Supplementary Information

Electrode-Dependent Interfacial Reactions and Ru Loss Suppression during Ozone-Based Atomic Layer Deposition of TiO_2 on Ru- and RuO_2-Based Electrodes

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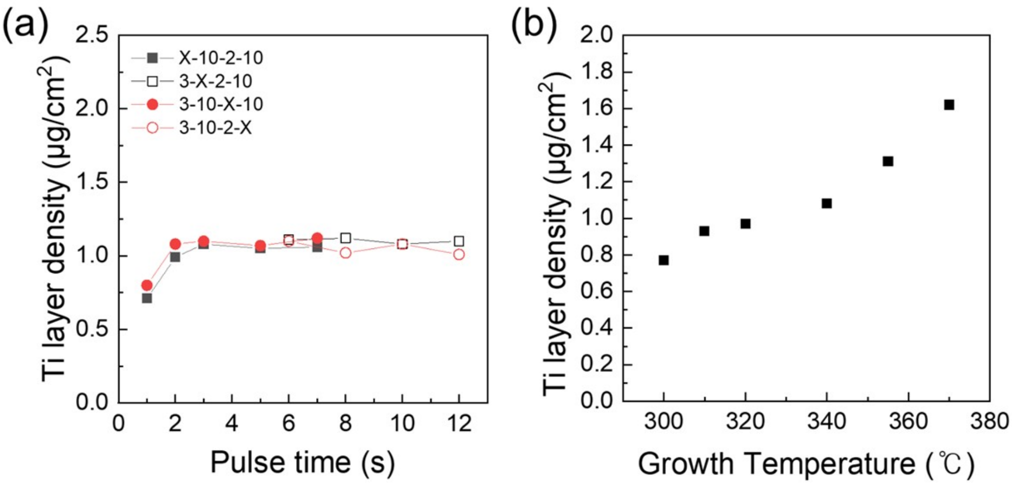

Fig. S1 Optimization of ALD process parameters and temperature dependence. **(a)** The Ti layer density of TiO_2 films deposited over 50 cycles on Ru substrates, with the pulse durations of the Ti precursor and O_3 feeding and purging varied as indicated in the legend. The Ti precursor feed reached self-limiting growth at pulse times longer than 3 s, while the O_3 feed saturated at 2 s. Both the Ti precursor and O_3 purge steps achieved effective removal with 10 s of purge time. Therefore, the final ALD sequence for one TiO_2 cycle was set as 3–10–2–10 s (Ti precursor feed–purge–O_3 feed–purge), corresponding to the conventional ALD sequence. **(b)** The Ti layer density of TiO_2 films deposited for 50 cycles at temperatures ranging from 300 to 370 °C using the conventional sequence determined in Fig. S1a. The Ti layer density gradually increases with temperature, then shows a distinct rise above 355 °C, indicating enhanced surface reactivity due to increased thermal energy. Since $(CpMe_5)Ti(OMe)_3$ remains thermally stable up to 400 °C,[1, 2] the sudden increase in growth rate above 355 °C is attributed to temperature-activated surface reactions rather than chemical vapor deposition (CVD)-type precursor thermal decomposition. Additionally, at higher temperatures, the increased reactivity of O_3 accelerates the decomposition of methoxy ligands, producing CO_2 and H_2O. The H_2O formed in this process can adsorb on the surface, providing additional reaction sites for precursor adsorption in subsequent ALD cycles.[3]

