Supporting Information

Thermal atomic layer deposition of rhenium nitride and rhenium metal thin films using methyltrioxorhenium

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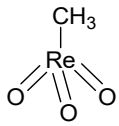
1. General Information

See the manuscript for experimental details.

Chart S1. Chemical structure of methyltrioxorhenium (MTO).



2. Deposition experiments with MTO only

2.1. XRF data

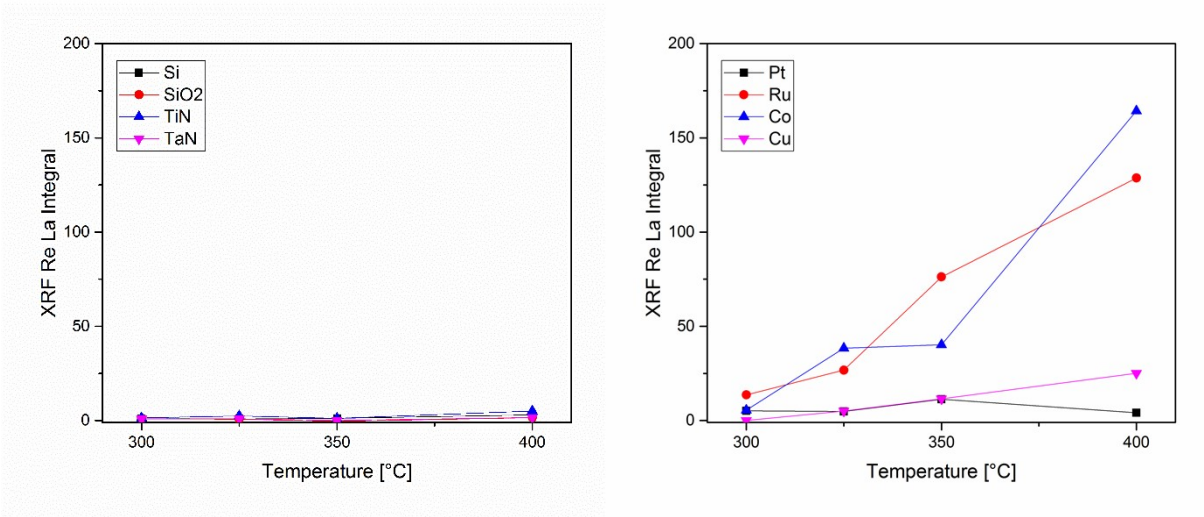


Figure S1. MTO self-decomposition behavior with respect to the deposition temperature on insulating (left) and metallic (right) substrate surfaces as evaluated by XRF

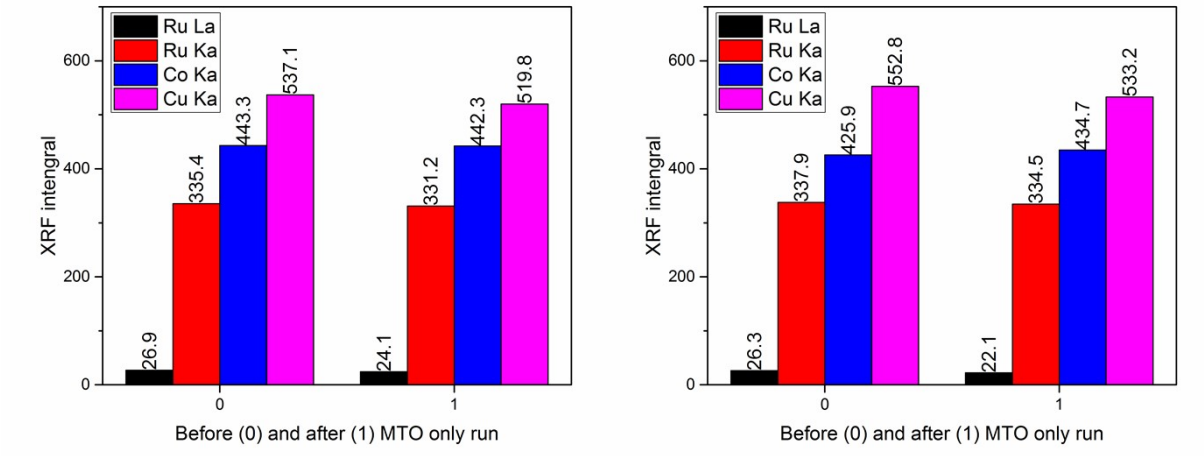


Figure S2. XRF counts of the metal substrates before and after MTO only deposition at 340 °C for 500 (left) and 1000 (right) cycles.

