Supporting Information for

Low Temperature Atomic Layer Deposition of Copper Films Using Borane Dimethylamine as the Reducing Co-Reagent

Lakmal C. Kalutarage,[†] Scott B. Clendenning,[‡] and Charles H. Winter*[,†]

[†]*Department of Chemistry, Wayne State University, Detroit, Michigan 48202*

[‡]*Components Research, Intel Corporation, Hillsboro, Oregon 97124*

Figure S1. X-Ray powder diffraction pattern of Cu powder obtained upon treatment of **1** with $BH_3(NHMe_2)$ at ambient temperature in tetrahydrofuran for 0.25 h. The reference diffraction pattern of Cu metal (JCPDS 04-0836) is overlaid on the experimental spectrum.

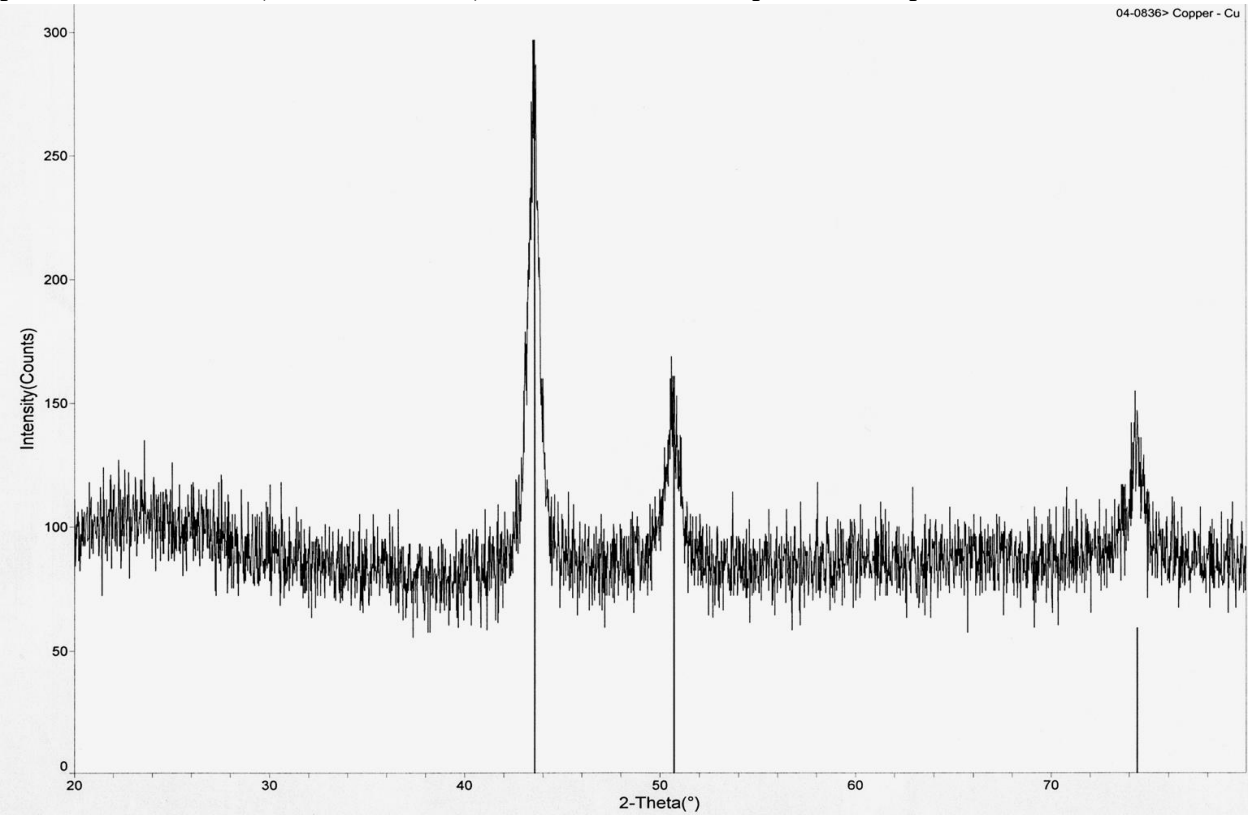


Figure S2. Side-view SEM image of a Ru substrate after the 50 nucleation cycles. The growth temperature was 150 °C. The 18 nm thickness includes 5 nm of Ru, so the height of the Cu features is 13 nm.

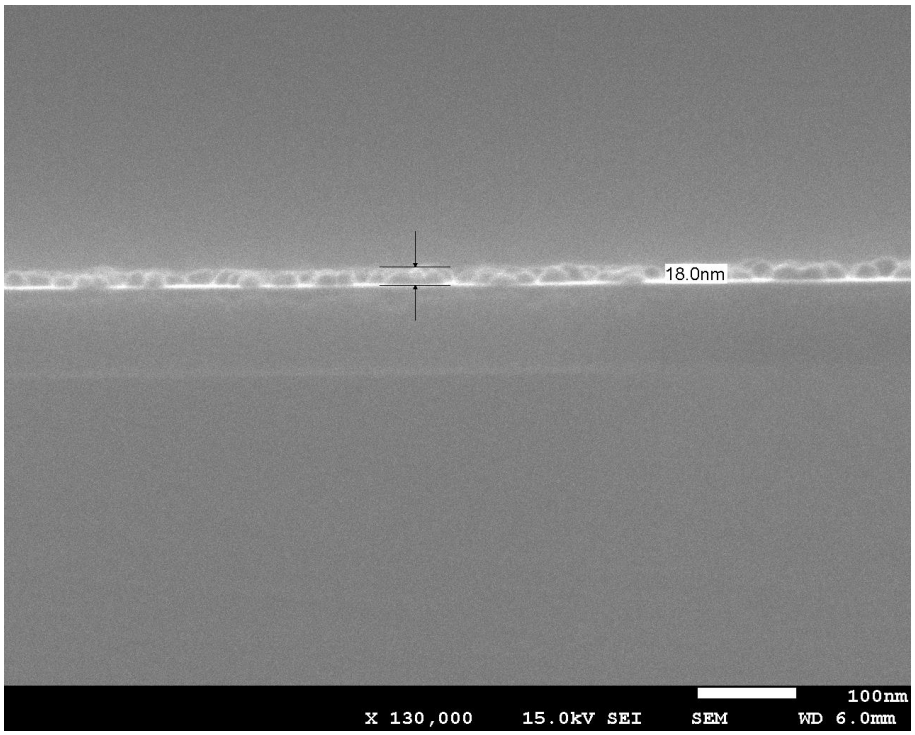


Figure S3. Growth rate versus pulse length of $BH_3(NHMe_2)$ at a substrate temperature of 150 °C.

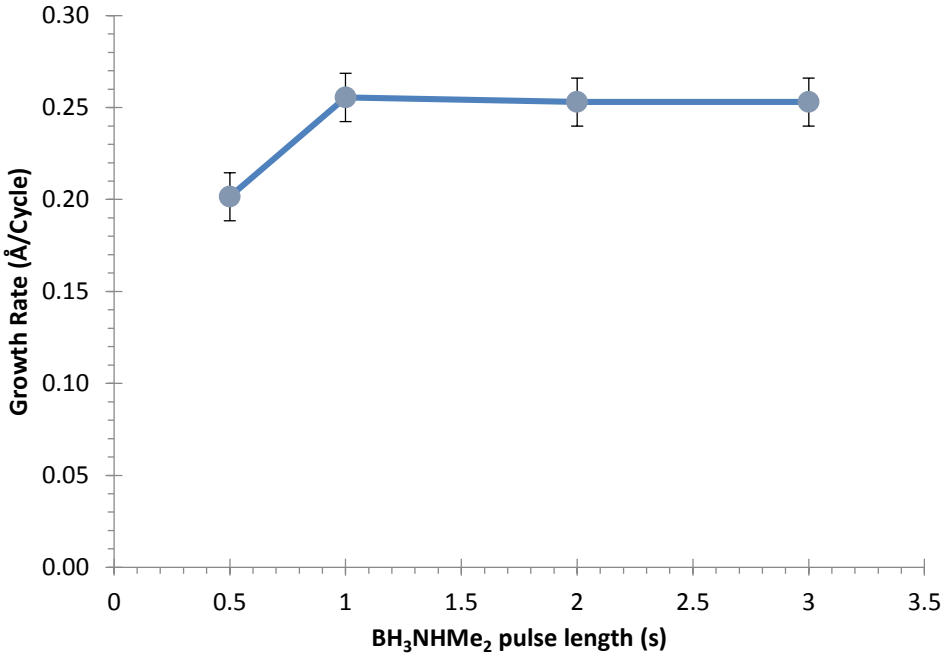


Figure S4. XPS survey scans of a 25 nm thick Cu film deposited at 120 °C with the two-step process on a Ru substrate.

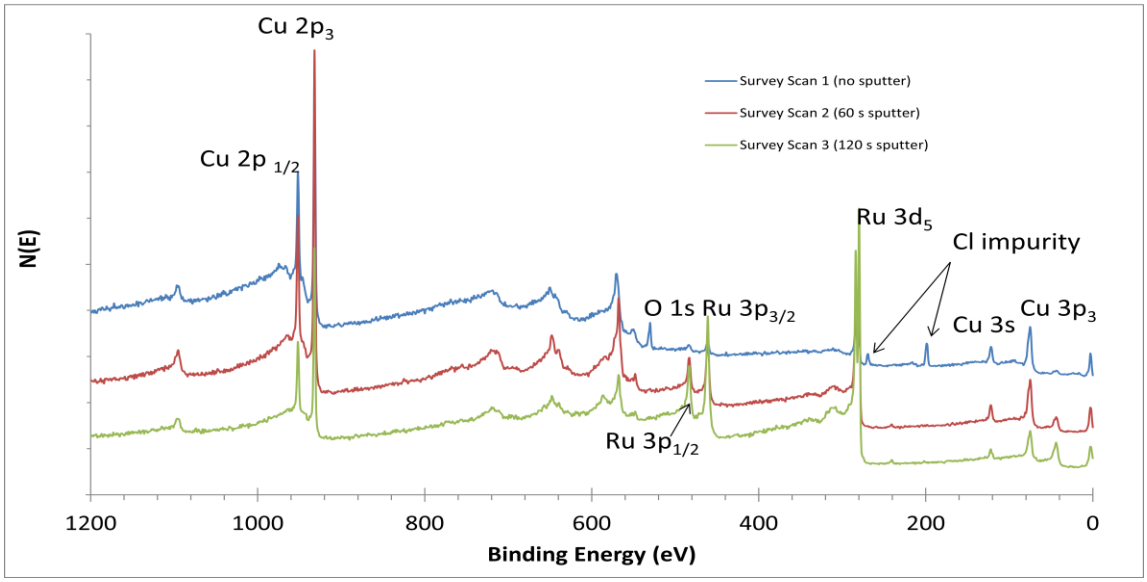


Figure S4. High resolution XPS scan of the Cu 2p region for a 25 nm thick Cu film deposited at 120 °C with the two-step process on a Ru substrate after 120 seconds of Ar ion sputtering.

