A systematic experimental evaluation of the thermal stability of Ru metal gate electrodes in direct contact with SiO$_2$ and Hf-based dielectric layers was performed and correlated with electrical device measurements. The distinctly different interfacial reactions in the Ru/SiO$_2$, Ru/HfO$_2$, and Ru/HfSiO$_x$ film systems were observed through cross-sectional high-resolution transmission electron microscopy, high angle annular dark field scanning transmission electron microscopy with electron-energy-loss spectra, and energy dispersive x-ray spectra analysis. Ru interacted with SiO$_2$, but remained stable on HfO$_2$ at 1000 °C. The onset of Ru/SiO$_2$ interfacial interactions is identified via silicon substrate pitting possibly from Ru diffusion into the dielectric in samples exposed to a 900 °C/10-s anneal. The dependence of capacitor device degradation with decreasing SiO$_2$ thickness suggests Ru diffuses through SiO$_2$, followed by an abrupt, rapid, nonuniform interaction of ruthenium silicide as Ru contacts the Si substrate. Local interdiffusion detected on Ru/HfSiO$_x$ samples may be due to phase separation of HfSiO$_x$ into HfO$_2$ grains within a SiO$_2$ matrix, suggesting that SiO$_2$ provides a diffusion pathway for Ru. Detailed evidence consistent with a dual reaction mechanism for the Ru/SiO$_2$ system at 1000 °C is presented. © 2005 American Institute of Physics.
20-nm-thick PVD Ru films deposited on 2-, 4-, 6-, and 8-nm-thick SiO₂ dielectric layers and capped with a 10-nm PVD TaN/100-nm poly-Si (phosphorus doped) gate contact were fabricated [Fig. 1(b)]. Capacitor patterning was performed before the 1000 °C/10-s RTA. High-frequency capacitance-voltage (C-V) measurements were used to study the oxide interface state-density changes induced by the metal electrode. PMOS Ru and ALD TiN electrode capacitors were also fabricated with 4-nm HfO₂ and (HfO₂)ₓ(SiO₂)₁₋ₓ, x=0.67, to compare the stability of Ru on the two Hf-based dielectrics and to enable direct physical comparison of the Ru/dielectric interface of each film system. The leakage current was measured with a HP4156B semiconductor parameter analyzer to quantify the amount of dielectric degradation corresponding to any interaction with Ru.

III. RESULTS AND DISCUSSION

A. Thermal stability of the Ru/SiO₂ system

Figure 2 illustrates the C-V plots of capacitors formed on various oxide thicknesses. The distortion of the C-V curves clearly increases with decreasing oxide thickness, from 8-nm SiO₂ (normal C-V) to 2-nm SiO₂ (gross C-V distortion). This observed distortion is attributed to changes in the SiO₂/Si interface state density, which is most likely caused by Ru metal atoms diffusing into the dielectric and/or Si atoms above. The distortion in the C-V curve occurs at the transition from depletion to inversion regions (Vₘ₉ = −0.5 to 0 V), which corresponds to the effect of acceptor-type traps. For 2-nm SiO₂ films, a significant amount of interface state-induced C-V distortion and high leakage current was observed, resulting in the failure to achieve saturation in accumulation capacitance.

HRTEM cross-sections in Fig. 3 demonstrate thermally induced physical variations of the Ru/SiO₂/Si film system after 700, 900, and 950 °C RTAs. The 700 °C sample in Fig. 3(a) exhibits abrupt interfaces between all materials (Ru/SiO₂/Si) with no observable difference from the as-deposited sample (not shown). Regions of randomly occurring substrate pitting and apparent oxidation were detected on the 900 °C sample, as indicated in Fig. 3(b), although the Ru/SiO₂ interface appears unaffected in this image. Figure