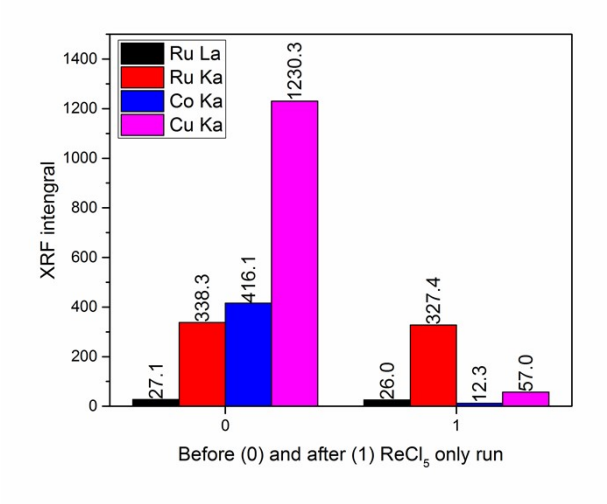


Figure S3. XRF counts of the metal substrates before and after $ReCl_5$ only deposition at 400 °C for 500 cycles.

3. ALD Thin Film Characterization Details

3.1. XRF data

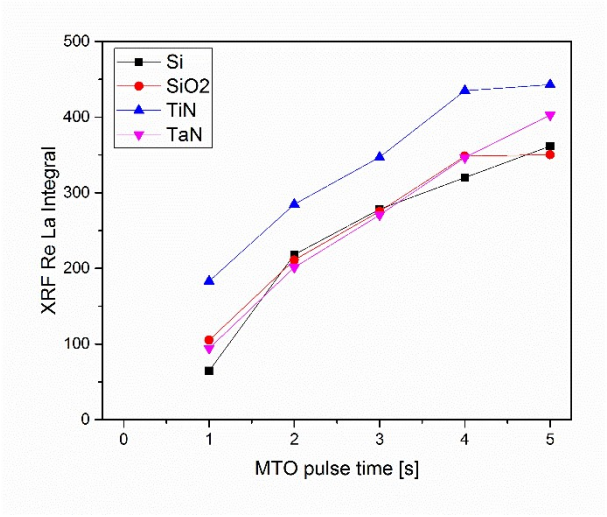


Figure S4. XRF counts with respect to the MTO pulse time for films grown at 340 °C with 500 cycles.

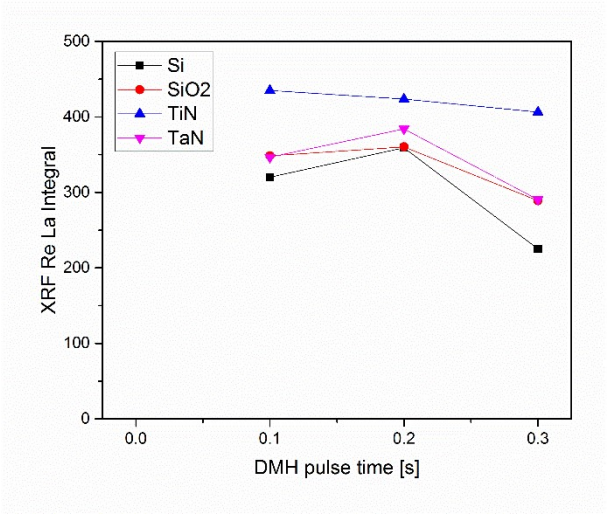


Figure S5. XRF counts with respect to the Me_2NNH_2 pulse time for films grown at 340 °C with 500 cycles.