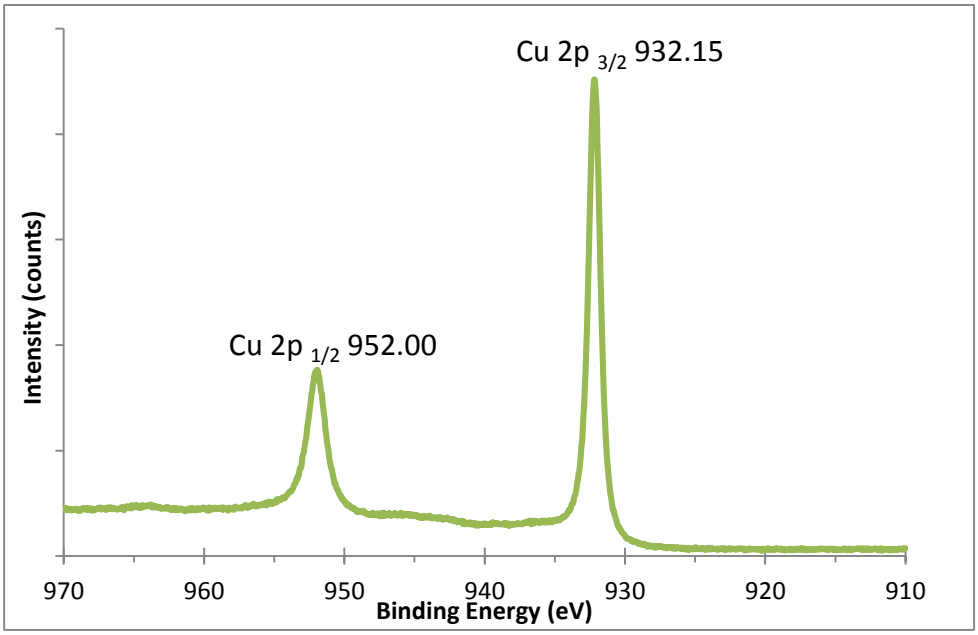


Figure S5. XPS survey scans of a 25 nm thick Cu film deposited at 140 °C with the two-step process on a Ru substrate.

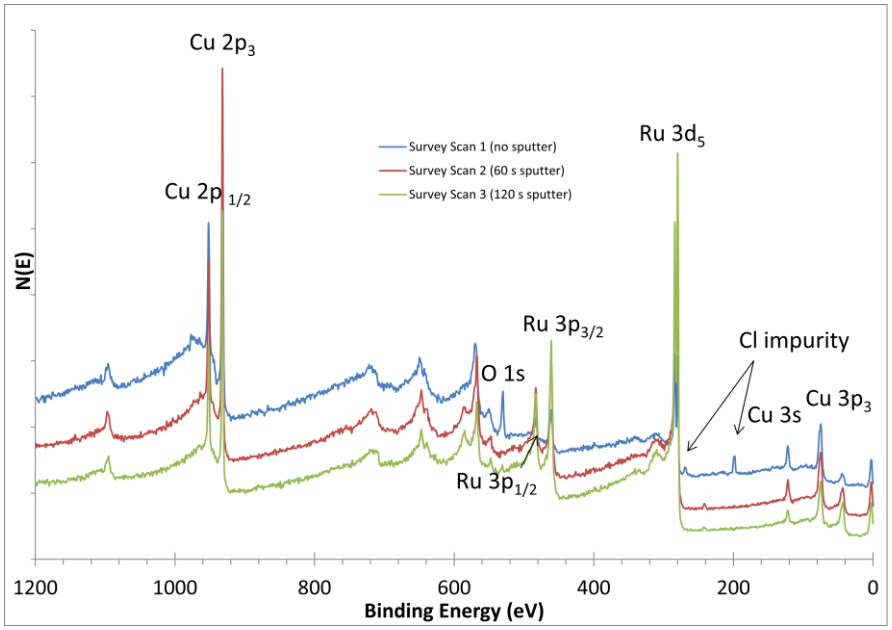


Figure S6. High Resolution XPS Scan of the Cu 2p Region for a 25 nm Thick Cu Film Deposited at 140 °C with the two-step process on a Ru substrate after 120 seconds of Ar ion sputtering.

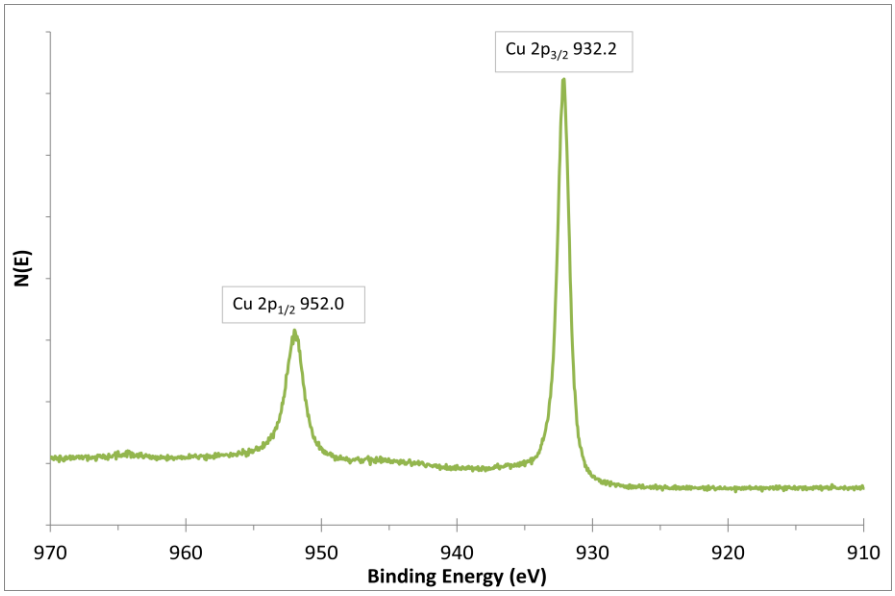


Figure S7. XPS survey scans of a 25 nm thick Cu film deposited at 160 °C with the two-step process on a Ru substrate.

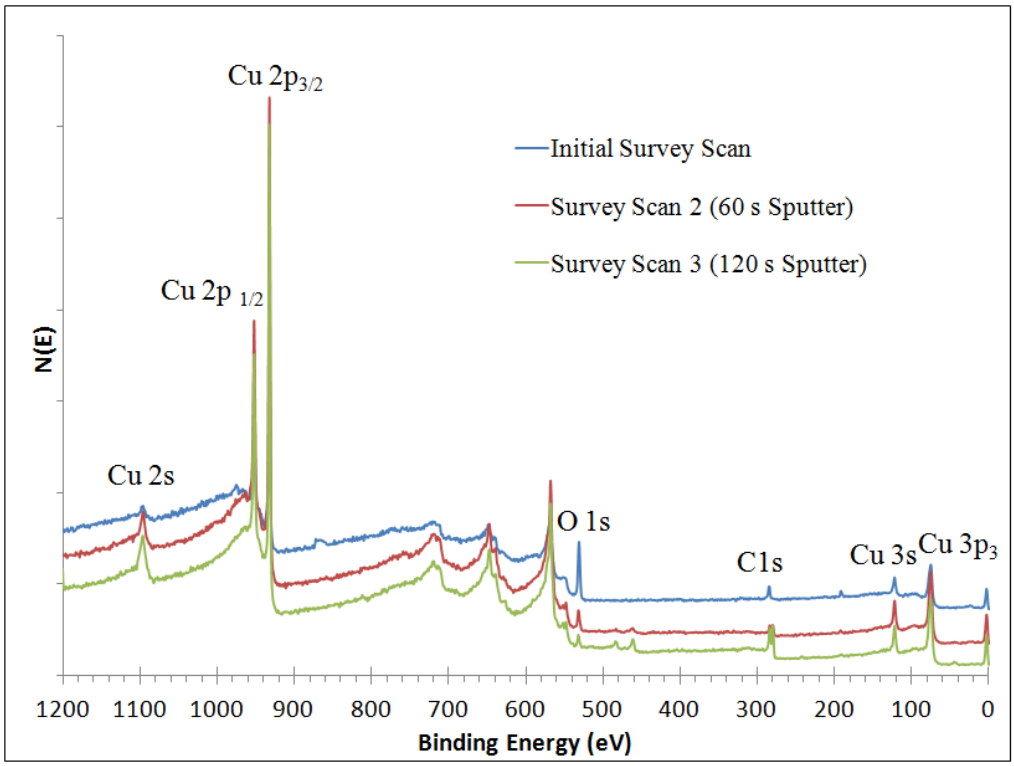


Figure S8. High Resolution XPS Scan of the Cu 2p Region for a 25 nm Thick Cu Film Deposited at 160 °C After 120 Seconds of Ar Ion Sputtering.

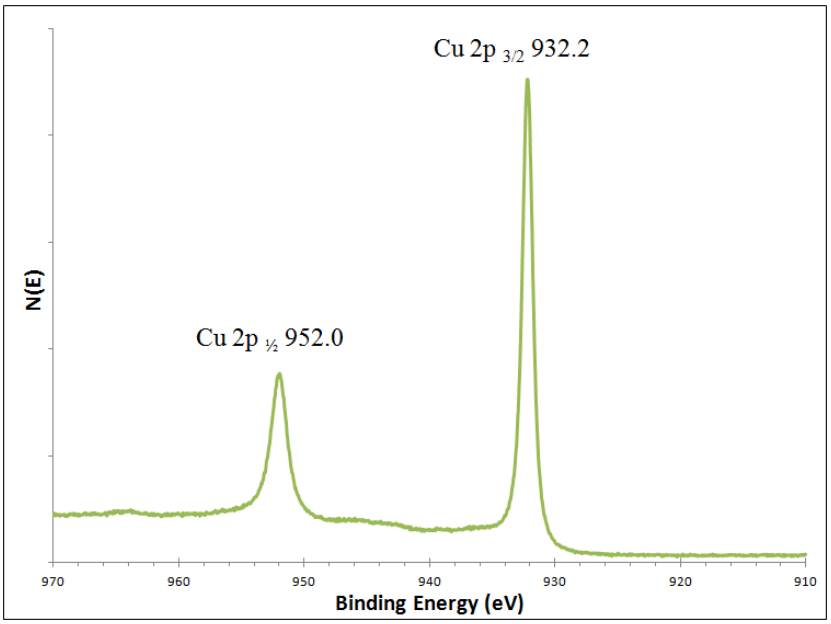


Figure S9. Cu LMM ionizations in the XPS spectrum a Cu film deposited at 160 °C with the two-step process on a Ru substrate after 120 seconds of Ar ion sputtering.

