Supplementary Information (SI) for Nanoscale.

Control of Cu morphology on TaN barrier and combined Ru-TaN barrier/liner substrates for nanoscale interconnects from atomistic kinetic Monte Carlo simulations

Samuel Aldana, Cara-Lena Nies, Michael Nolan**

Contents

Section 1: Activation energies estimation

We used DFT calculations to evaluate how Ru incorporation in a TaN substrate affects Cu migration. The results indicate that the incorporation of Ru increases the interaction strength between the substrate and deposited Cu, making upward migration from substrate to the top of the first Cu layer progressively more difficult. This trend is evident when comparing TaN and Ru25, where a similar change in coordination number (CN) (- 5 atoms from the substrate and +1 Cu) results in a higher activation energy for the Ru25 substrate (0.67 eV) compared to TaN (0.58 eV), as shown in Table S1 and Fig. S1a-S1b (TaN) and Fig. S2c-S2d (Ru25). Additionally, upward migration with a loss of 2 atoms from the Ru50 substrate leads to an activation energy of 0.62 eV. In contrast, the loss of 4 atoms from the Ru25 substrate, double the number, leads to an activation energy of 0.92 eV, just 0.3 eV higher. Note that when 3 atoms are lost from the Ru50 substrate along with 1 Cu atom, yielding the same CN as in the Ru25 case, the activation energy is even higher, at 1.03 eV. These findings clearly indicate that the substrate's strength increases with higher Ru content, align with previous studies.[1]

For the TaN case, losing 3 atoms from the substrate and gaining 2 Cu atoms results in an activation energy of 0.16 eV. Thus, the activation energy without the CN contribution would be slightly lower, so we selected 0.13 eV for (111) surfaces and 0.19 for (001) surfaces. Given that Ru incorporation increases the activation energy for upward migration, we assumed values of 0.18 eV for (111) and 0.23 eV for (001) surfaces for Ru25, while higher values were chosen for Ru50: 0.28 eV for (111) and 0.38 eV for (001). These selected values reflect the trend observed in Table S1.

When comparing these values with the homoepitaxial case, caution is advised.1 Besides typical differences in activation energies between MD and DFT calculations, the DFT-derived values are obtained from a model that represents a crystal still in the formation stage, rather than a perfect crytal, as illustrated in Figure S1 (TaN), S2 (Ru25) and S3 (Ru50).

Table S1: Activation energies obtained from DFT calculations for the upward migration from substrate to the top of the first layer of Cu. The upward migration for the case of Cu on an fcc Cu crystal is obtained by MD calculations[2].

Substrate	CN in Position 1	Activation energy (eV)	CN in Position 2	CN change
TaN	5 TaN + 3 Cu (Fig. S1a)	0.58	4 Cu (Fig. S1b)	- 5 TaN + 1 Cu
TaN	3 TaN + 2 Cu (Fig. S1c)	0.16	4 Cu (Fig. S1d)	- 3 TaN + 2 Cu
Ru25	4 Ru25 + 2 Cu (Fig. S2a)	0.92	2 Cu (Fig. S2b)	- 4 Ru25
Ru25	5 Ru25 + 2 Cu (Fig. S2c)	0.67	3 Cu (Fig. S2d)	- 5 Ru25 + 1 Cu
Ru50	2 Ru50 + 2 Cu (Fig. S3a)	0.62	2 Cu (Fig. S3b)	- 2 Ru50
Ru50	3 Ru50 + 3 Cu (Fig. S3c)	1.03	2 Cu (Fig. S3d)	- 3 Ru50 - 1 Cu
Homoepitaxial (111) face	5 Cu	0.763[2]	2 Cu	- 3 Cu
Homoepitaxial (001) face	5 Cu	0.978[2]	2 Cu	- 3 Cu

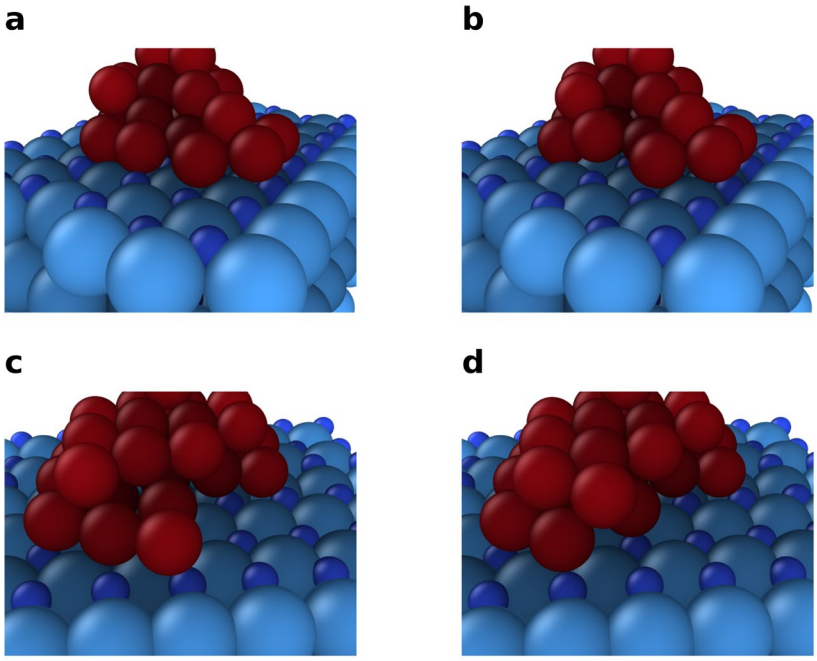

Figure S1: Transitions of a Cu atom from the TaN substrate to the upper Cu layer. The transition from state (a) to state (b) requires an activation energy of 0.58 eV, while the transition from state (c) to state (d) requires an activation energy of 0.16 eV.