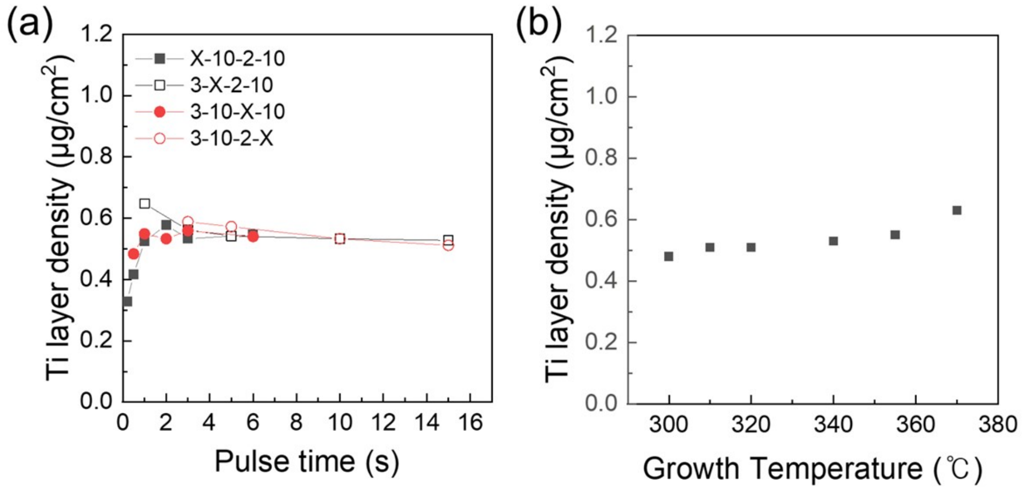

Fig. S2 Comparison of ALD growth characteristics on Si substrates. **(a)** ALD saturation behavior on Si substrates. Consistent with the results on Ru substrates, self-limiting growth was achieved with an optimized ALD sequence of 3–10–2–10 s. **(b)** TiO_2 deposition amount over 50 cycles on Si substrates as a function of temperature. While the deposition increases with temperature, as on Ru substrates, the magnitude of this increase is much less pronounced. This is because, unlike on Ru substrates, there is no substrate-induced overgrowth on Si.

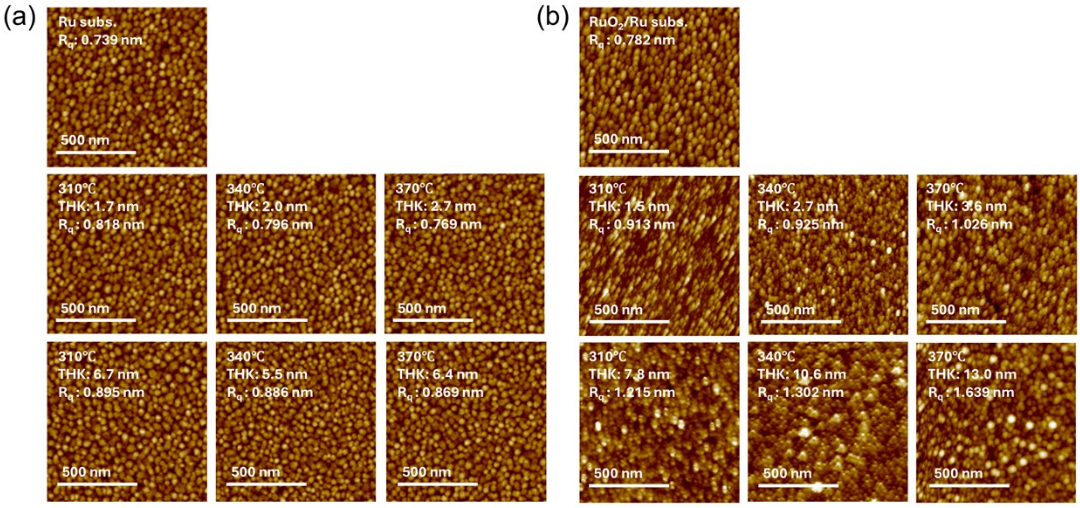

Fig. S3 AFM images of TiO_2 films deposited on (a) Ru, and (b) RuO_2/Ru bottom electrodes during the initial ALD cycles. The images correspond to the samples used for the RMS roughness analysis in Figure 4b.