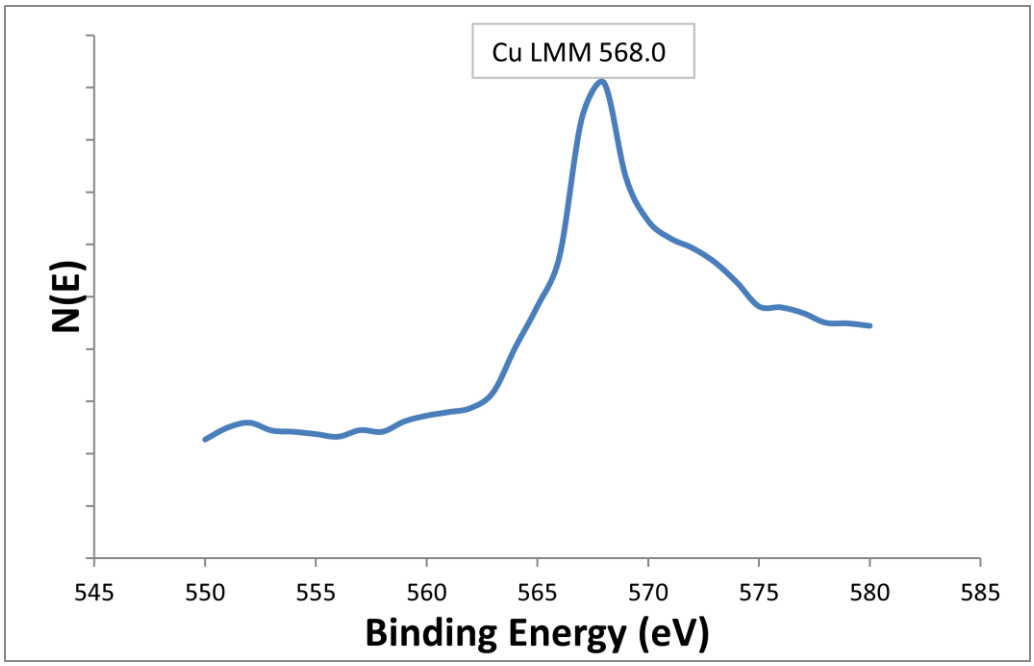


Figure S10. Powder X-ray diffraction pattern of a Cu film deposited at 150 °C with the two-step process on a Ru substrate after annealing for 3 hours at 300 °C under Ar.

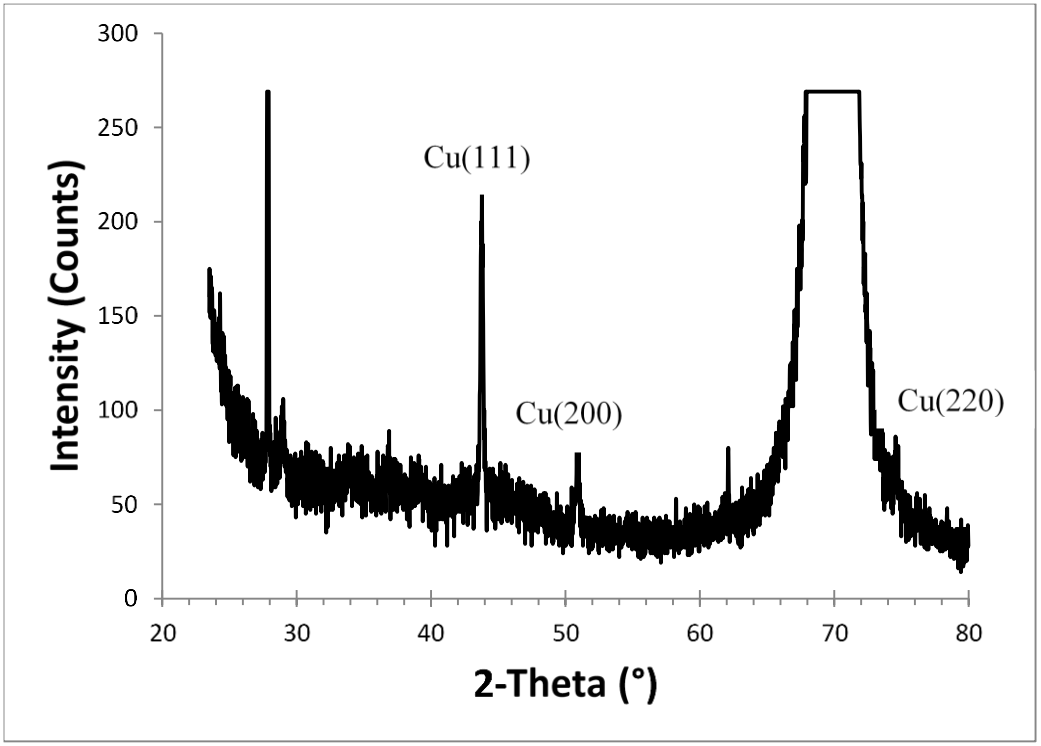


Figure S11. A plot of growth rate versus pulse length for a Cu film grown by the three-step process at 150 °C on a Pd substrate.

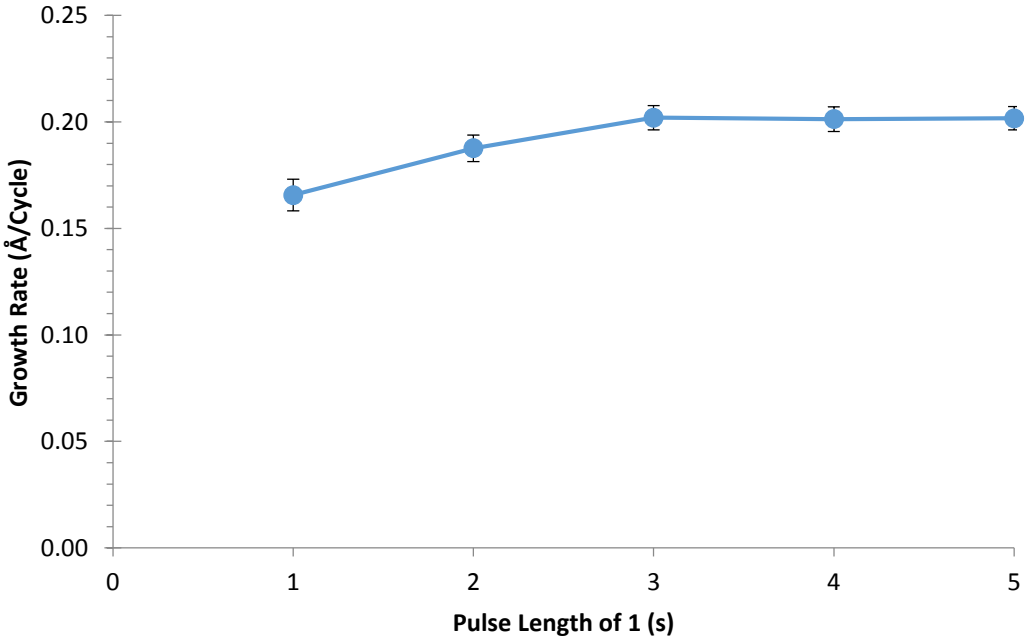


Figure S12. A plot of growth rate versus pulse length for a Cu film grown by the three-step process at 150 °C on a Pt substrate.

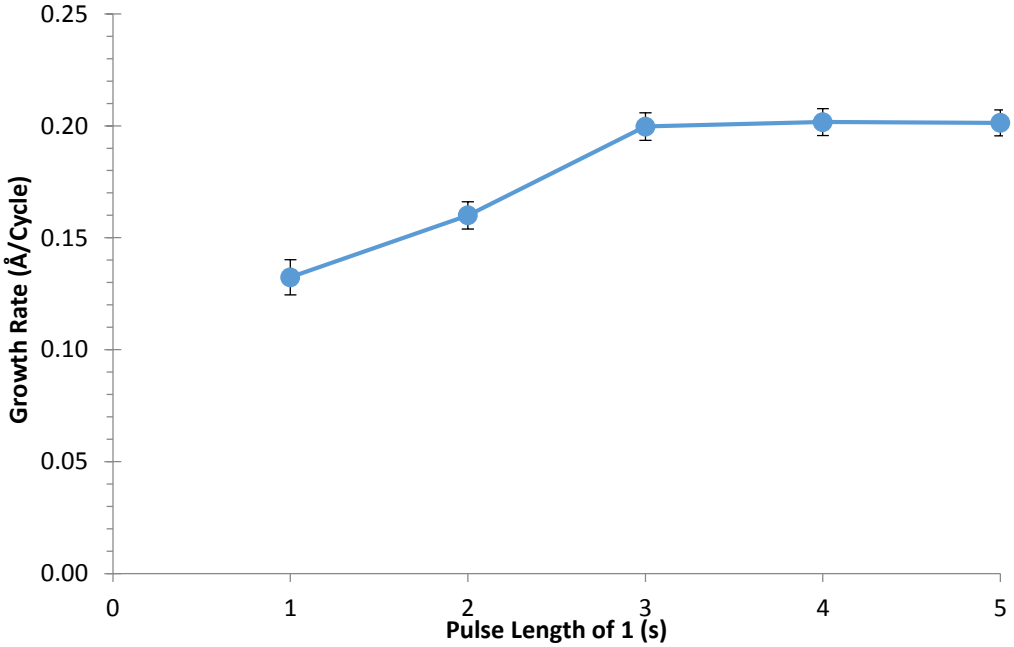


Figure S13. A plot of growth rate versus formic acid pulse length for a Cu film grown by the three-step process at 150 °C on a Pd substrate.