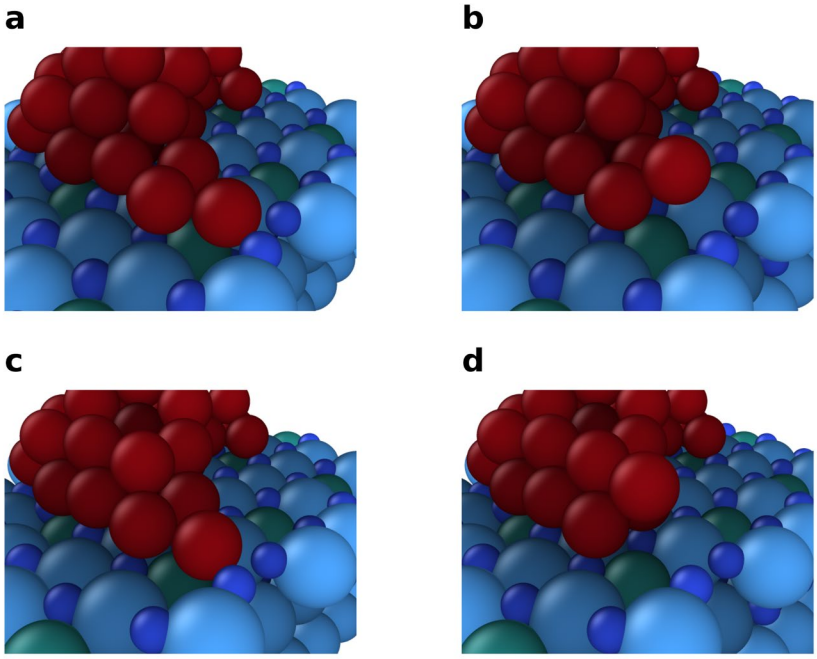

Figure S2: Transitions of a Cu atom from the Ru25 substrate to the upper Cu layer. The transition from state (a) to state (b) requires an activation energy of 0.92 eV, while the transition from state (c) to state (d) requires an activation energy of 0.67 eV.

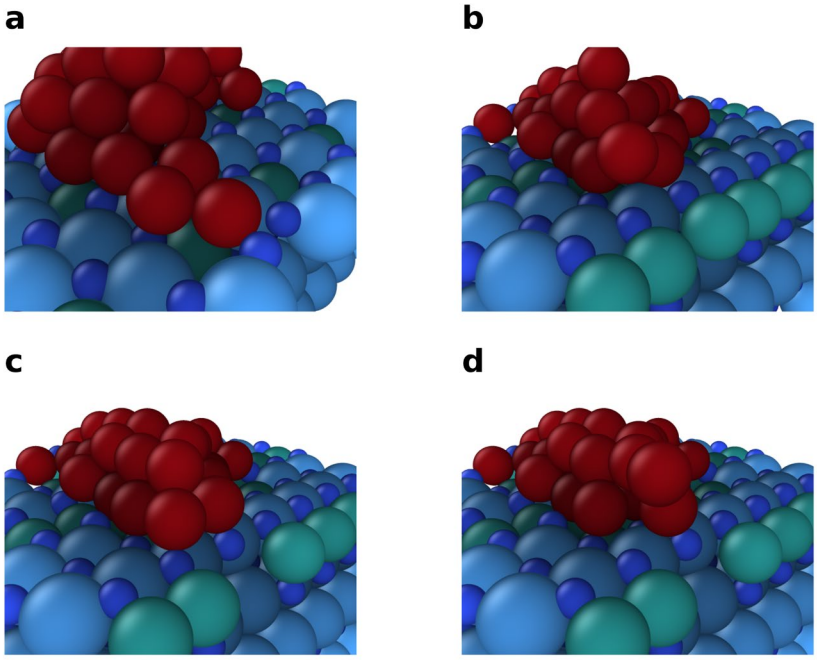

Figure S3: Transitions of a Cu atom from the Ru50 substrate to the upper Cu layer. The transition from state (a) to state (b) requires an activation energy of 0.62 eV, while the transition from state (c) to state (d) requires an activation energy of 1.03 eV.

Table S2: Activation energies obtained from DFT calculations for the upward migration from one Cu layer to the next one. The upward migration for the homoepitaxial case is obtained by MD calculations[2].

Substrate	CN in Position 1	Activation energy (eV)	CN in Position 2	CN change	Activation energy without CN contribution (eV)
TaN (001)	7 Cu (Fig. S4a)	0.69	4 Cu (Fig. S4b)	- 3 Cu	0.24
TaN (001)	3 Cu (Fig. S4c)	0.22	2 Cu (Fig. S4d)	- 1 Cu	0.07
Ru25 (N/A)	5 Cu (Fig. S5a)	0.67	3 Cu (Fig. S5b)	- 2 Cu	0.37
Ru25 (111)	3 Cu (Fig. S5c)	0.49	2 Cu (Fig. S5d)	- 1 Cu	0.34
Ru50 (N/A)	5 Cu (Fig. S6a)	0.72	2 Cu (Fig. S6b)	- 3 Cu	0.27
Ru50 (N/A)	2 Cu (Fig. S6c)	0.83	1 Cu (Fig. S6d)	- 1 Cu	0.68
Homoepitaxial (111) face	5 Cu	0.763[2]	2 Cu	- 3 Cu	0.313
Homoepitaxial (001) face	5 Cu	0.978[2]	2 Cu	- 3 Cu	0.528

As shown in Table S2, the migration of a Cu atom between adjacent Cu layers deposited on TaN substrate involves an activation energy of 0.22 eV for a CN change of one Cu atom. Consequently, the contribution of each atom to the activation energy due to CN should be less than 0.22 eV. In our study, we have set this value at 0.15 eV/atom, which is sufficiently high to ensure that deposited Cu can form clusters even at elevated temperatures (800 K). The activation energy without the CN contribution for Cu migration between Cu layers for TaN substrate ranges between 0.07 and 0.24 eV, so we select an intermediete value of 0.13 eV. In line with the observed trend, we selected activation energies of 0.20 eV for Ru25 and 0.28 eV for Ru50.

Ru incorporation into the substrate impacts not only the Cu directly in contact with the substrate but also the subsequent layers[1]. As shown in Table S2, the activation energy for Cu migration between layers on a TaN substrate is lower compared to substrates containing Ru and the homoepitaxial case, as TaN is a weakly interacting substrate. The addition of Ru increases the interaction strength of the substrate, resulting in higher activation energies for migration between layers. The elevated values observed for Ru25 may be attributed to the crystallographic surfaces still being in the formation stage (see Fig. S5). Additionally, the high

value found for Ru50 (0.68 eV, excluding CN contribution) may be due to migration being supported by a single atom (see Fig. S6d).

The activation energies used in this study serve as effective activation energies, given that exact values for every individual process and possible configurations are not available. To address this, we calibrated our kMC simulations using activation energies derived from DFT calculations or previously reported values[2]. This calibration process involves comparing 29-atoms island morphology from our kMC simulations and MD calculations at different temperatures (300 K, 500 K and 800 K), as shown in Figure S3 in ref. 1.