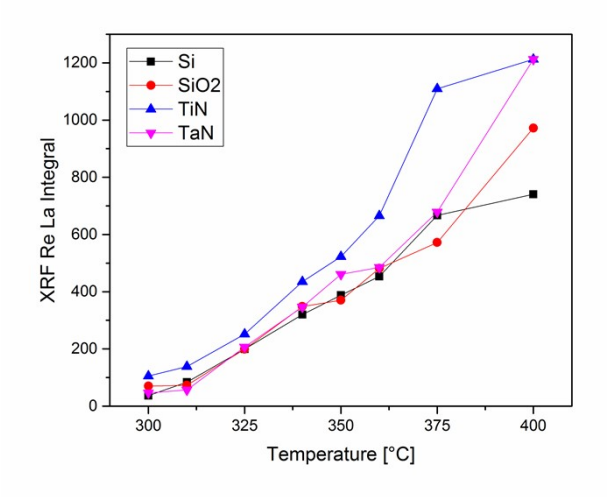


Figure S6. XRF counts with respect to the deposition temperature for films grown with 500 cycles.

3.2. SEM images of temperature series

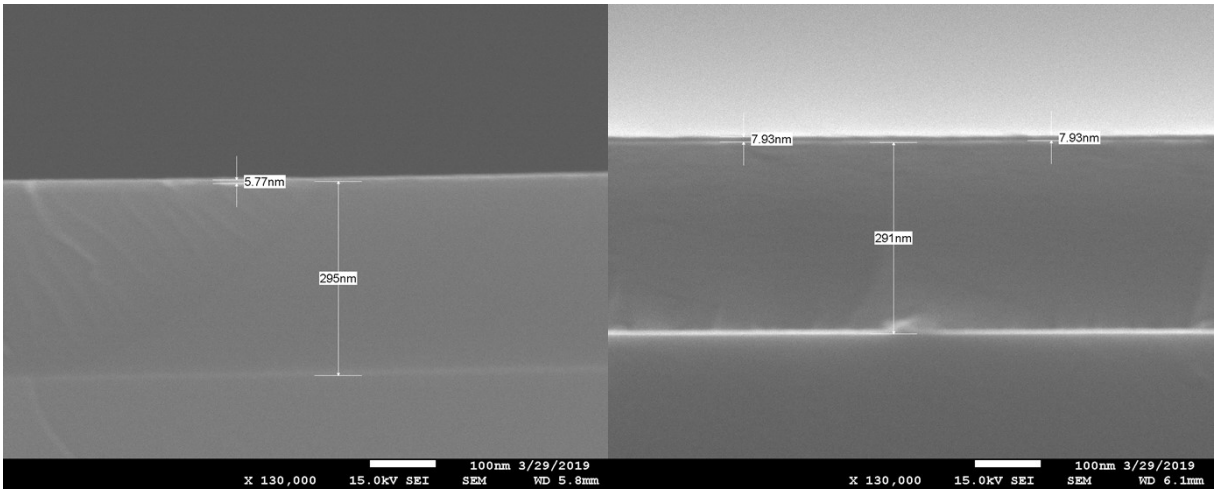


Figure S7. SEM cross-sections of Re films grown at 300 °C (left) and 310 °C (right) for 500 cycles.