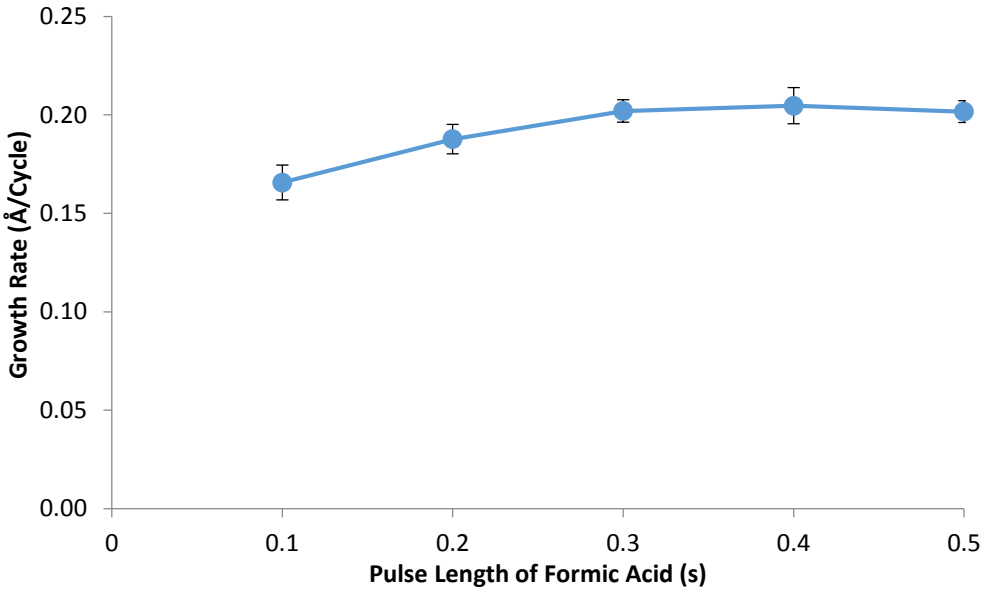


Figure S14. A plot of growth rate versus formic acid pulse length for a Cu film grown by the three-step process at 150 °C on a Pt substrate.

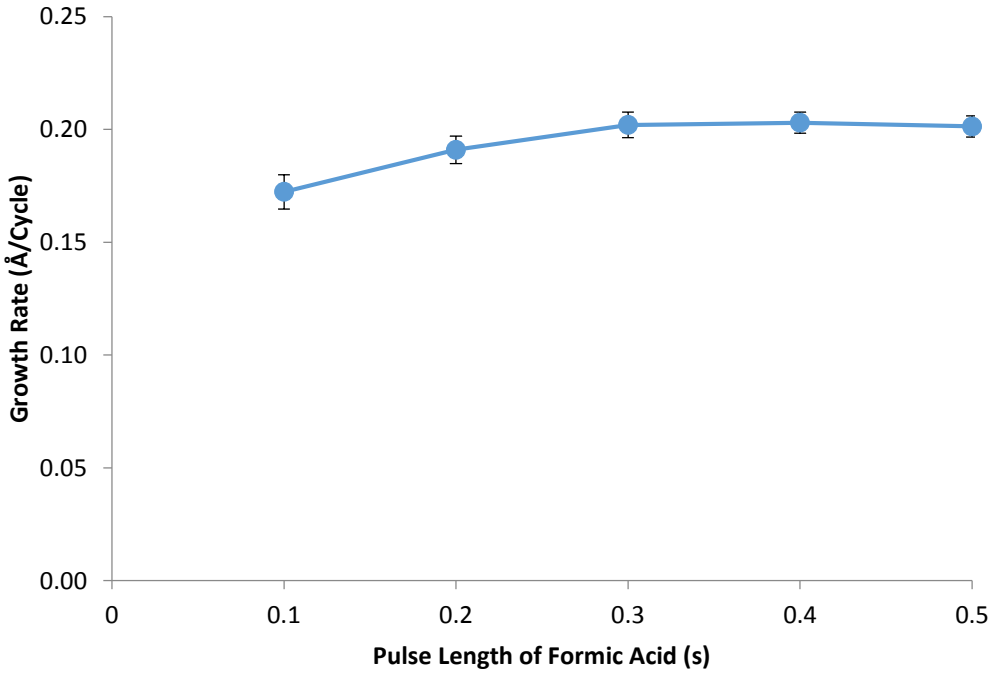


Figure S15. A plot of growth rate versus $BH_3(NHMe_2)$ pulse length for a Cu film grown by the three-step process at 150 °C on a Pd substrate.

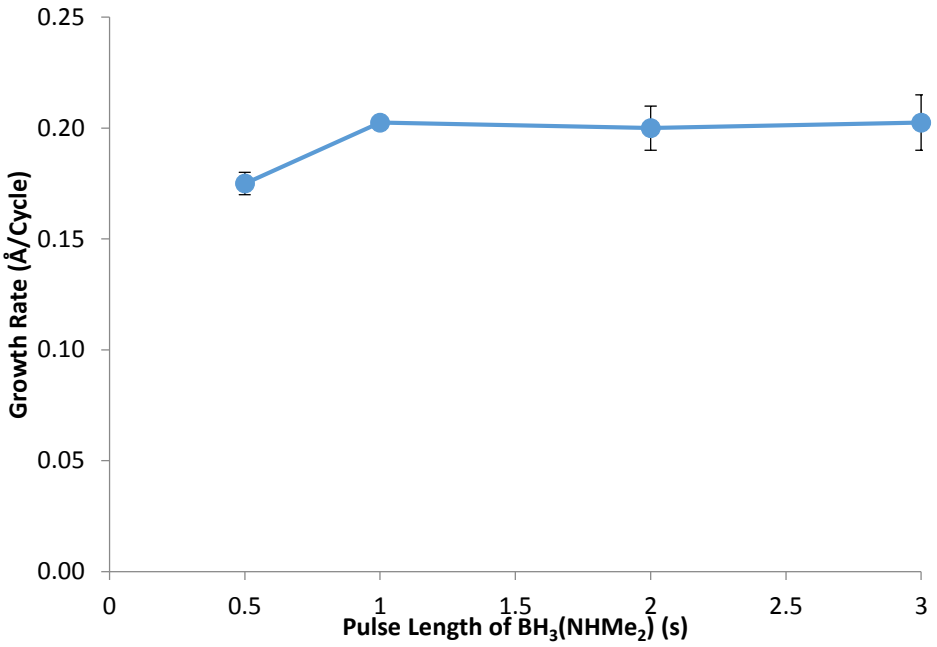


Figure S16. A plot of growth rate versus $BH_3(NHMe_2)$ pulse length for a Cu film grown by the three-step process at 150 °C on a Pt substrate.

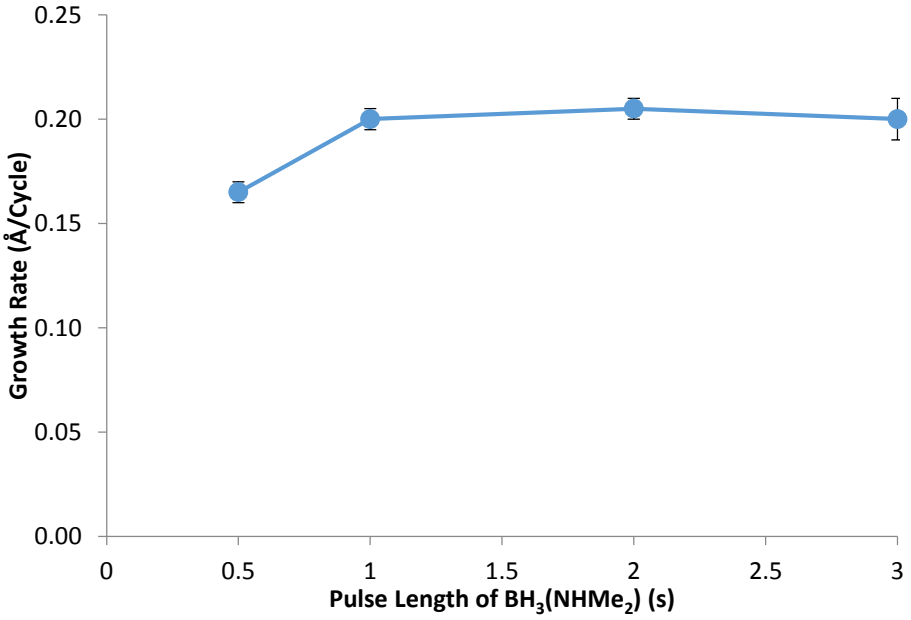


Figure S17. A plot of growth rate versus deposition temperature for a Cu film grown by the three-step process at 150 °C on a Pt substrate.

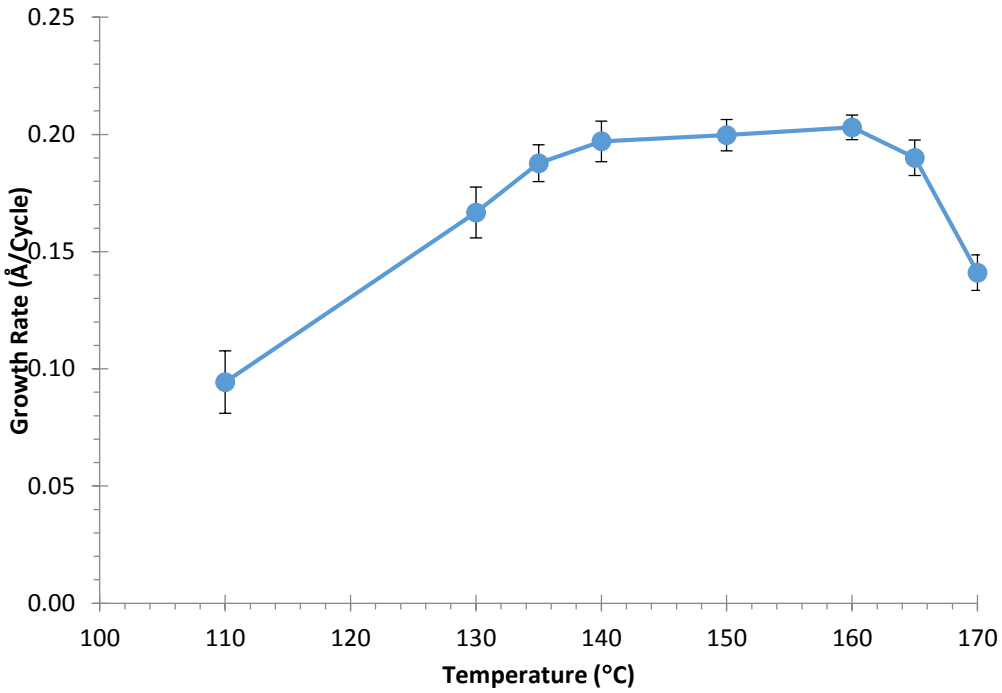


Figure S18. XPS survey scans of a 20 nm thick Cu film deposited at 140 °C with the three-step process on a Pd substrate.