![Image](image_url)
3(c) clearly illustrates a breakthrough of the SiO$_2$ dielectric with corresponding interaction in the Si substrate for the sample exposed to 950 °C. Significant density distribution variation in the HAADF-STEM dark field image suggests intermixing across the interfaces [Fig. 3(d)]. While HRTEM images are primarily sensitive to crystallinity, the intensity in HAADF-STEM images is roughly proportional to the atomic number squared ($Z^2$) and thus clearly delineates the brighter, higher density Ru ($Z=44$) from the dark, relatively low-density SiO$_2$ (average $Z=10$) and substrate Si ($Z=14$). In addition to the evidence for intermixing at the Ru/Si substrate interface, contrast for the initial SiO$_2$ layer is not distinguishable. The STEM, EELS, and EDXS data were recorded simultaneously while stepping the electron probe across the gate stack system in cross section. Microscopy and spectroscopic data-recording details have been discussed previously. The EELS profiling through the gate stack for the 900 °C sample in Fig. 4 indicates, by the Ru signal position and slope, that Ru has migrated into the SiO$_2$ interfacial layer. These data illustrate an increase in the extent of Ru diffusion into the SiO$_2$ layer as a function of temperature with the onset at or below 900 °C. At 950 °C [Figs. 3(c) and 3(d)], Ru breaches the SiO$_2$ bottom interface and makes contact with the Si substrate, causing localized silicidation reactions. Such ruthenium silicidation has been reported to occur at temperatures as low as 450 °C. Increasing the thickness of the SiO$_2$ interfacial layer could reduce the amount of Ru reaching the Si substrate (by increasing the temperature/time dependence); however, thick oxides would compromise operating performance and are not suitable for future generation devices with metal electrode applications.

Figure 5 exhibits a HRTEM cross-section image, HAADF-STEM Z-contrast image, and EELS elemental chemical profile plot from the same 20-nm PVD Ru film on a 2-nm SiO$_2$ sample following a 1000 °C/10-s anneal. The extreme interaction of Ru and SiO$_2$ is evident since the SiO$_2$ dielectric is not detectable and Ru is converted to ruthenium silicide. It is expected that Si is the dominant diffusing atom, characterized by voiding along the Si substrate interface, which is consistent with the silicidation reaction reported. However, concentration gradients of Si extending only a few nanometers or less into the Ru layer were detected; this may be due to reduced sensitivity by EELS for Si in the presence of higher $Z$ materials such as Ru. In the HAADF-STEM image, a low-density interface is found between Ru and TaN. Elemental analysis of this layer identified that the material...
begins diffusing into the underlying SiO₂ layer at 700 °C. When Ru contacts the Si substrate, Ru₂Si₃ silicide formation is immediately triggered with Si as the dominant diffusing atom. The Ru silicide reaction detected here is consistent with the diffusion mechanism for ruthenium silicide formation wherein Si diffuses up into the Ru layer and reacts with Ru to form Ru₂Si₃. In the case of Ru alloys, the reaction is nucleation controlled and initially forms the intermediate phase of RuSi. The reaction between Ru and SiO₂ is less favorable from theoretical thermal dynamic calculations that expect a positive Gibbs free energy for the Ru and SiO₂ reaction (Metal+SiO₂→M-oxide+M-silicide, ΔG>0). However, in thin SiO₂ films, especially near the Si/SiO₂ interface, Si and O atoms may not be forming complete tetrahedral structures as in the bulk SiO₂ film and thus could be more reactive with the Ru atoms, easily traveling into three monolayers of SiO₂. Another possible reaction mechanism is dielectric degradation due to oxygen diffusing upward into the Ru, which could not be detected because of instrumentation limits. Further investigation is required for greater understanding of the reaction mechanism and other factors which may induce instability, such as influence from the capping layer, effect of annealing ambient, and actual thermal budget in response to annealing temperature. Overall, the stability of Ru in SiO₂ devices is limited due to the potential Ru diffusion triggering a Si substrate reaction. Consequently, stability can be maintained only on thick dielectrics.