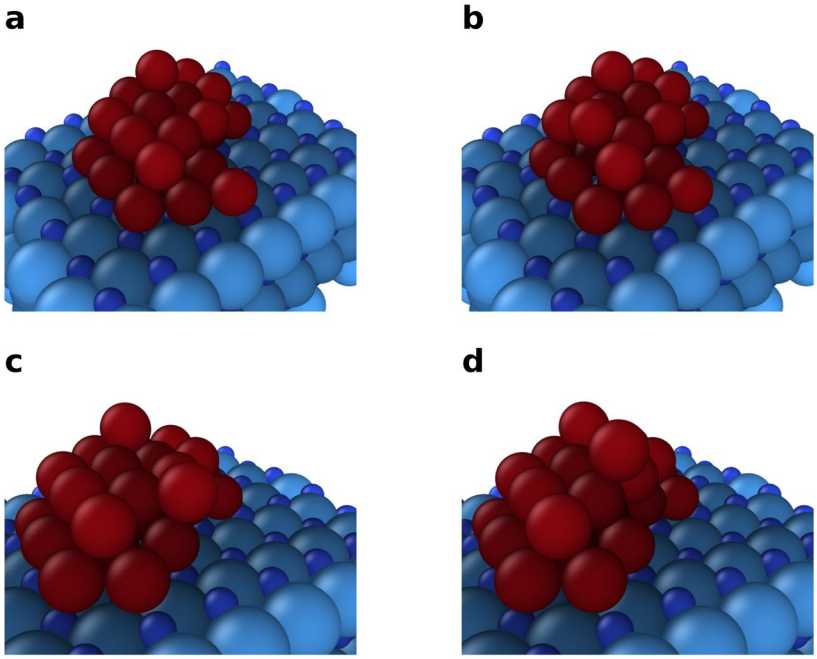

Figure S4: Transitions of a Cu atom between adjacent Cu layers deposited on a TaN substrate. The transition from state (a) to state (b) requires an activation energy of 0.69 eV, while the transition from state (c) to state (d) requires an activation energy of 0.22 eV.

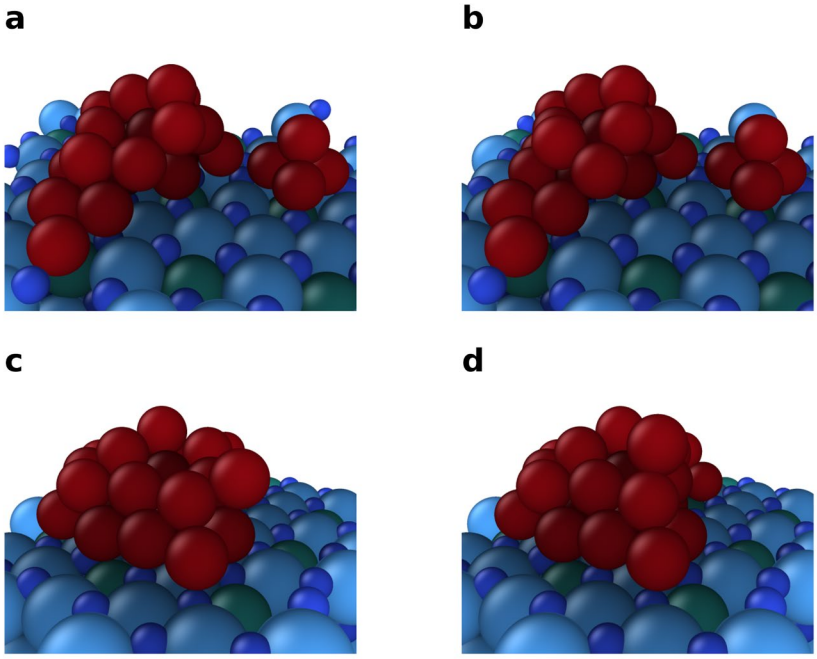

Figure S5: Transitions of a Cu atom between adjacent Cu layers deposited on a Ru25 substrate. The transition from state (a) to state (b) requires an activation energy of 0.67 eV, while the transition from state (c) to state (d) requires an activation energy of 0.49 eV.

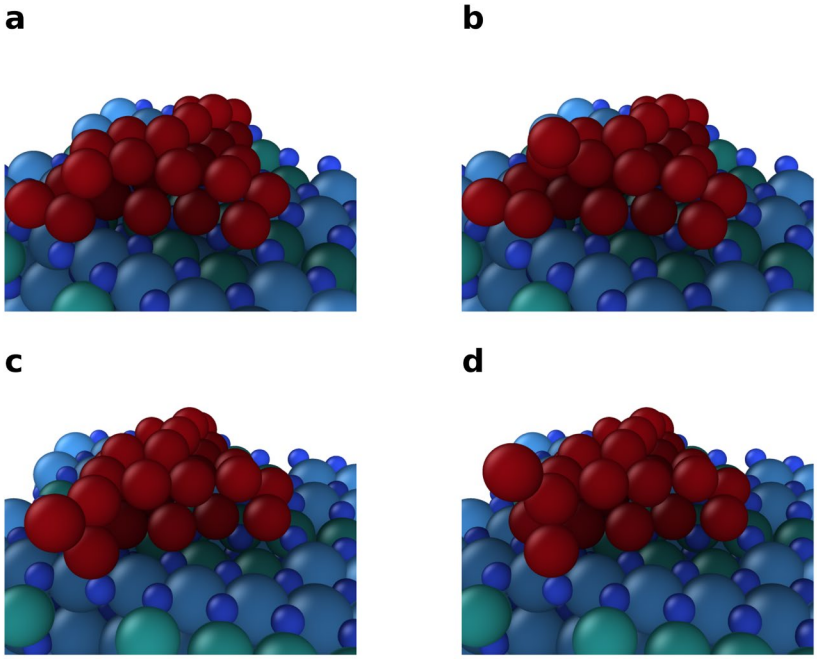

Figure S6: Transitions of a Cu atom between adjacent Cu layers deposited on a Ru50 substrate. The transition from state (a) to state (b) requires an activation energy of 0.72 eV, while the transition from state (c) to state (d) requires an activation energy of 0.83 eV.