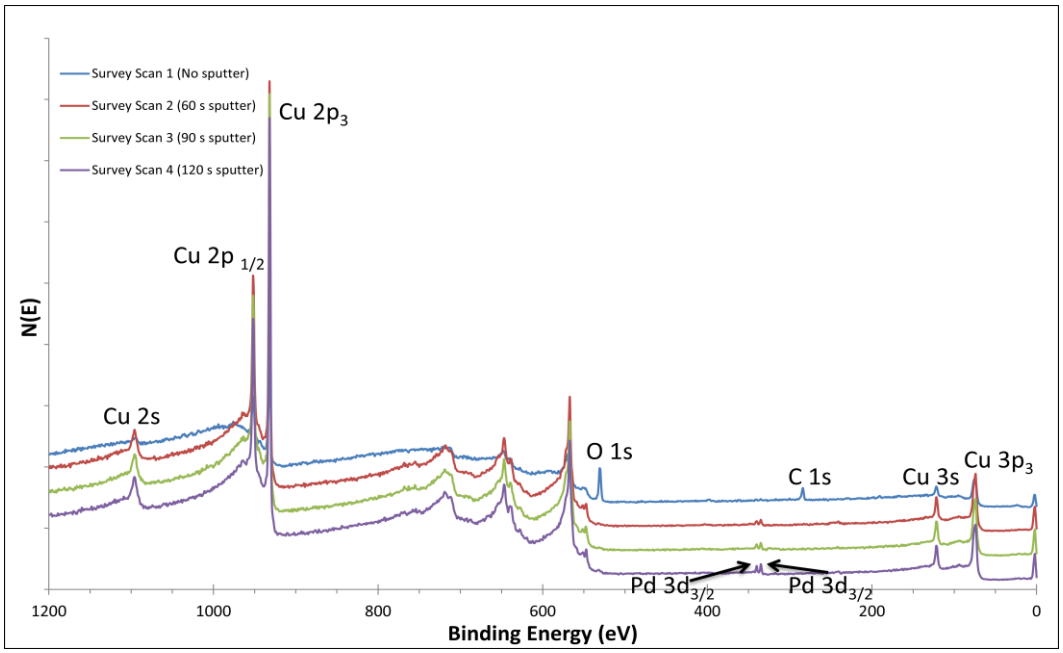


Figure S19. High resolution XPS scan of the Cu 2p region for a 20 nm thick Cu film deposited at 140 °C with the three-step process on a Pd substrate after 120 seconds of Ar ion sputtering.

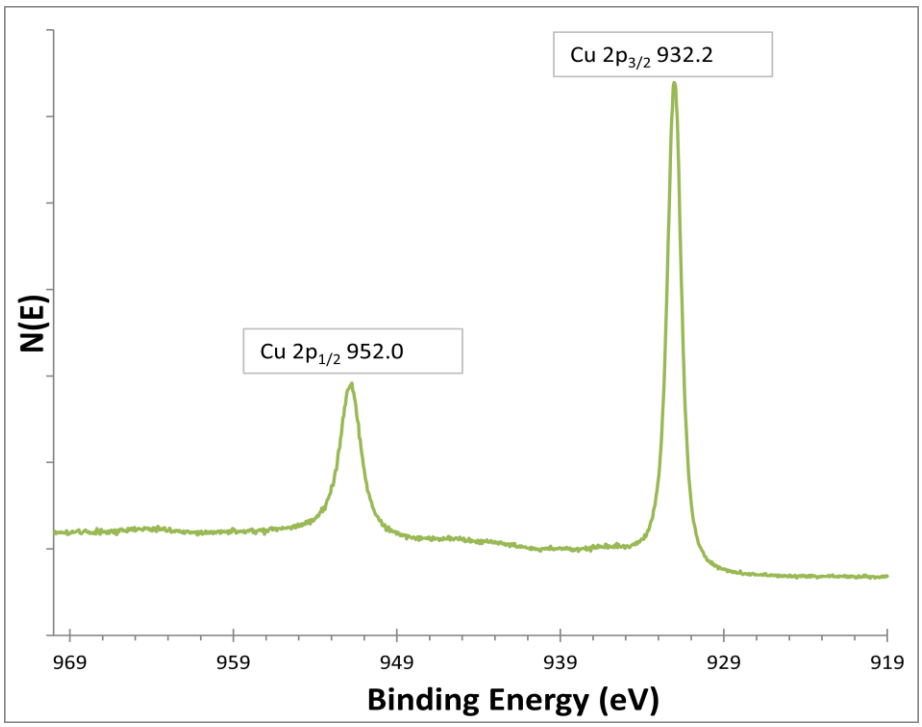


Figure S20. XPS survey scans of a 20 nm thick Cu film deposited at 140 °C with the three-step process on a Pt substrate.

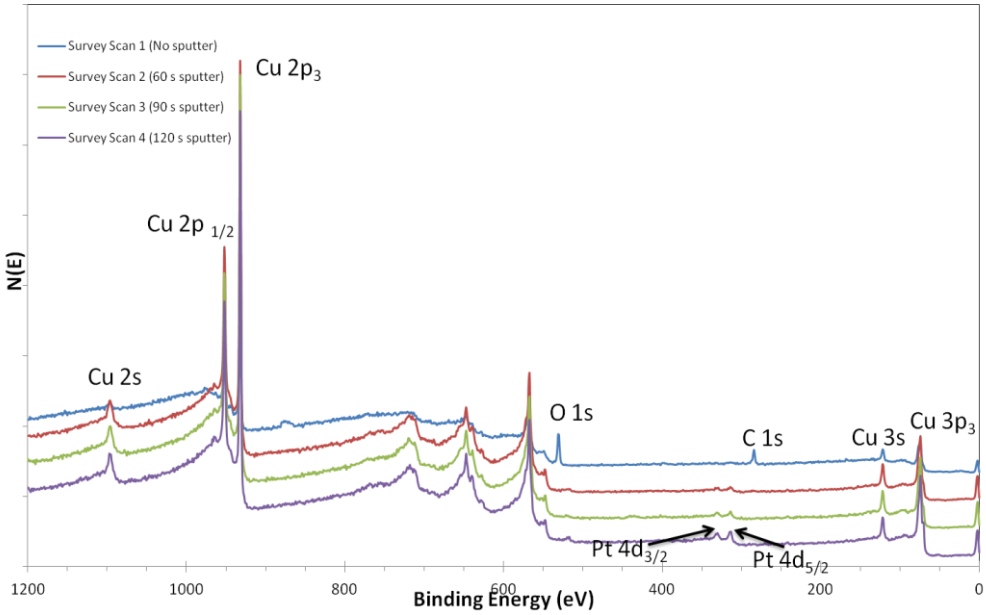


Figure S21. High resolution XPS scan of the Cu 2p region for a 20 nm thick Cu film deposited at 140 °C with the three-step process on a Pt substrate after 120 seconds of Ar ion sputtering.

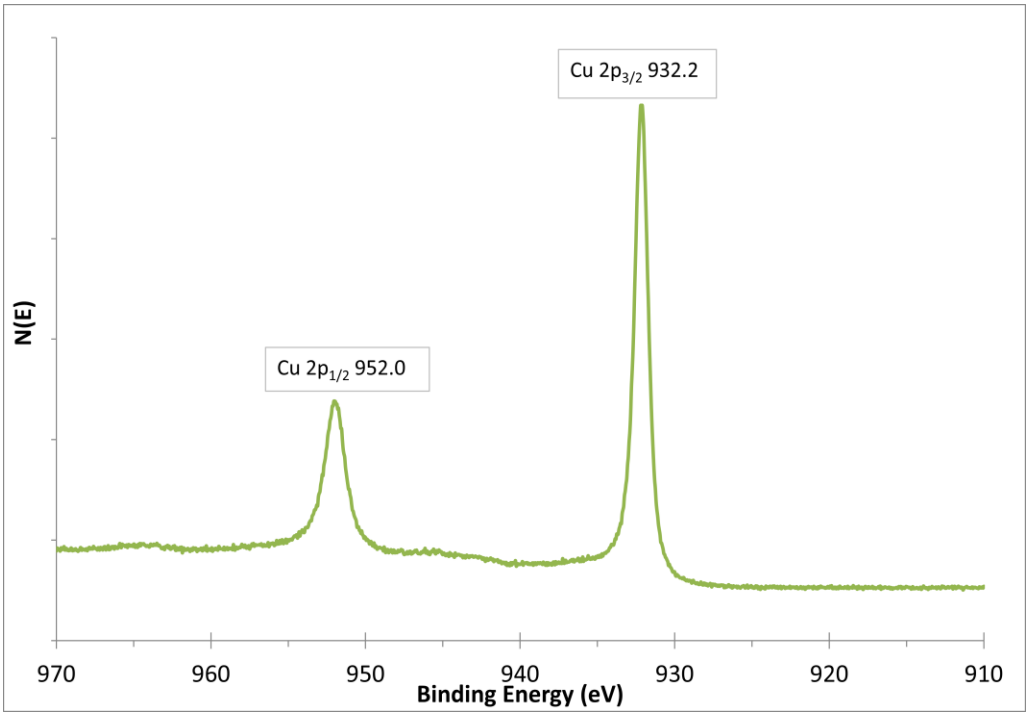


Figure S22. XPS survey scans of a 20 nm thick Cu film deposited at 150 °C with the three-step process on a Pd substrate.

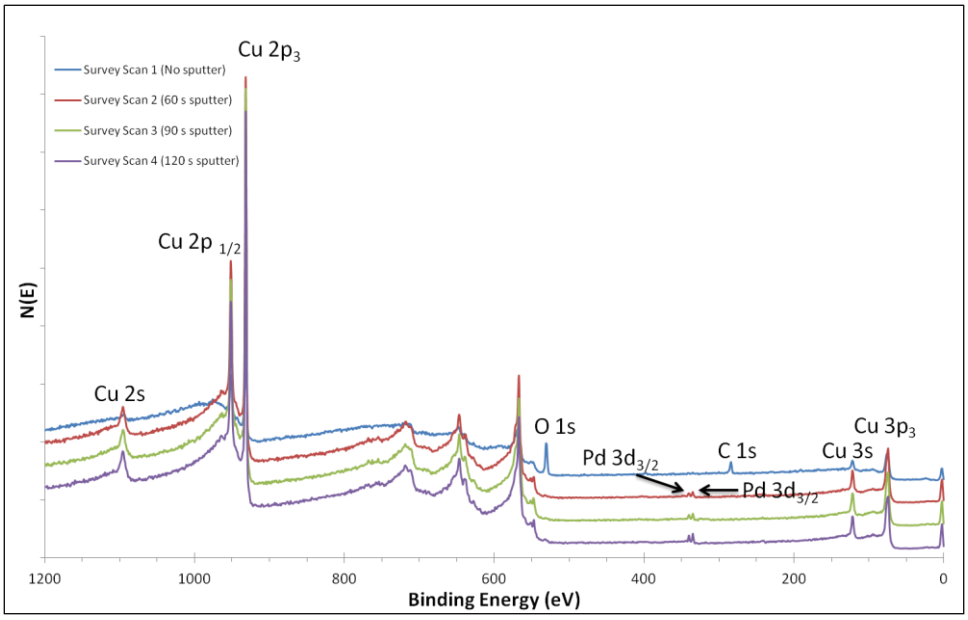


Figure S23. High resolution XPS scan of the Cu 2p region for a 20 nm thick Cu film deposited at 150 °C with the three-step process on a Pd substrate after 120 seconds of Ar ion sputtering.