B. Thermal stability of the Ru on Hf-based dielectric systems

Having determined that Ru diffuses into SiO₂ below the thermal stability evaluation temperature of 1000 °C, it was critical to examine the thermal stability of Ru in direct contact with Hf-based high-k dielectrics, given the performance requirements for the 45-nm CMOS technology node. This is particularly significant for Hf silicate dielectric materials since it has been shown that the formation of a stable silicate is thermodynamically unfavorable and that over a wide range of compositions the films spontaneously phase separate into polycrystalline HfO₂ grains embedded in an amorphous SiO₂-like microstructure after annealing. Figure 6 shows HRTEM cross-section images of 20-nm PVD Ru on 4.5-nm-thick Hf-based dielectric films with (a) HfO₂ and (HfO₂)ₓ(SiO₂)₁₋ₓ, with (b) x=0.67 and (c) x=0.25 after 1000 °C anneal. Change in Ru density is only observed for the SiO₂ rich HfSiOₓ film.

FIG. 6. HRTEM image of (a) Ru/4.5-nm HfO₂ and (HfO₂)ₓ(SiO₂)₁₋ₓ, with (b) x=0.67 and (c) x=0.25 after 1000 °C anneal. Change in Ru density is only observed for the SiO₂ rich HfSiOₓ film.

FIG. 5. HRTEM image, HAADF-STEM, and EELS analysis of a Ru on 2-nm SiO₂ sample exposed to 1000 °C. Reaction of Ru and SiO₂ is observed.

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ture of the (uncapped) SiO₂-rich Hf silicate composition film following a 1000 °C/60-s anneal clearly indicates Hf-free regions of the film that are expected to react with Ru in the manner described for Ru/SiO₂.

A broad-range temperature study of Ru deposited on (HfO₂)ₓ(SiO₂)₁₋ₓ, x=0.67, films was performed to examine the stability of Ru on Hf-rich Hf silicate. Several x=0.67 samples annealed at temperature from 700–1000 °C (at 100 °C increments) were measured; the end-point sample temperature are shown in Fig. 8. The Hf Lα EDXS signal profile is not shown so that the Ru/dielectric interface could be seen more clearly. From the EELS profiles of the gate stack shown in Fig. 8, no Ru was detected in the dielectric. Also Ru diffusion, characterized by the broadening of the Ru signal slope toward the high-k interface, was not observed. However, a significantly higher amount of gate leakage current was observed with the Ru/Hf silicate device than with the TiN control, while Ru and TiN has similar leakage current properties on HfO₂. Higher leakage current for Ru/Hf silicate resulted in a distortion in the C-V plot compared to that of HfO₂.

IV. CONCLUSIONS

The Ru/HfO₂ film system was found to be thermally stable up to 1000 °C. However, Ru/SiO₂ samples exhibit increasing Ru migration as a function of the anneal temperature. The amount of Ru detected in Hf silicate films of x =0.67 and x=0.25 compositions (exposed to 1000 °C) increases with the mol % SiO₂, suggesting that SiO₂ provides a diffusion pathway for Ru. Increasing the dielectric thickness could suppress the amount of Ru diffusing through the dielectric, but would compromise device performance. Electrical measurements of C-V and gate leakage current data for Ru/HfO₂ and Ru/Hf silicates are consistent with the trend of greater Ru migration with increased mol % SiO₂ of the dielectric.

FIG. 7. Plane-view HRTEM image of (HfO₂)ₓ(SiO₂)₁₋ₓ, x=0.25, after 1000 °C 60-s anneal showing phase separation of SiO₂ and HfO₂ regions.

FIG. 8. HAADF-STEM and EELS analysis of a Ru on 4.5-nm (HfO₂)ₓ(SiO₂)₁₋ₓ (x=0.25) annealed between 700 and 1000 °C. No clear interdiffusion of Ru into the dielectric is observed.

FIG. 9. Comparison plots of the PMOS capacitor. (a) Leakage current density vs voltage of Ru compared with control TiN on 4-nm Hf silicate and HfO₂. (b) C-V of Ru on Hf silicate compared to HfO₂. A significantly higher amount in leakage current for Ru/Hf silicate is observed compared with TiN, while Ru and TiN has similar leakage current properties on HfO₂. Higher leakage current for Ru/Hf silicate resulted in a distortion in the C-V plot compared to that of HfO₂.
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