Section 2: Surface of deposited Cu films

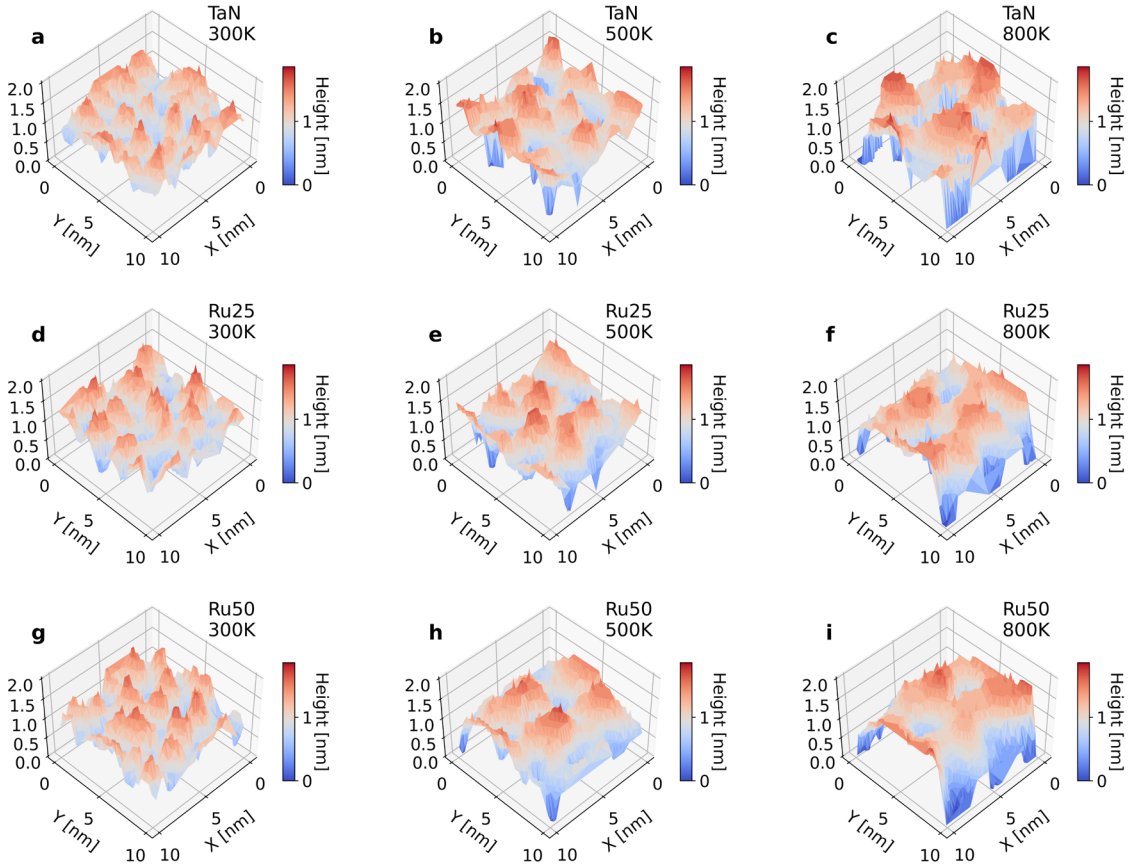

Figure S7: Surface of deposited Cu employing a partial pressure of P=0.5 Pa. Rows are different substrates: TaN (a, b, c), Ru25 (d, e, f) and Ru50 (g, h, i). Different columns represent varying temperature: 300 K (a, d, g), 500 K (b, e, h) and 800 K (c, f, i).

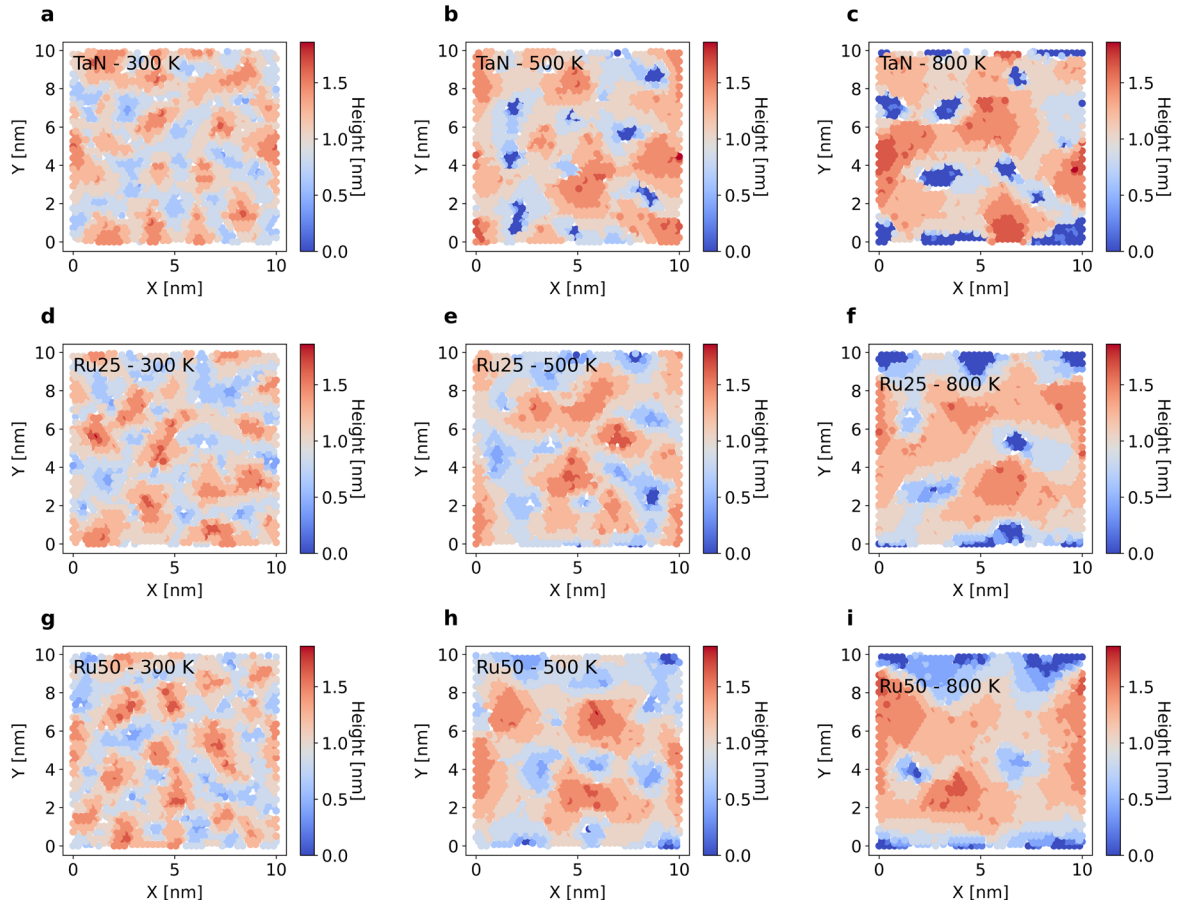

Figure S8: Height color maps of deposited Cu employing a partial pressure of P=0.5 Pa. Rows are different substrates: TaN (a, b, c), Ru25 (d, e, f) and Ru50 (g, h, i). Different columns represent varying temperature: 300 K (a, d, g), 500 K (b, e, h) and 800 K (c, f, i).