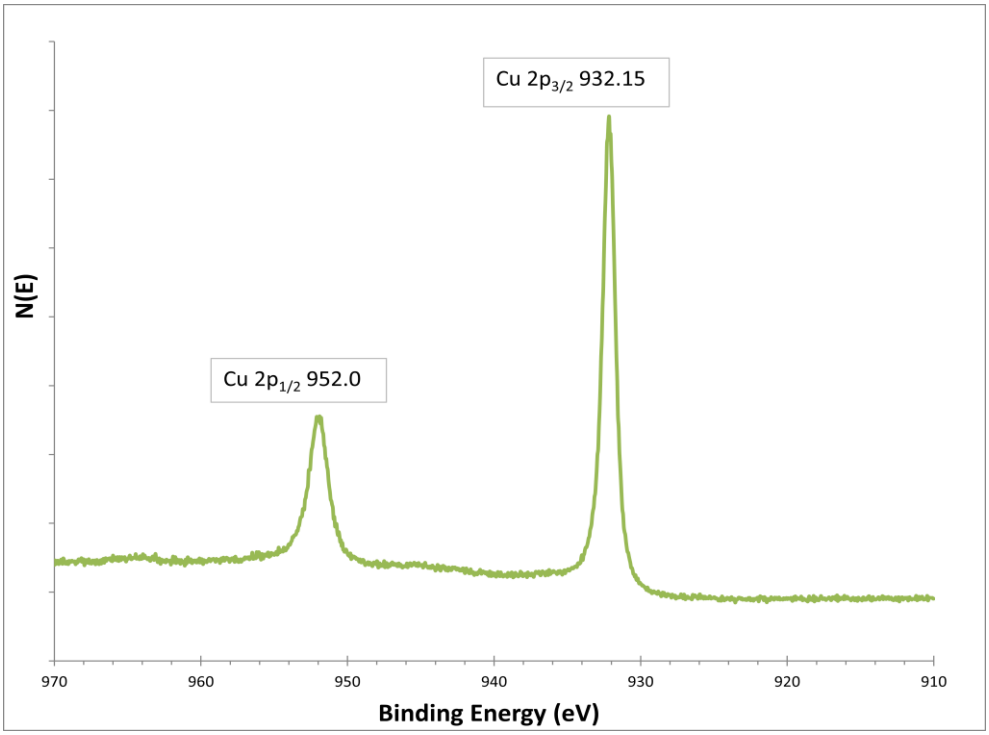


Figure S24. XPS survey scans of a 20 nm thick Cu film deposited at 150 °C with the three-step process on a Pt substrate. The Pt 3d ionizations appear at ca. 320 eV in the sputtered samples.

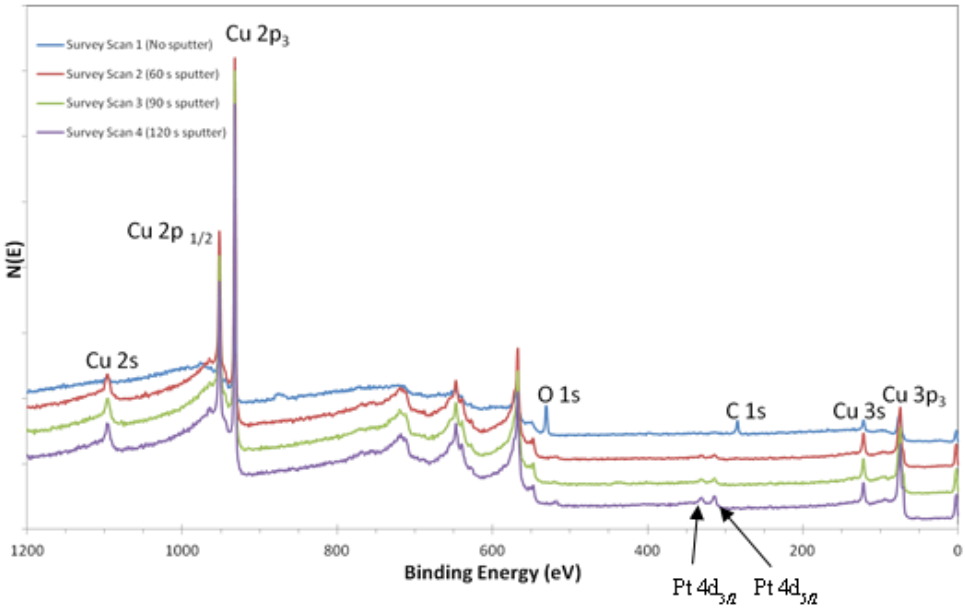


Figure S25. High resolution XPS scan of the Cu 2p region for a 20 nm thick Cu film deposited at 150 °C with the three-step process on a Pt substrate after 120 seconds of Ar ion sputtering.

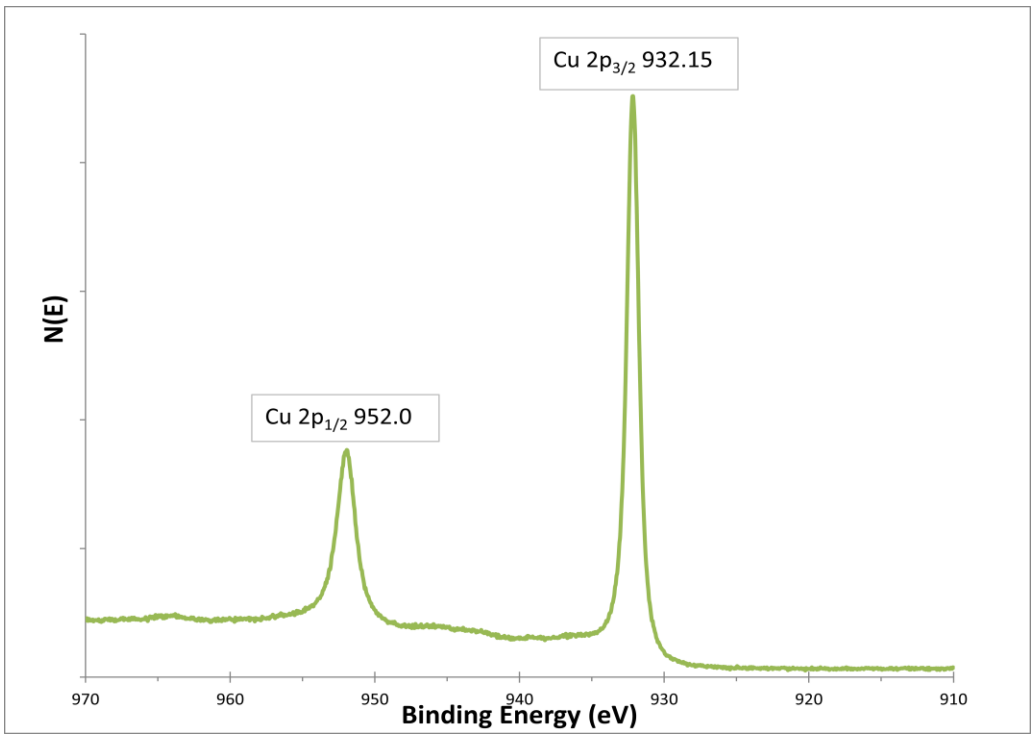


Figure S26. XPS survey scans of a 20 nm thick Cu film deposited at 160 °C with the three-step process on a Pd substrate.

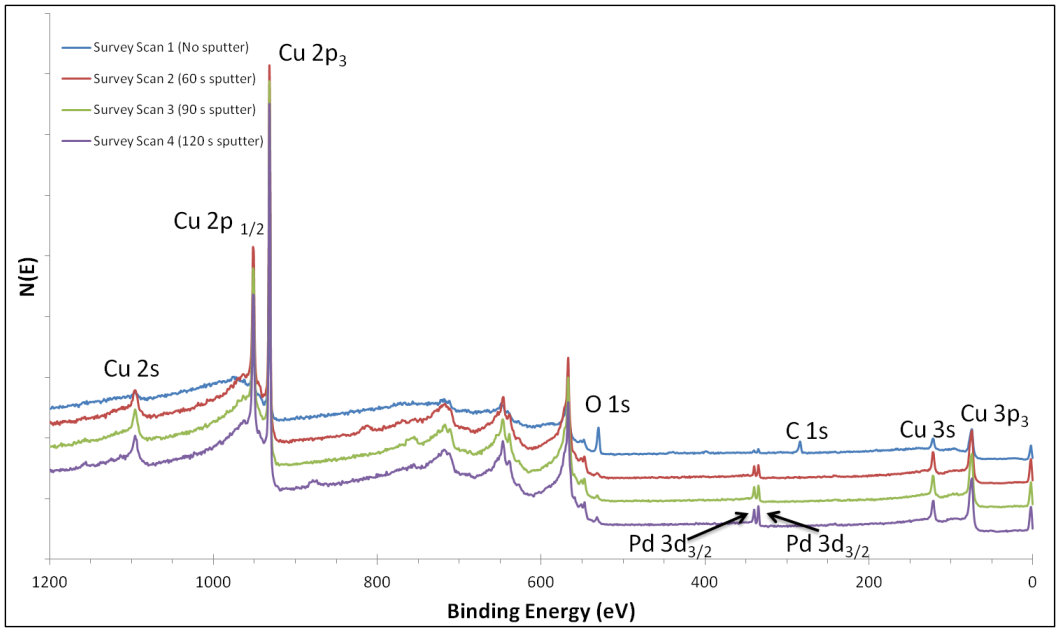


Figure S27. High resolution XPS scan of the Cu 2p region for a 20 nm thick Cu film deposited at 160 °C with the three-step process on a Pd substrate after 120 seconds of Ar ion sputtering.