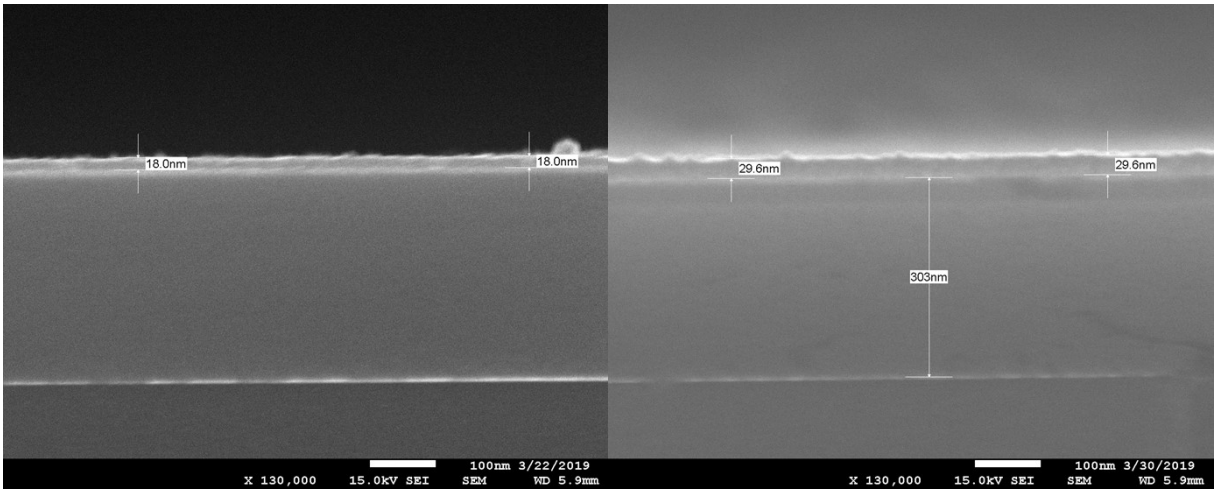


Figure S8. SEM cross-sections of Re films grown at 325 °C (left) and 340 °C (right) for 500 cycles.

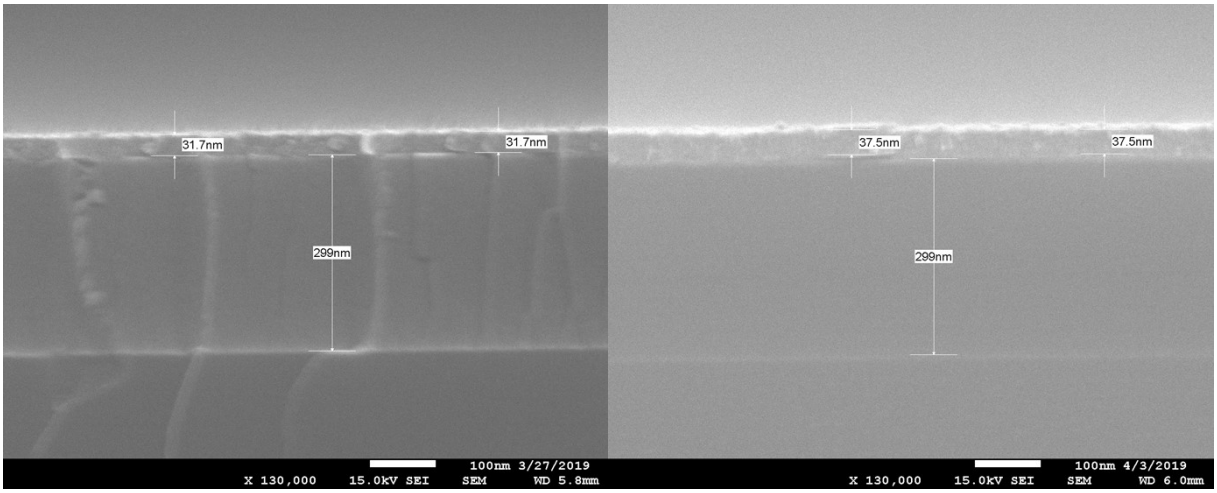


Figure S9. SEM cross-sections of Re films grown at 350 °C (left) and 360 °C (right) for 500 cycles.