Section 3: Influence of partial pressures on Cu film deposition

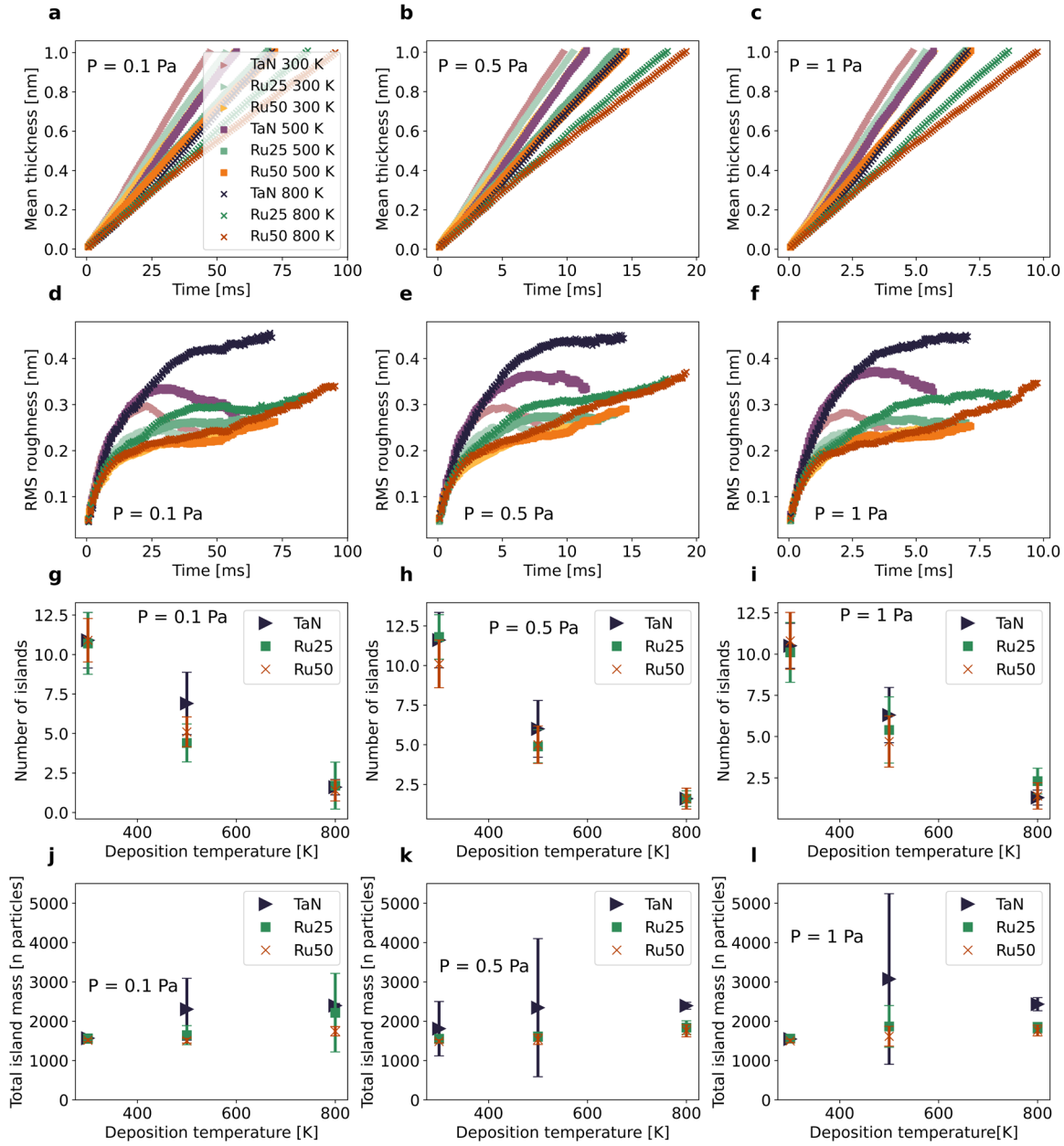

Figure S9: Time evolution of thickness (a, b, c), RMS roughness (d, e, f) number of islands (g, h, i) and total island mass (j, k, l) in deposition processes at different temperatures. Subfigures (a-f) present data from 9 independent simulations each. Subfigures (g-l) show the averaged results from 10 simulations per data point, with error bars as the standard deviation, totaling 90 independent simulations in each figure. Different category of colors represent different substrates (purple for TaN, blue for Ru25 and brown for Ru50), with darker colors for higher temperatures. Along the rows, the partial pressure increases as P=0.1 Pa (a, d, g, j), P=0.5 Pa (b, e, h, k) and P=1 Pa (c, f, i, l).

