufficient surface passivation, Si-cap thickness cannot be scaled. In fact, Si-cap thickness is one of the key parameters in achieving low interface state density D_{it} (4), (5). An introduction of a high-k interfacial layer instead of a chemical oxide SiO₂ could potentially help to scale down the equivalent oxide thickness. Integrating thulium silicate (TmSiO) as a replacement of SiO₂ interfacial layer has been demonstrated on silicon (6), and a hole and electron mobility enhancement compared to SiO₂/HfO₂ gate stacks has been achieved for EOT < 1 nm (7). Moreover, we have previously shown the compatibility of Tm₂O₃ with Ge by demonstrating GeO_x/Tm₂O₃ gate stacks with $D_{it} < 5 \cdot 10^{11} \text{ eV}^{-1} \text{ cm}^{-2}$ (8). In this work, we integrate TmSiO in Si-cap process to achieve D_{it} comparable to GeO₂ passivation while simultaneously achieving low oxide trap density. As Si-cap process conditions has

been shown to impact the quality of resulting gate stack (9), we also investigate how small changes in Si-cap growth temperature affect the interface state density of the gate stack.

Experiments

Si-passivated Ge MOS capacitors were fabricated on virtual Ge substrates as schematically depicted in Figure 1 (a). Ge strain relaxed buffers (SRBs) were epitaxially grown on (100) oriented 100 mm Si wafers by reduced pressure chemical vapor deposition (20 torr, ASM Epsilon 2000) in a two-step process using GeH_4 precursor (10). Phosphine (PH_3 5% in H_2) was used as a dopant resulting in doping concentration of $1\text{--}3 \cdot 10^{16} \text{ cm}^{-3}$. Si-caps were deposited in the same reactor at a nominal temperature of 400°C using Si_2H_6 . The growth temperature was also varied by $\pm 3^\circ\text{C}$ in order to test the robustness of the process conditions. Si growth was confirmed by testing that the surface of the wafer was hydrophobic, by spectroscopic ellipsometry and transmission electron microscopy (TEM). While trying to keep Si-cap exposure to air to a minimum, 400 nm SiO_2 was deposited by plasma-enhanced chemical vapor deposition and active areas were defined.

Figure 1. (a) Process flow of Ge/Si/TmSiO/Tm₂O₃/HfO₂/TiN MOS capacitor fabrication. TmSiO interfacial layer is formed by ALD growth of Tm_2O_3 followed by RTA at 550°C in N_2 for 60 s. Interfacial layer formation is then followed by high-k HfO_2 deposition and O_3 PDA in ALD. ALD TiN is used as a gate metal. The resulting gate stack is schematically shown in (b) and cross-section TEM of the gate is shown in (c).

Following the patterning of the active areas, the gate stacks were formed. The remaining SiO₂ from the active areas was removed with 1 % HF, and Tm₂O₃ was deposited by atomic layer deposition (ALD) at 225 °C using TmCp₃ and H₂O precursors (11) with a target thickness of 7.4 nm. Rapid thermal anneal (RTA) at 550 °C for 60 s in N₂ was used for thulium silicate (TmSiO) interfacial layer formation. High-k HfO₂ was deposited by ALD at 350 °C using HfD04 and H₂O precursors (target thickness 5.6 nm) followed by a post deposition anneal (PDA) in O₃ for 10 min. Gate stack was completed by TiN gate metal deposition at 425 °C by ALD (TiCl₄ and NH₃ precursors) and 500 nm Al was deposited by sputtering for electrical probing purposes. After patterning, forming gas anneal (FGA) of 10% H₂ in N₂ at 400 °C for 30 min was performed. The resulting gate stack is schematically depicted in Figure 1 (b) and Figure 1 (c) shows a cross-section TEM of the gate stack indicating the layers. The TmSiO thickness is ~1 nm leaving an unreacted Si layer of ~0.5 nm. Reference MOSCAPs with Ge/GeO_x/Tm₂O₃/HfO₂ gate stacks were also fabricated as described in (8) with addition of ALD HfO₂ and FGA.