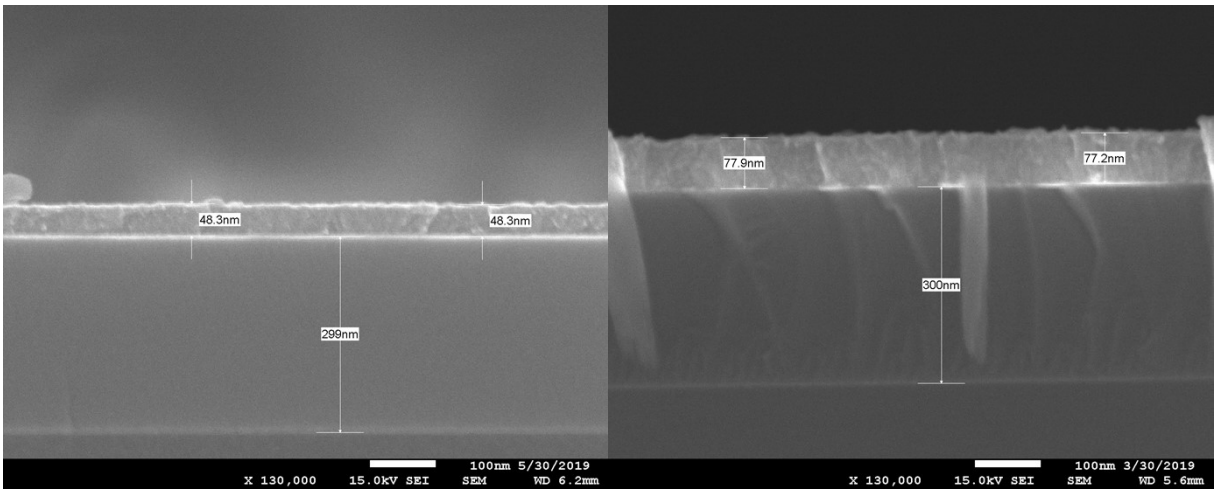


Figure S10. SEM cross-sections of Re films grown at 375 °C (left) and 400 °C (right) for 500 cycles.

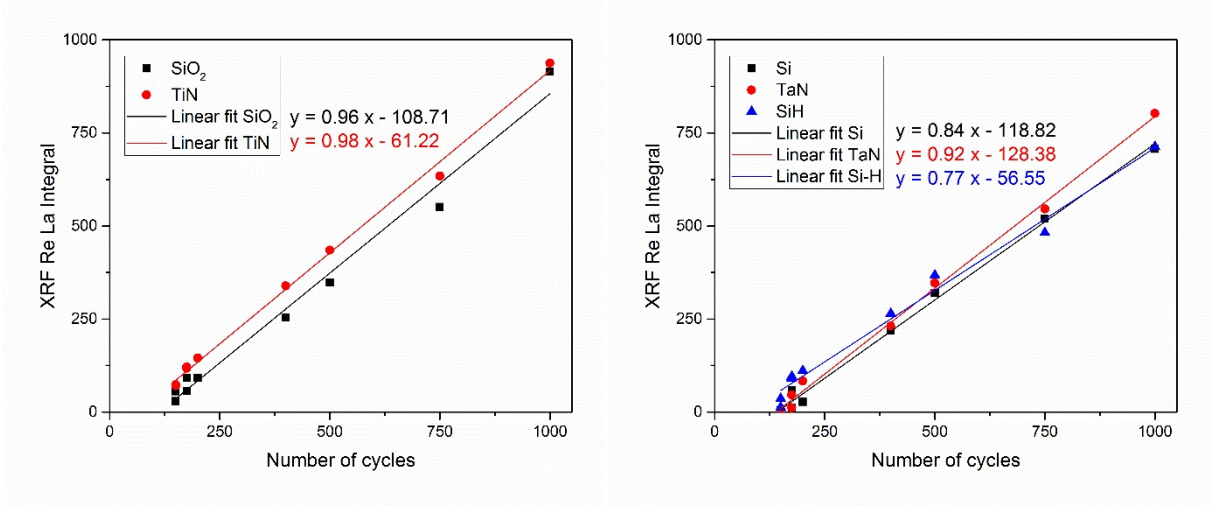


Figure S11. XRF counts versus number of cycles for Re films grown at 340 °C on various substrates.