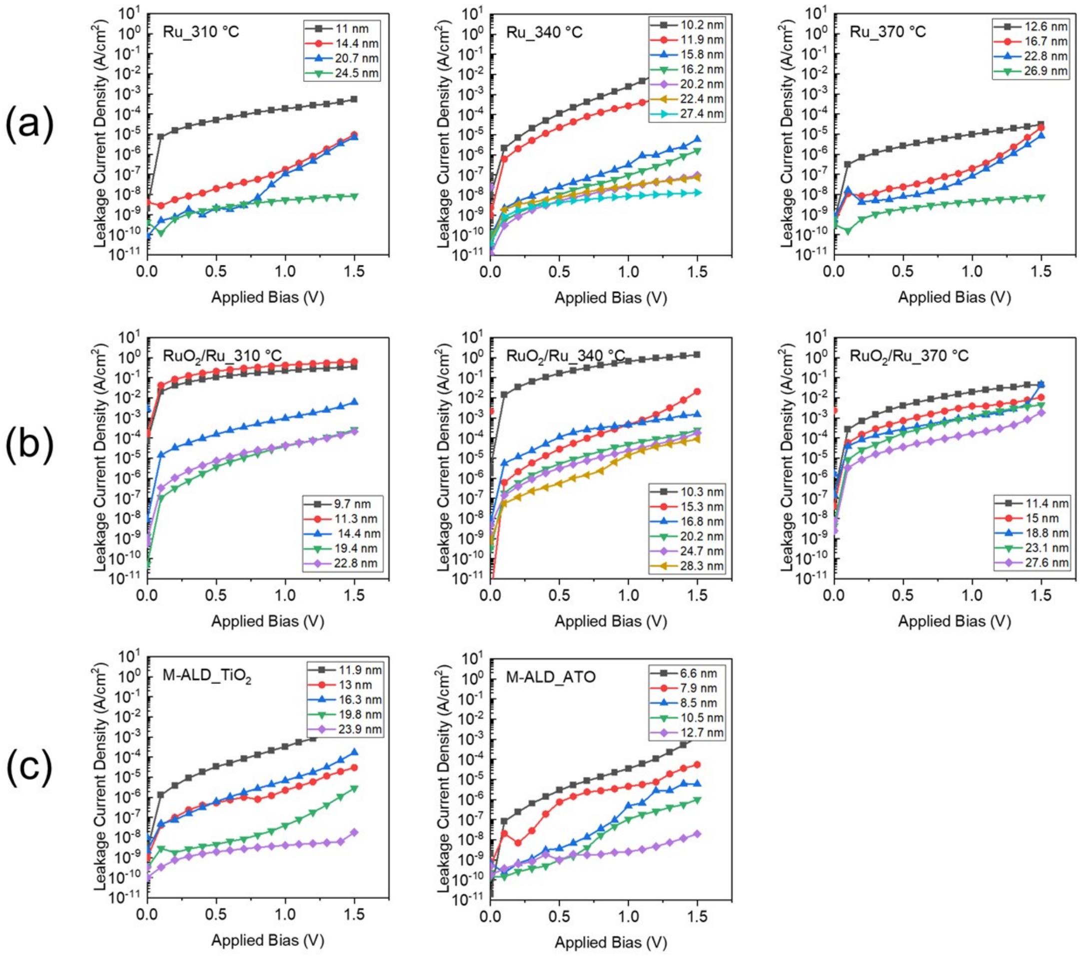

Fig. S4 Representative J–V curves of MIM capacitors used for the leakage-current analysis. (a) J–V curves of TiO_2 films deposited on Ru bottom electrodes at 310, 340, and 370 °C using the conventional ALD process. (b) J–V curves of TiO_2 films deposited on RuO_2/Ru bottom electrodes at 310, 340, and 370 °C using the conventional ALD process. (c) J–V curves of TiO_2 and ATO films deposited on Ru bottom electrodes using the sequential process. The bottom electrode was grounded, and the bias was applied to the top electrode.

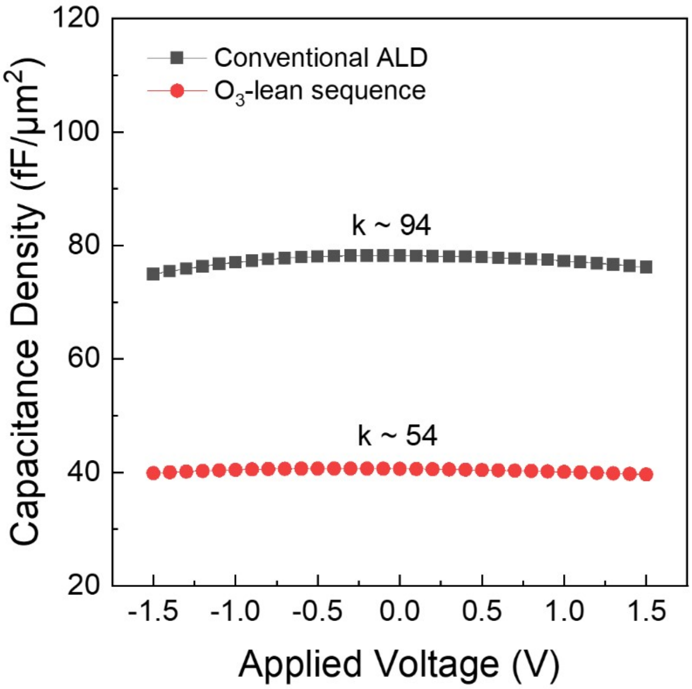

Fig. S5 Comparison of ALD growth characteristics on Si substrates. (a) ALD saturation behavior on Si substrates. Consistent with the results on Ru substrates, self-limiting growth was achieved with an optimized ALD sequence of 3–10–2–10 s. (b) TiO_2 deposition amount over 50 cycles on Si substrates as a function of temperature. While the deposition increases with temperature, as on Ru substrates, the magnitude of this increase is much less pronounced. This is because, unlike on Ru substrates, there is no substrate-induced overgrowth on Si.

References

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3 Y. Cho, S. Hyeon Kim, B. Seok Kim, Y. Kim and W. Jeon, Physical Chemistry Chemical Physics, 2021, 23, 2568–2574.