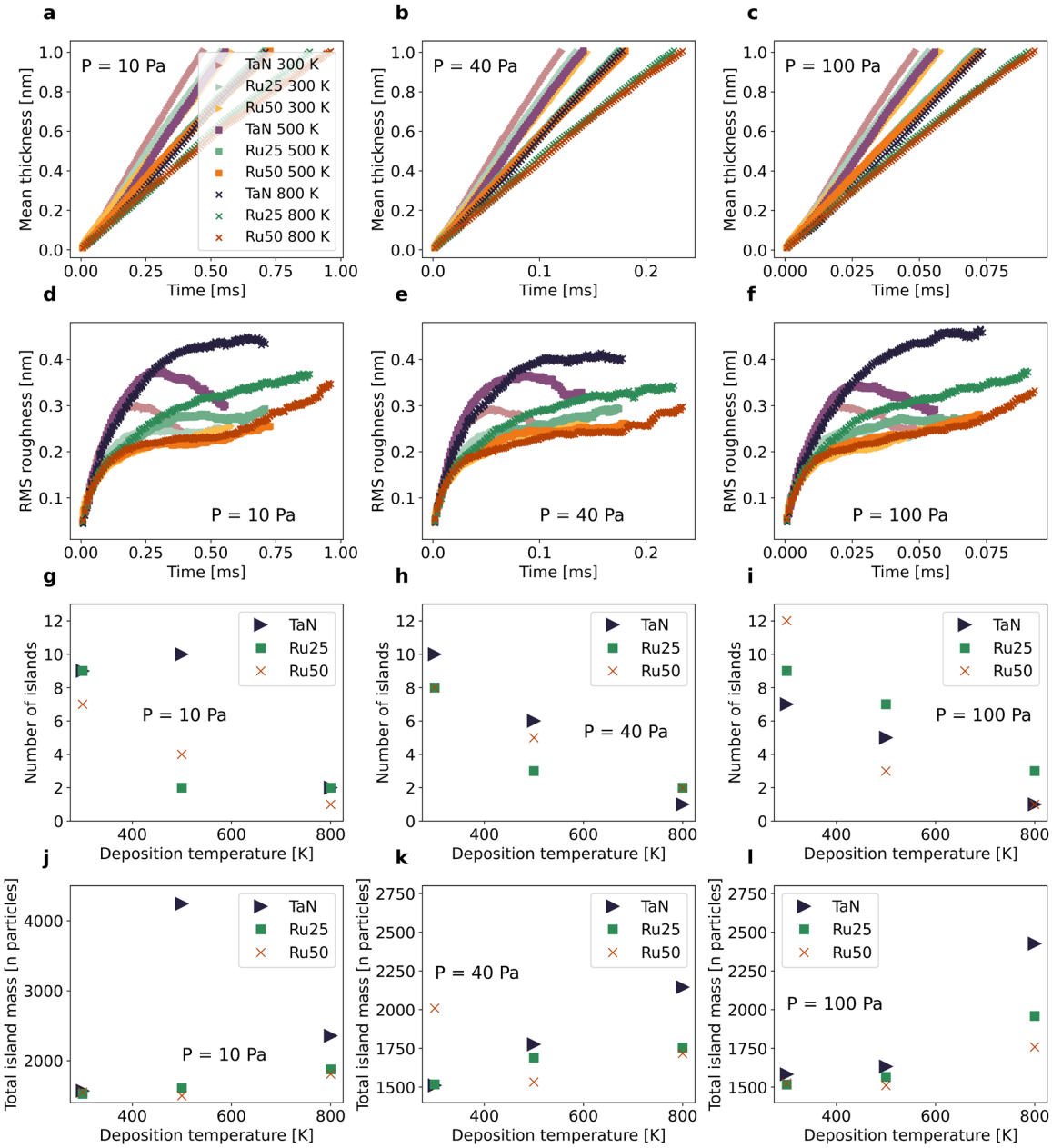

Figure S10: Time evolution of thickness (a, b, c), RMS roughness (d, e, f) number of islands (g, h, i) and total island mass (j, k, l) in deposition processes at different temperatures. Each subfigure consist of 9 independent simulations. Different category of colors represent different substrates (purple for TaN, blue for Ru25 and brown for Ru50), with darker colors for higher temperatures. Along the rows, the partial pressure increases as $P = 10\ Pa$ (a, d, g, j), $P = 40\ Pa$ (b, e, h, k) and $P = 100\ Pa$ (c, f, i, l).

Section 4: Root Mean Square Roughness of Cu film

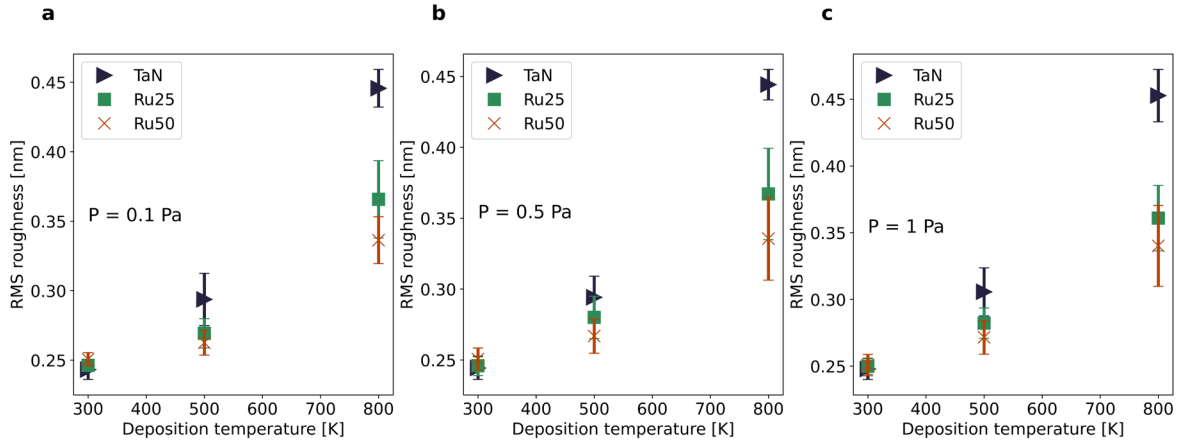

Figure S11: RMS roughness for growth simulations conducted on TaN, Ru25 and Ru50 at different temperatures (300 K, 500 K and 800 K) for a range of partial pressures: 0.1 (a), 0.5 (b) and 1 Pa (c). Ten growth simulations were averaged per data point, with error bars as the standard deviation.