3.3. XPS spectra and EELS depth profile.

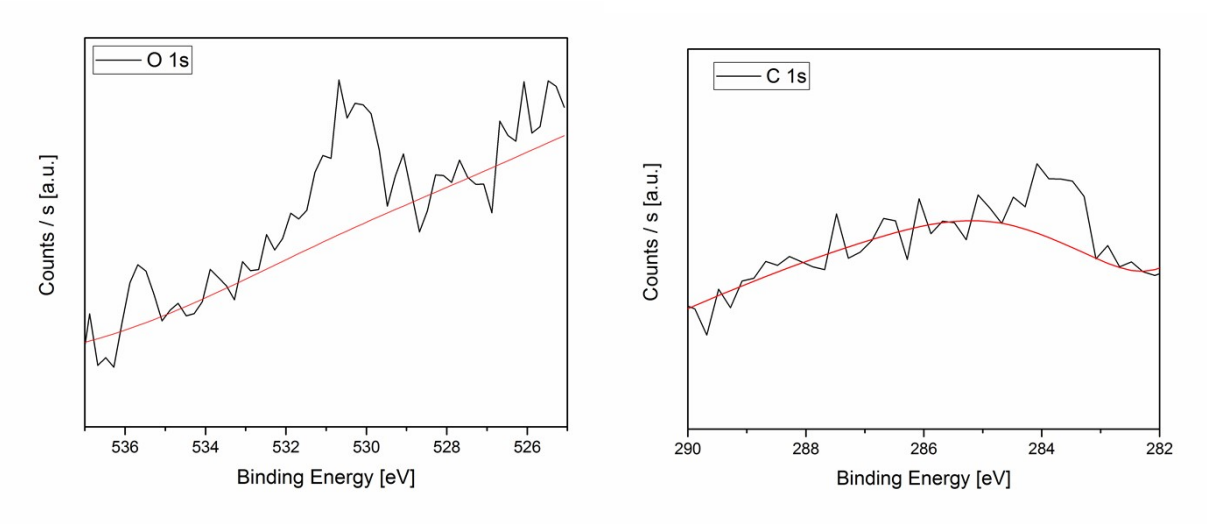


Figure S12. High resolution O 1s (left) and C 1s (right) XPS spectra of 70 nm thick Re films grown at 340 °C on Si with native oxide substrate.

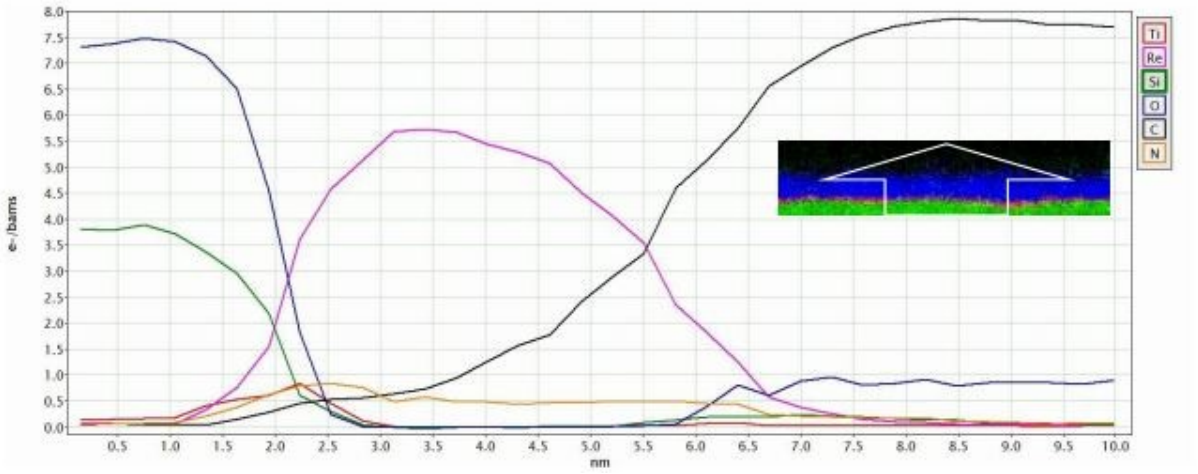


Figure S13. EELS spectra of a 3.7 nm Re film grown on 1 nm thick *in situ* TiN layer at 340 °C on SiO_2.