Electrical characterization of MOS capacitors was performed with Cascade 12000 wafer prober and Keithley SCS 4200. Interface state density in the midgap was evaluated from capacitance-voltage (CV) characteristics for 10 devices of each sample using a method described in (12).

Results and Discussion

Si-passivated Ge gate stacks with TmSiO interfacial layer

Well behaved CV characteristics of a typical Ge/Si/TmSiO/Tm₂O₃/HfO₂/TiN MOS capacitor with Si-cap grown at a nominal temperature of 400 °C for 40 min are displayed in Figure 2 (a). Almost no frequency dispersion is observed. Interface state density and equivalent oxide thickness were extracted from CV characteristics of 10 MOSCAPs over a 100 mm wafer. D_{it} was found to be ~3·10¹¹ eV⁻¹cm⁻² and EOT of 3.75-3.8 nm as displayed in Figure 2 (b). Reference MOSCAPs with Ge/GeO_x/Tm₂O₃/HfO₂ gates exhibit a similar D_{it} of 2·10¹¹ cm⁻²eV⁻¹. The interface state density of Si-passivated Ge gates is also consistent with TmSiO/Tm₂O₃ gate stacks previously shown on silicon, which yielded D_{it} ~10¹¹ eV⁻¹cm⁻² (6), demonstrating that no significant D_{it} degradation occurs when transferring the gate stack process to Si-passivated germanium.

One of the challenges in Ge gate stacks is to simultaneously achieve high mobility and superior reliability. While low interface state density is a good indication of high mobility, low oxide trap density can show a potential for superior reliability. Oxide trap density N_{ox} was extracted from the hysteresis of a dual CV sweep for both Si-cap and the reference GeO_x MOS capacitors as displayed in Figure 3 as a function of the oxide electric field E_{ox} and is defined as:

$$E_{ox} = \frac{V_{G,max} - V_{FB}}{CET} \quad [1]$$

Here V_{G,max} is the highest voltage to which the dual sweep was performed, V_{FB} is the flatband voltage and CET is capacitance equivalent thickness. The Si-passivated gates exhibit a hysteresis of only ~3 mV at E_{ox} of 4 MV/cm corresponding to N_{ox} of 1.5·10¹⁰ cm⁻². It is more than 20 times lower than the oxide trap density of the reference

GeO_x devices, showing the superiority of Si-passivated gates. Low oxide trap density in Ge/Si/TmSiO/Tm₂O₃/HfO₂/TiN gate stacks indicates a potential for improved reliability.

Figure 2. (a) CV characteristics of Ge/Si/TmSiO/Tm₂O₃/HfO₂/TiN gate stacks with Si-cap growth at nominal temperature of 400 °C for 40 min. (b) Interface state density is 2-4 · 10¹¹ eV⁻¹cm⁻² at EOT of 3.75-3.8 nm.

Figure 3. Oxide trap density N_{ox} extracted from CV hysteresis as a function of oxide electric field E_{ox}. Si-cap devices exhibit more than 20 times lower oxide trap density than the reference GeO_x devices.

Influence of process parameters on interface state density

Si layer thickness plays an important role in achieving low interface state density in Si-passivated gate stacks (4), (9). A Si thickness deviation of 1-2 monolayers can cause significant D_{it} degradation. As epitaxial growth rate is sensitive to temperature, small