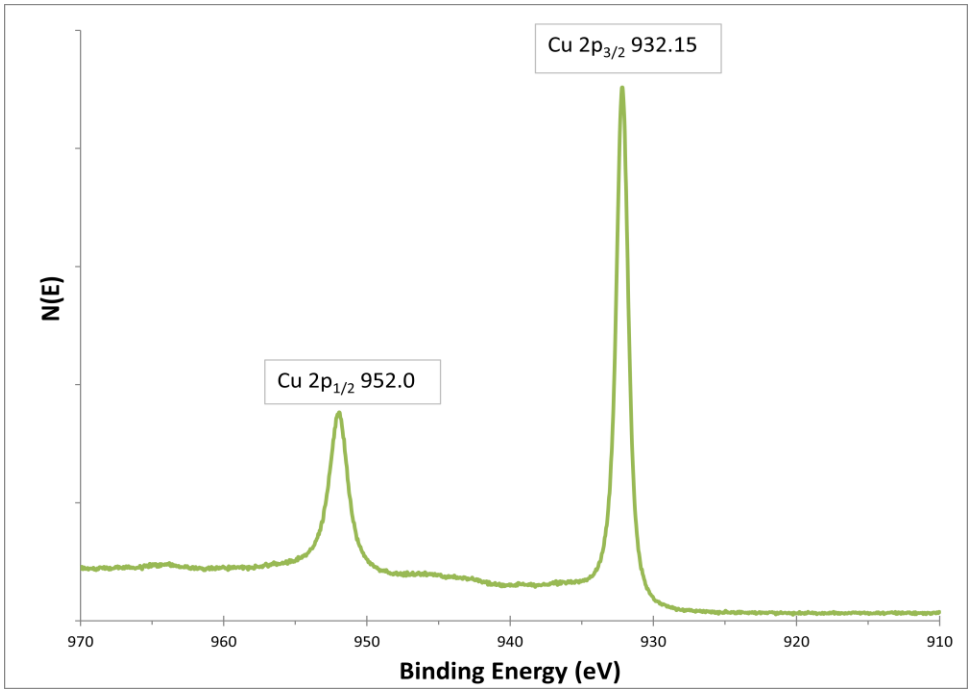


Figure S28. XPS survey scans of a 20 nm thick Cu film deposited at 160 °C with the three-step process on a Pt substrate.

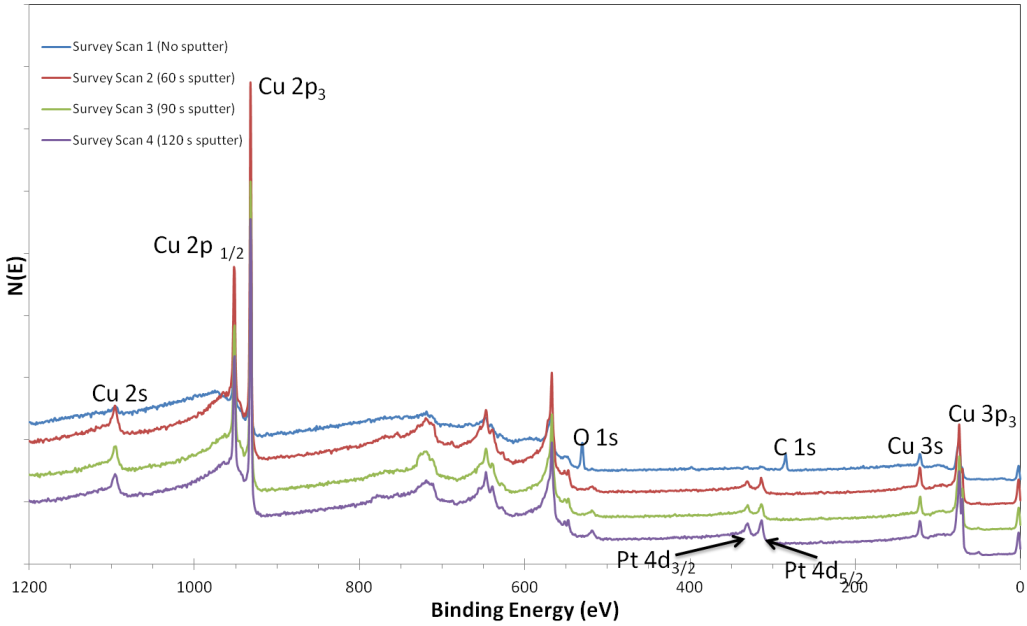


Figure S29. High resolution XPS scan of the Cu 2p region for a 20 nm thick Cu film deposited at 160 °C with the three-step process on a Pt substrate after 120 seconds of Ar ion sputtering.

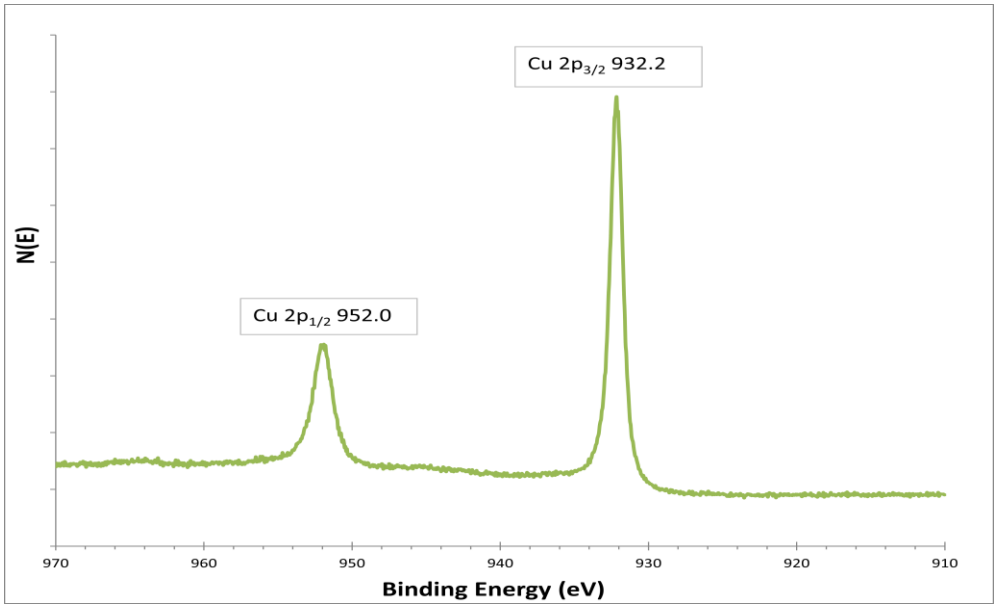


Figure S30. Representative X-ray diffraction pattern of a 30 nm thick Cu film deposited at 160 °C on a Pd substrate.

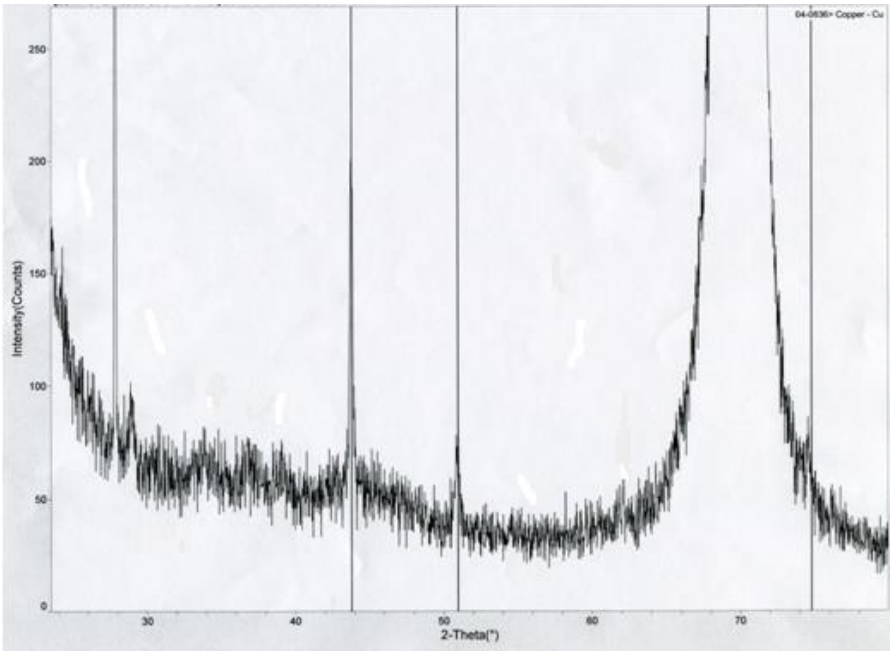


Figure S31. AFM images of 20 nm thick three-step Cu film surfaces grown on Pt substrates at 140 °C (top, rms roughness = 1.8 nm) and 160 °C (bottom, rms roughness = 1.8 nm).

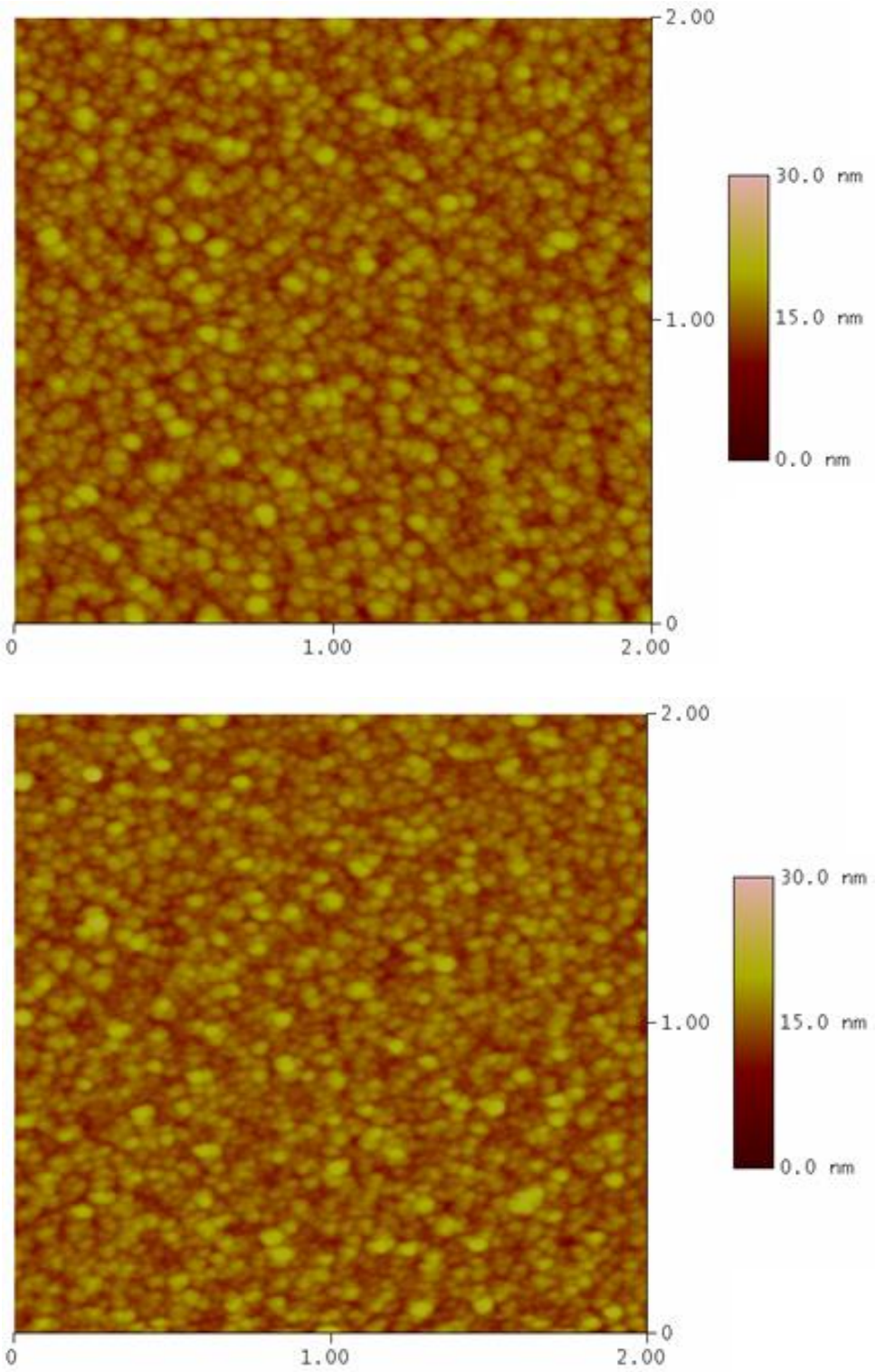


Figure S32. A plot of sheet resistivity versus number of growth cycles for a Cu film grown by the three-step process on a Pd substrate at 150 °C. The sheet resistivity of the as-received Pd substrate is 15 Ω/Sq and drops to 14 Ω/Sq after annealing the bare substrate at 150 °C for the same amount of time each deposition required.