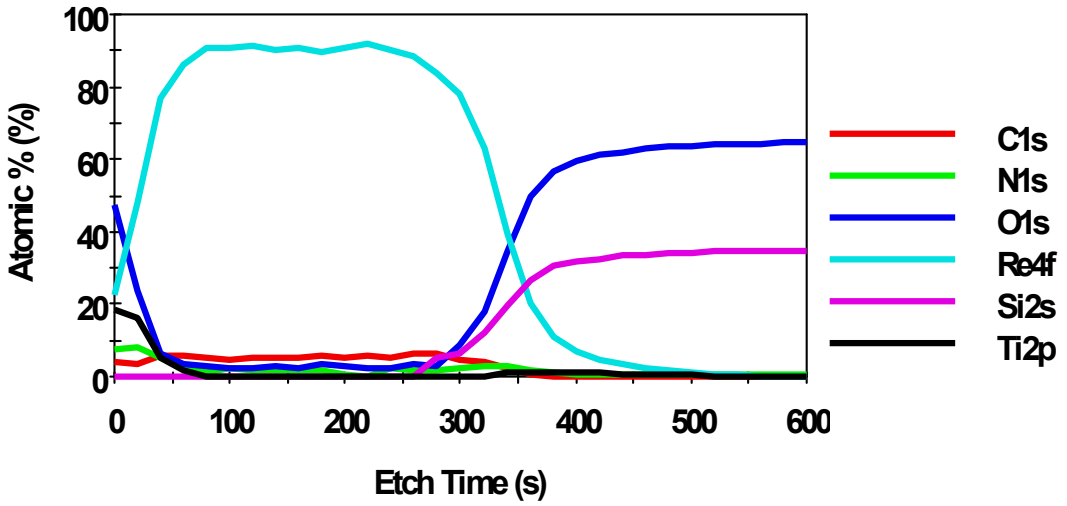


Figure S14. XPS spectra of a Re thin film annealed under H_2 atmosphere (12 Torr, 400 °C, 1 h) followed by heating to 600 °C (Ar, 10 min). The film was about 20 nm thick prior to annealing and was grown at 340 °C.

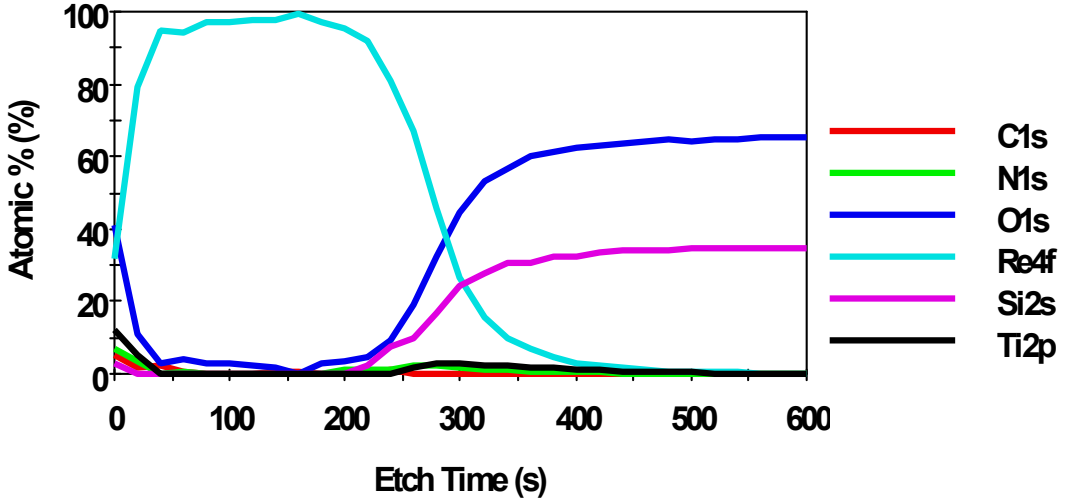


Figure S15. XPS spectra of a Re thin film annealed under NH_3 atmosphere (11 Torr, 400 °C, 1 h) followed by heating to 600 °C (Ar, 10 min). The film was about 20 nm thick prior to annealing and was grown at 340 °C.