temperature deviations could potentially alter the Si layer thickness significantly, thus increasing the interface state density of the gate stack. The influence of Si-cap growth temperature on D_{it} was investigated by introducing a small (up to ± 3 °C) deviation from the nominal growth temperature while keeping the growth time constant at 40 min. The interface state density versus the deviation from the nominal temperature is displayed in Figure 4 where each point shows an average over 10 MOSCAPs and the error bars indicate one standard deviation. Even one degree deviation from the nominal temperature increases D_{it} 1.5-2 times, from $3 \cdot 10^{11}$ eV⁻¹cm⁻² to $4.5 \cdot 10^{11}$ eV⁻¹cm⁻² and $6.5 \cdot 10^{11}$ eV⁻¹cm⁻² for -1 °C and 1 °C deviation, respectively. If the growth temperature deviates from the nominal temperature more (± 3 °C), D_{it} rises to above 10^{12} eV⁻¹cm⁻². The strong dependence of D_{it} on Si-cap growth temperature could be explained by the exponential growth rate dependence on temperature for Si growth temperatures <650 °C (13). Small growth temperature differences could alter Si-cap thickness enough to significantly influence the interface state density which has been shown to be very sensitive to Si-cap thickness (4), (9). In addition, the variation of the interface state density within a wafer becomes larger as the growth temperature deviates from the nominal temperature more. At the nominal growth temperature, the standard deviation is less than $3 \cdot 10^{10}$ eV⁻¹cm⁻² while at ± 3 °C deviation from the nominal temperature, the standard deviation is more than $2 \cdot 10^{11}$ eV⁻¹cm⁻². Hence, temperature control when depositing Si-caps for Ge passivation is of a paramount importance for achieving low and uniform interface state density.

Figure 4. Interface state density in Si-passivated gate stacks versus deviation from nominal growth temperature. Growth time is set at 40 min. Each point is an average over 10 measured MOS capacitors, and error bars indicate one standard deviation.

To further investigate the influence of the process parameters on the interface state density in Si-passivated gate stacks, Si-cap deposition time was varied. D_{it} of Ge/Si/TmSiO/Tm₂O₃/HfO₂/TiN gate stacks with Si-caps grown at three different temperatures (nominal 400 °C $\pm$ 1 °C) for 30-60 min is displayed in Figure 5. The lowest D_{it} for all growth temperatures is achieved at 40 min growth time and is $4.5 \cdot 10^{11}$ eV⁻¹cm⁻², $3 \cdot 10^{11}$ eV⁻¹cm⁻² and $6.5 \cdot 10^{11}$ eV⁻¹cm⁻² for -1 °C, 0 °C and 1 °C deviation from nominal temperature, respectively. For shorter growth times interface state density increases

rapidly, reaching more than $10^{12} \text{ eV}^{-1}\text{cm}^{-2}$ already at 35 min growth time for Si-caps grown 1°C above the nominal temperature. A similar tendency is seen for longer growth times where D_{it} is above $10^{12} \text{ eV}^{-1}\text{cm}^{-2}$ at 50 min growth time for all growth temperatures. Compared to other growth temperatures, the samples with Si-cap grown at 1°C higher than nominal temperature exhibit degraded D_{it} for all growth times. On the other hand, interface state density of the samples with Si layer grown at the nominal temperature and 1°C below becomes comparable for longer deposition times.

Figure 5. Interface state density of Ge/Si/TmSiO/Tm₂O₃/HfO₂/TiN gates as a function of the Si-cap growth time. The Si layer was grown at a nominal temperature of 400°C and at two temperatures $\pm 1^\circ\text{C}$ from the nominal temperature. The average over 10 measured devices is displayed and the standard deviation is indicated with error bars.

Conclusion

A Si-cap process with high-k TmSiO interfacial layer has been demonstrated on Ge MOS devices yielding an average $D_{it} \sim 3 \cdot 10^{11} \text{ eV}^{-1}\text{cm}^{-2}$ over 10 devices with a standard deviation of $< 3 \cdot 10^{10} \text{ eV}^{-1}\text{cm}^{-2}$. This result is similar to GeO_x/Tm₂O₃ passivation as well as with Si devices employing TmSiO interfacial layer. Si-capped Ge gates with a TmSiO interfacial layer also enable a significant improvement in oxide trap density compared to GeO_x passivation, exhibiting a potential for superior reliability. Furthermore, a strong dependence of the interface state density on Si-cap growth temperature has been shown, when a substantial D_{it} degradation was observed at only $\pm 3^\circ\text{C}$ deviation from the nominal growth temperature.

Acknowledgments

This work was supported by the Swedish Foundation for Strategic research. Fredrik Gustavsson is acknowledged for TEM images.

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