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Supplementary information

# Thermal Atomic Layer Etching of Copper via Sequential Chlorination and Volatility-Controlled Hydration

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## Supplementary Figures

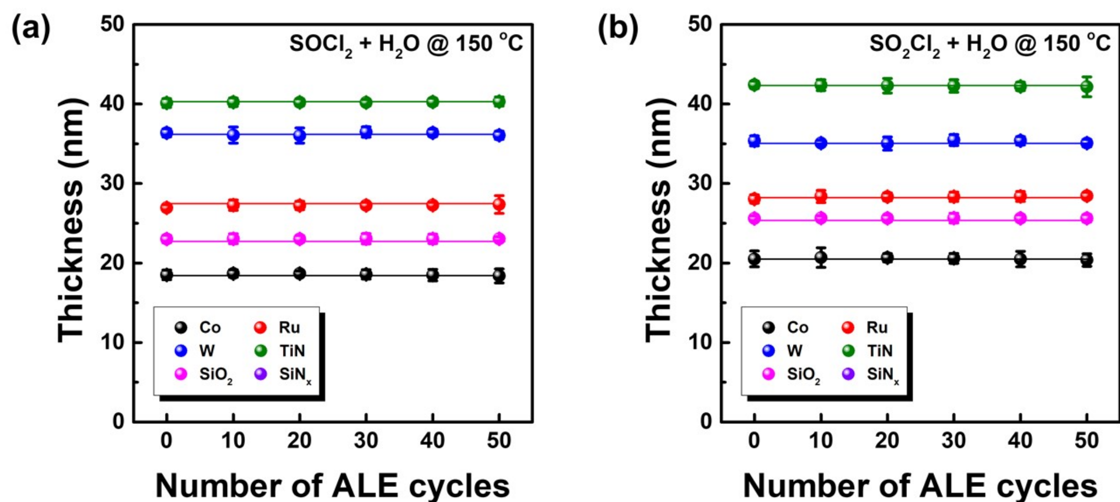


**Fig. S1.** Thickness evolution of various thin films as a function of the number of ALE cycles at 150 °C using (a) $SOCl_2/H_2O$ and (b) $SO_2Cl_2/H_2O$ processes. No measurable thickness change is observed for Co, Ru, W, TiN, $SiO_2$, and $SiN_x$ films over 50 ALE cycles for either chemistry, indicating negligible etching of non-Cu materials and confirming the high material selectivity of the chlorination–hydration ALE process toward Cu.

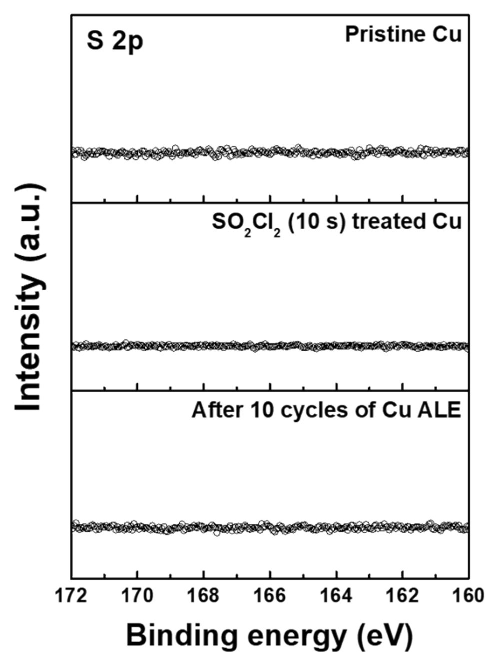


**Fig. S2.** S 2p XPS spectra of a pristine Cu film, a Cu film after $SO_2Cl_2$ exposure, and a Cu film subjected to 10 ALE cycles at 150 °C. No discernible sulfur-related signals are detected in any condition, confirming that sulfur species do not remain on the Cu surface and do not contribute to the surface modification or etching mechanism.