3.4. TEM images

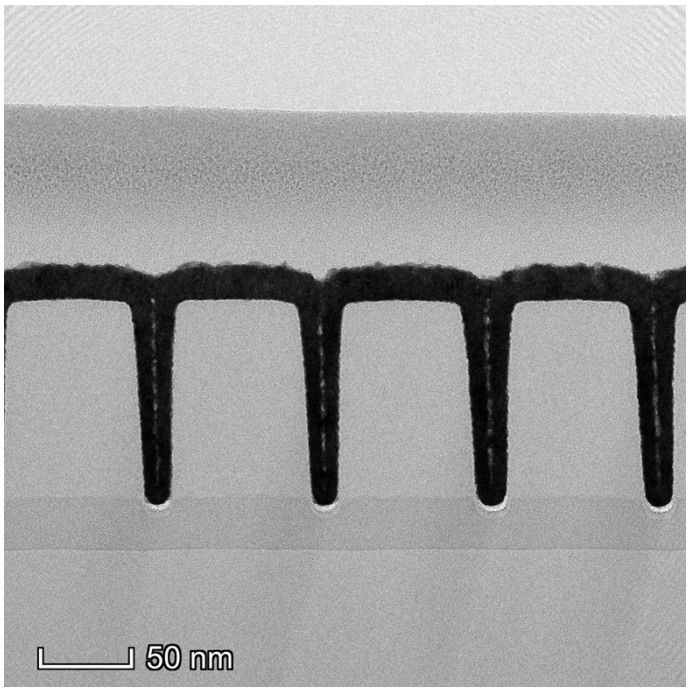


Figure S16. TEM images of Re thin film grown on *in-situ* TiN coated structures annealed under H_2 atmosphere (12 Torr, 400 °C, 1 h) followed by heating to 600 °C (Ar, 10 min)

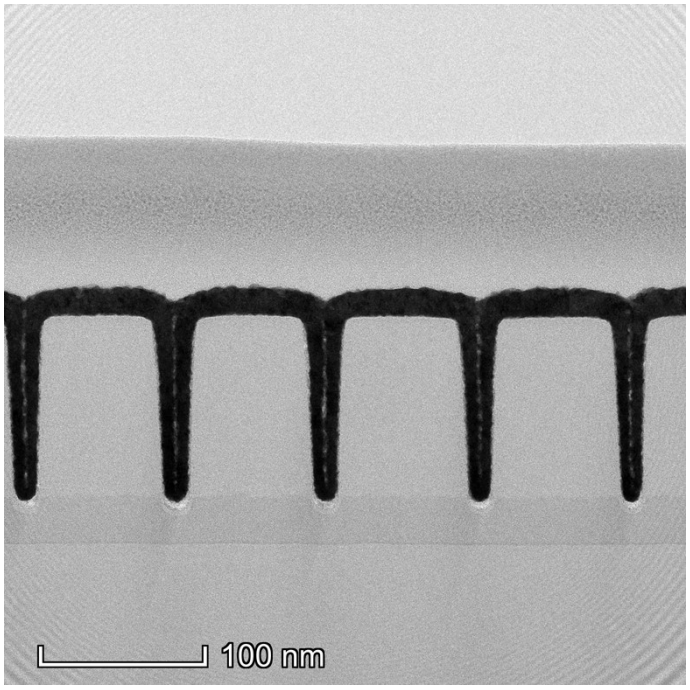


Figure S17. TEM images of Re thin film grown on *in-situ* TiN coated structures annealed under NH_3 atmosphere (11 Torr, 400 °C, 1 h) followed by heating to 600 °C (Ar, 10 min)