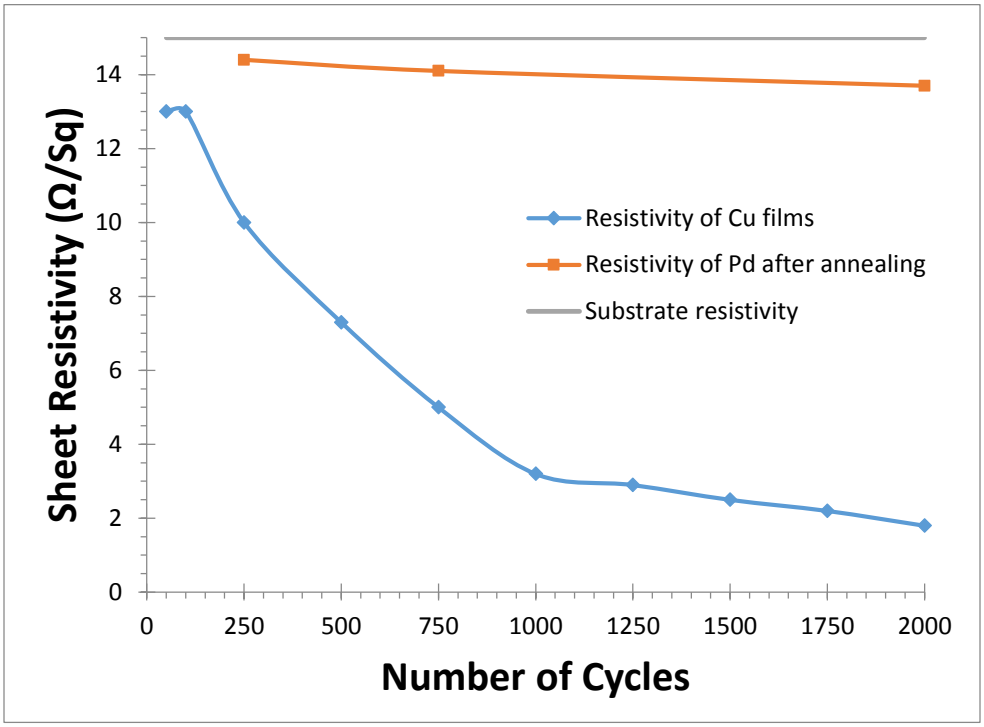


Figure S33. A plot of sheet resistivity versus number of growth cycles for a Cu film grown by the three-step process on a Pt substrate at 150 °C. The sheet resistivity of the as-received Pt substrate is 39 Ω/Sq and drops to 31 Ω/Sq after annealing the bare substrate at 150 °C for the same amount of time each deposition required.

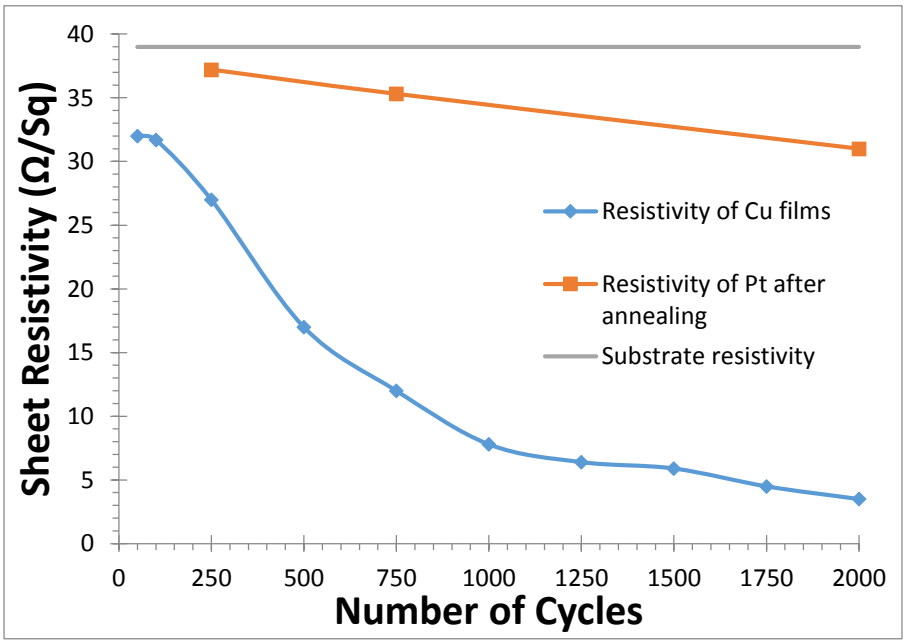
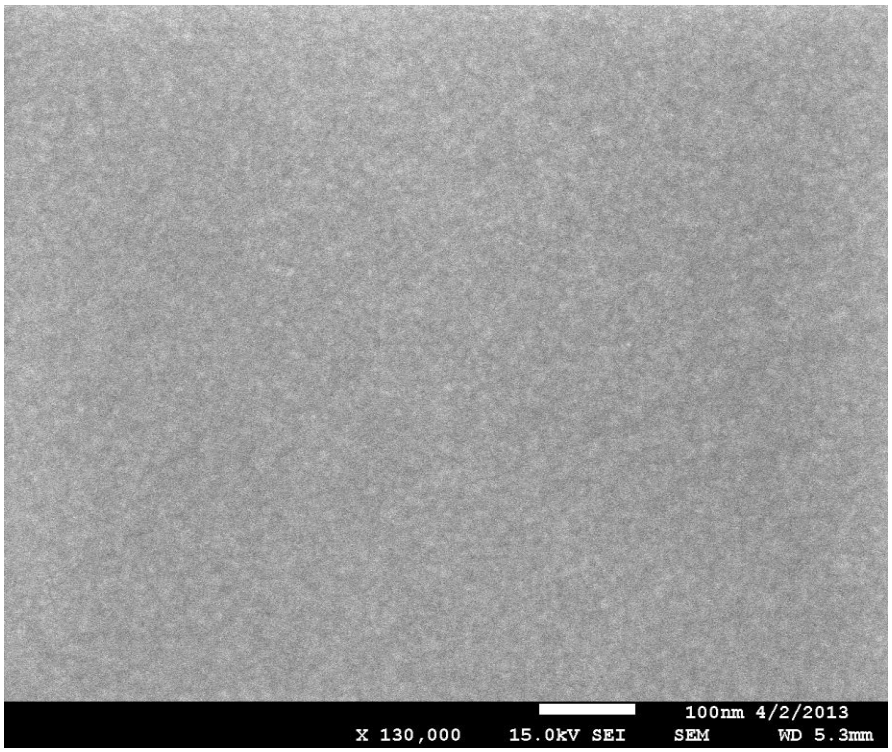


Figure S34. SEM images of a Cu film grown at 150 °C by the three-step process on a Pd substrate after 100 growth cycles (top-down image is top view, bottom image is side view).



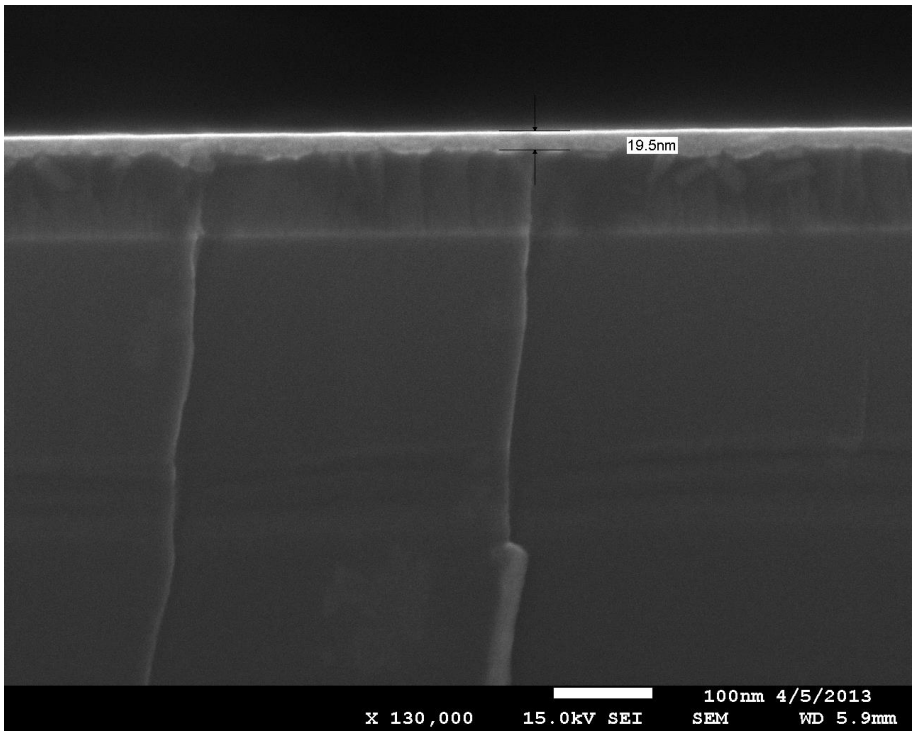


Figure S35. SEM images of a Cu film grown at 150 °C by the three-step process on a Pt substrate after 100 growth cycles (top-down image is top view, bottom image is side view).