Section 5: Mean island size

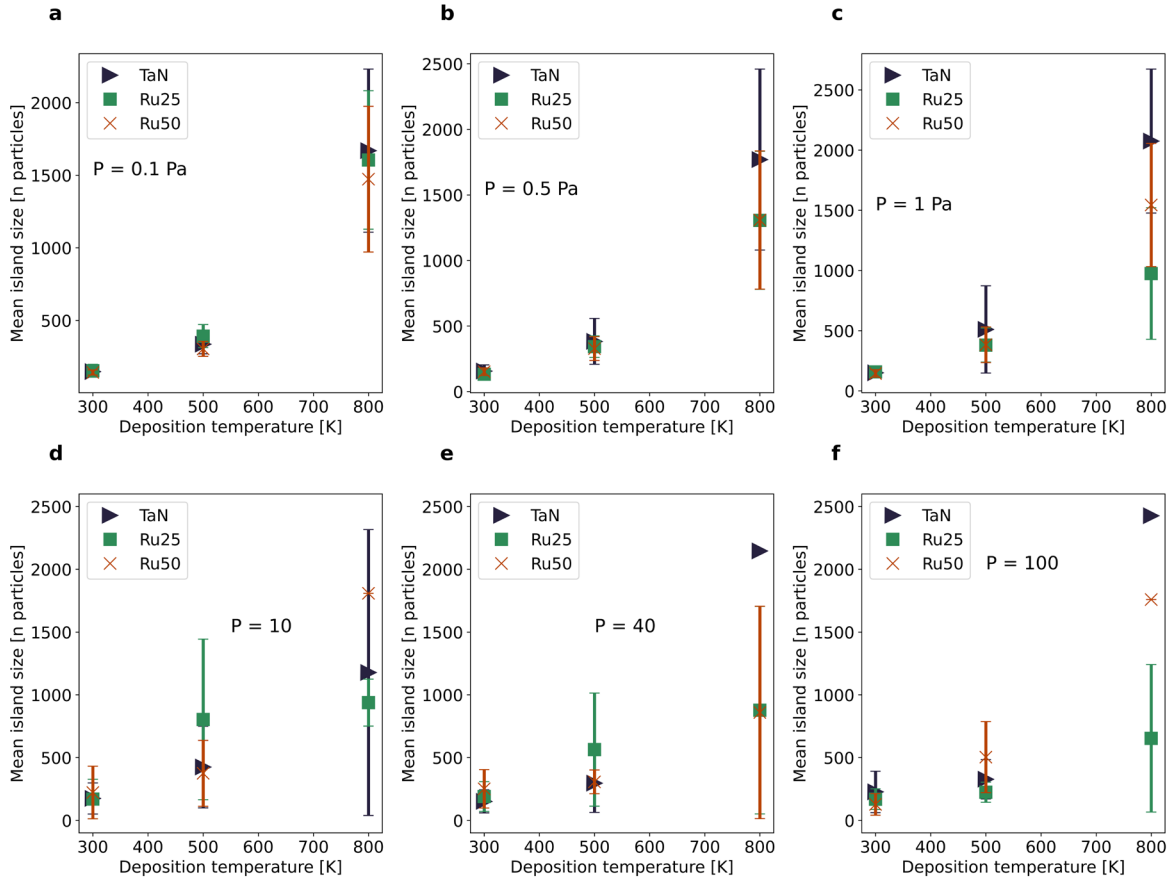

Figure S12: Mean island size for growth simulations on TaN, Ru25 and Ru50 at different temperatures (300 K, 500 K and 800 K) across a range of partial pressures: 0.1 Pa (a), 0.5 Pa (b), 1 Pa (c), 10 Pa (d), 40 Pa (e) and 100 Pa (f). Subfigures (a-c) show the averaged results from 10 simulations per data point, with error bars as the standard deviation, resulting in a total of 90 independent simulations per figure. Subfigures (d-f) present data from 9 independent simulations, with each data point corresponding to a single simulation.

Section 6: Substrate exposure and total uncovered area

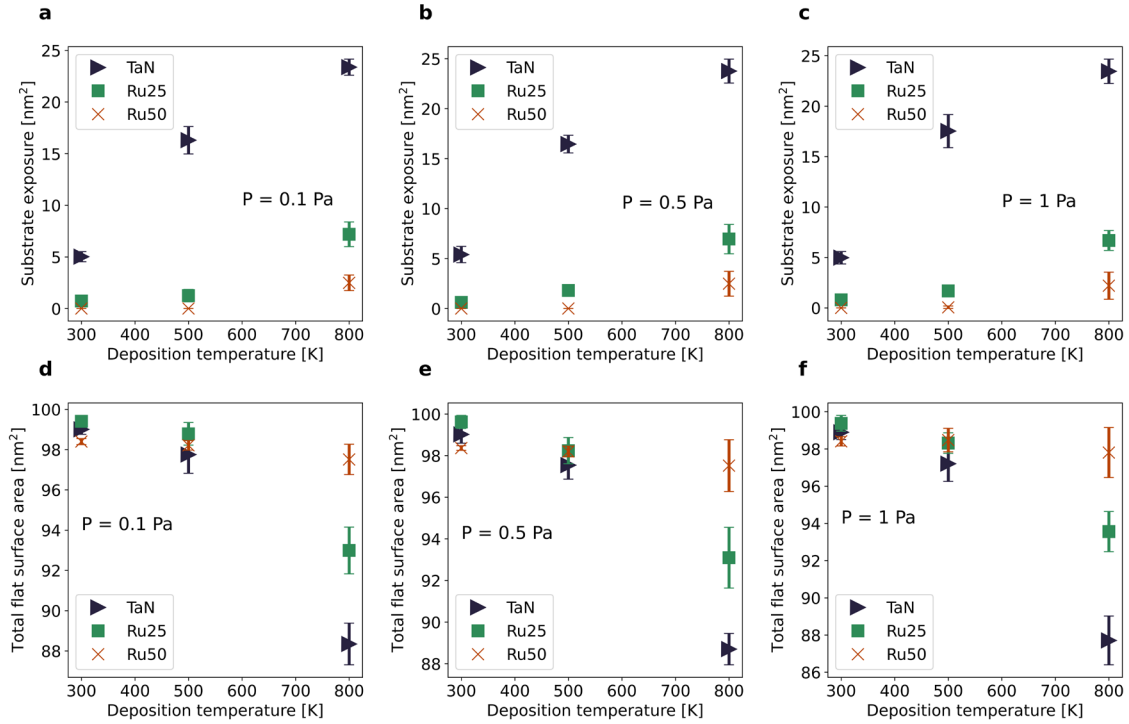

Figure S13: Substrate exposure for three partial pressures P = 0.1 Pa (a), P = 0.5 Pa (b) and P = 1 Pa (c). Total uncovered area for three partial pressures P = 0.1 Pa (d), P = 0.5 Pa (e) and P = 1 Pa (f). Ten growth simulations were averaged per data point on TaN, Ru25 and Ru50 at different temperatures (300 K, 500 K and 800 K) across the range of partial pressures. Error bars are the standard deviation.