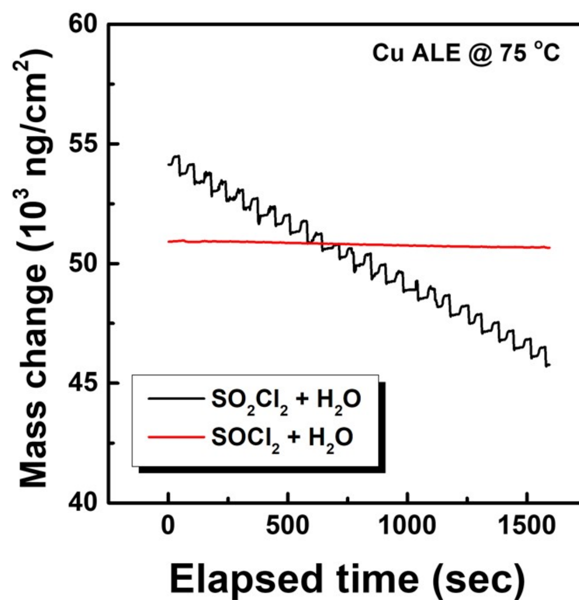


**Fig. S3.** Comparison of in situ QCM mass evolution during 25 cycles of alternating $SOCl_2/H_2O$ and $SO_2Cl_2/H_2O$ exposures. While $SO_2Cl_2/H_2O$ cycles exhibit clear, cycle-resolved mass changes associated with chlorination and hydration, the $SOCl_2/H_2O$ process shows no measurable net mass loss, corroborating the lack of effective Cu etching with $SOCl_2$ under identical conditions.

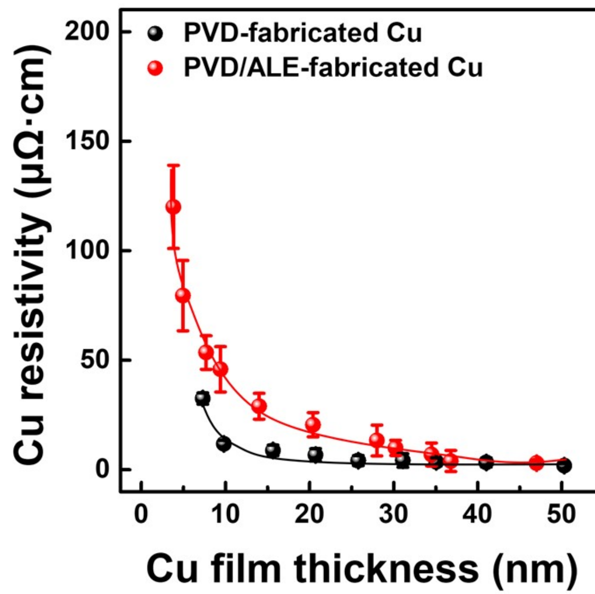


**Fig. S4.** Electrical resistivity of Cu thin films as a function of film thickness, comparing films fabricated solely by PVD with those initially deposited to 50 nm by PVD and subsequently thinned by ALE. Reliable resistivity measurements are enabled at reduced thicknesses for PVD/ALE-treated films, reflecting improved film continuity compared to PVD-only Cu films at comparable thicknesses.

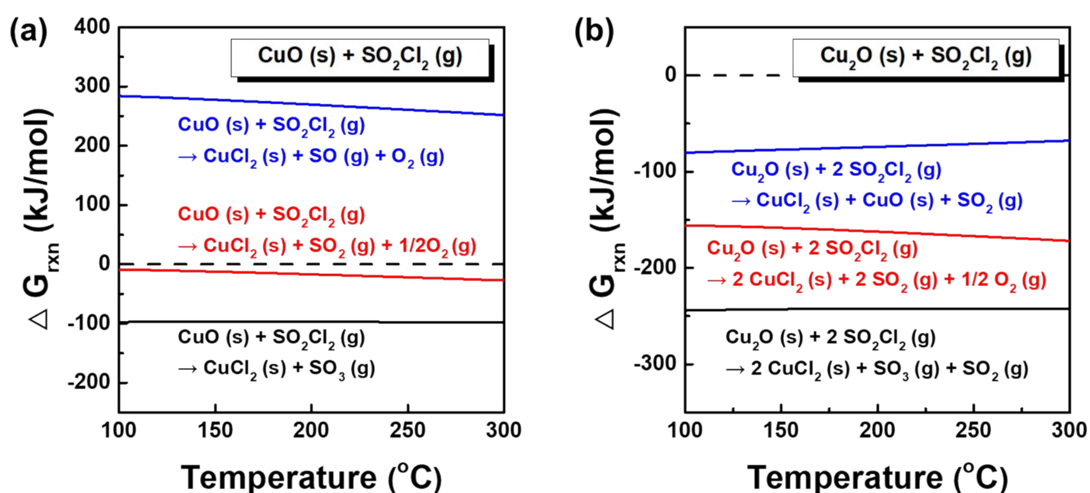


**Fig. S5.** Thermodynamic evaluation and comparison of plausible $SO_2Cl_2$-induced chlorination pathways for CuO and $Cu_2O$ based on calculated Gibbs free energy changes ($\Delta G_{rxn}^{o}$). For both oxides, reaction pathways leading to $CuCl_2$ formation exhibit the lowest $\Delta G_{rxn}^{o}$ values across the investigated temperature range, indicating that $SO_2Cl_2$-driven chlorination is thermodynamically favorable for both metallic Cu and its representative native oxides.