Section 7: Neighbors analysis

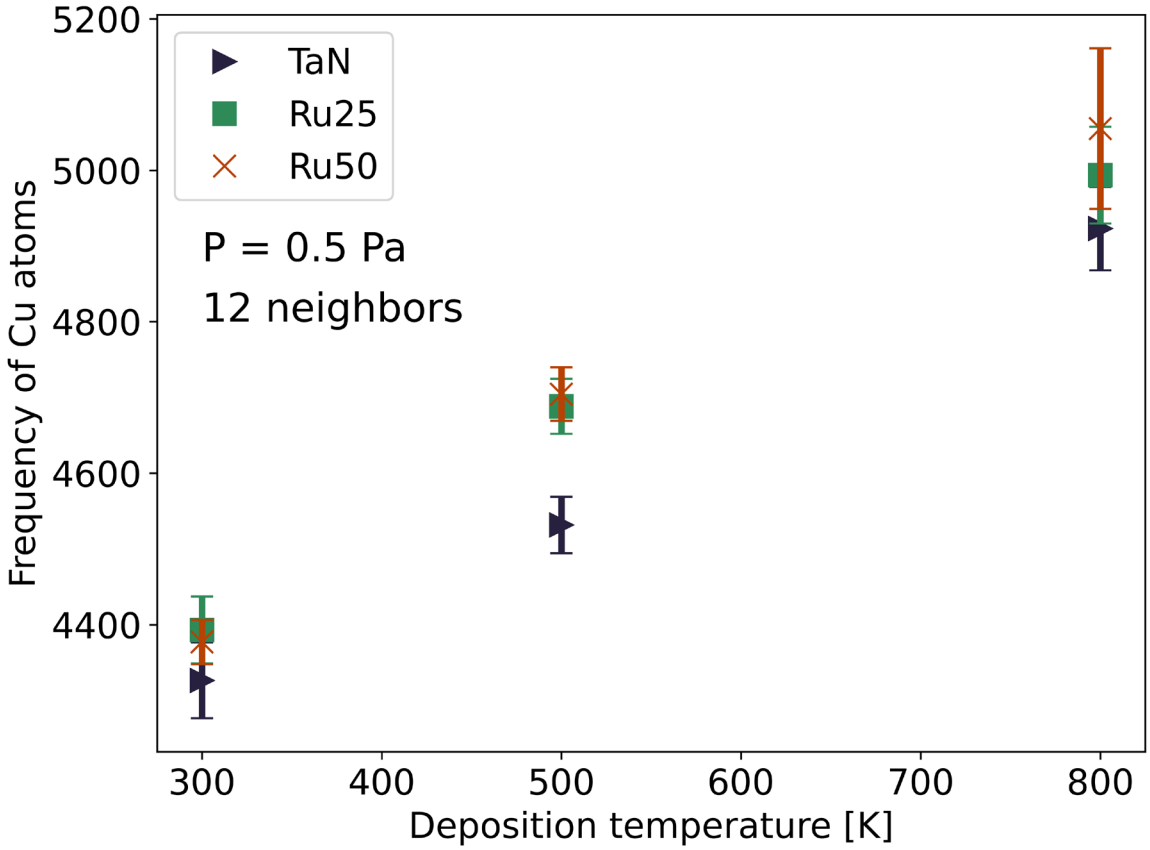

Figure S14: Frequency of Cu atoms with 12 nearest neighbors, averaged over 10 simulations, for TaN, Ru25 and Ru50 substrates across temperatures of 300 K, 500 K and 800 K. All simulations were conducted at a partial pressure of P = 0.5 Pa.

Section 8: Impact of Annealing

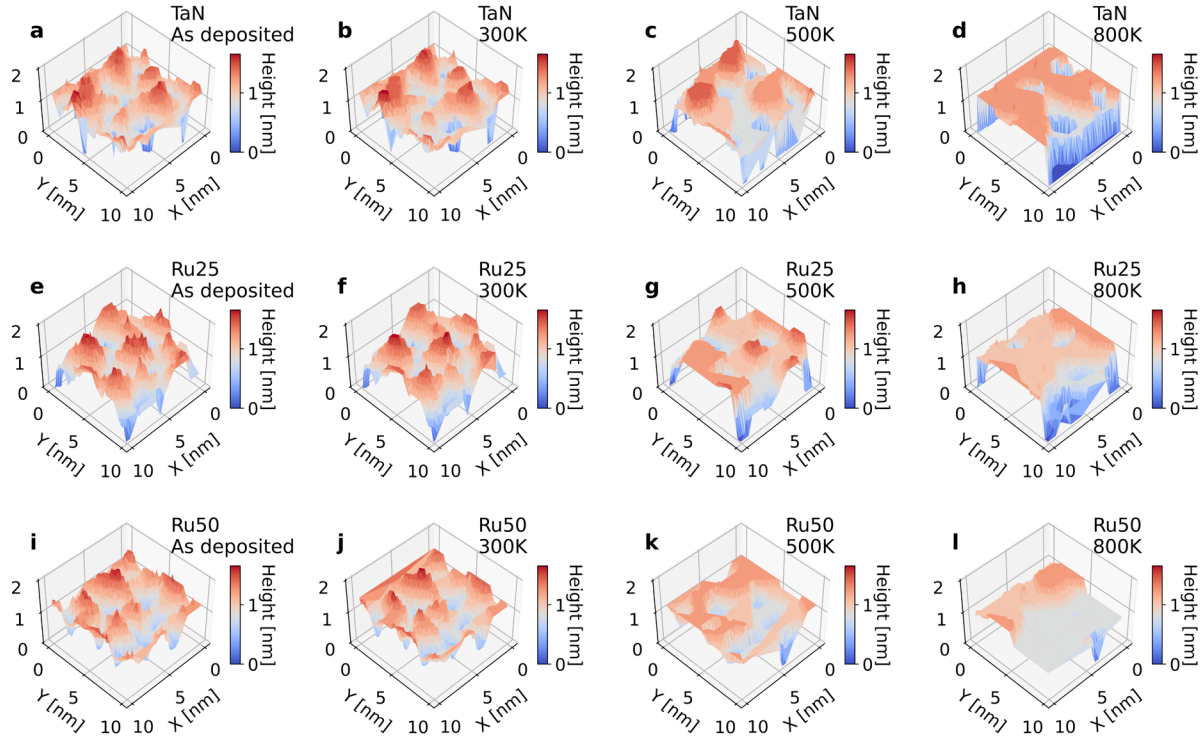

Figure S15: Surface of deposited Cu employing a partial pressure of P=0.5 Pa. Rows are different substrates: TaN (a, b, c, d), Ru25 (e, f, g, h) and Ru50 (i, j, k, l). First column represent the film deposited at 500 K for the different substrates, while the other columns are the layer surfaces annealed at varying temperature: 300 K (b, f, j), 500 K (c, g, k) and 800 K (d, h, l).

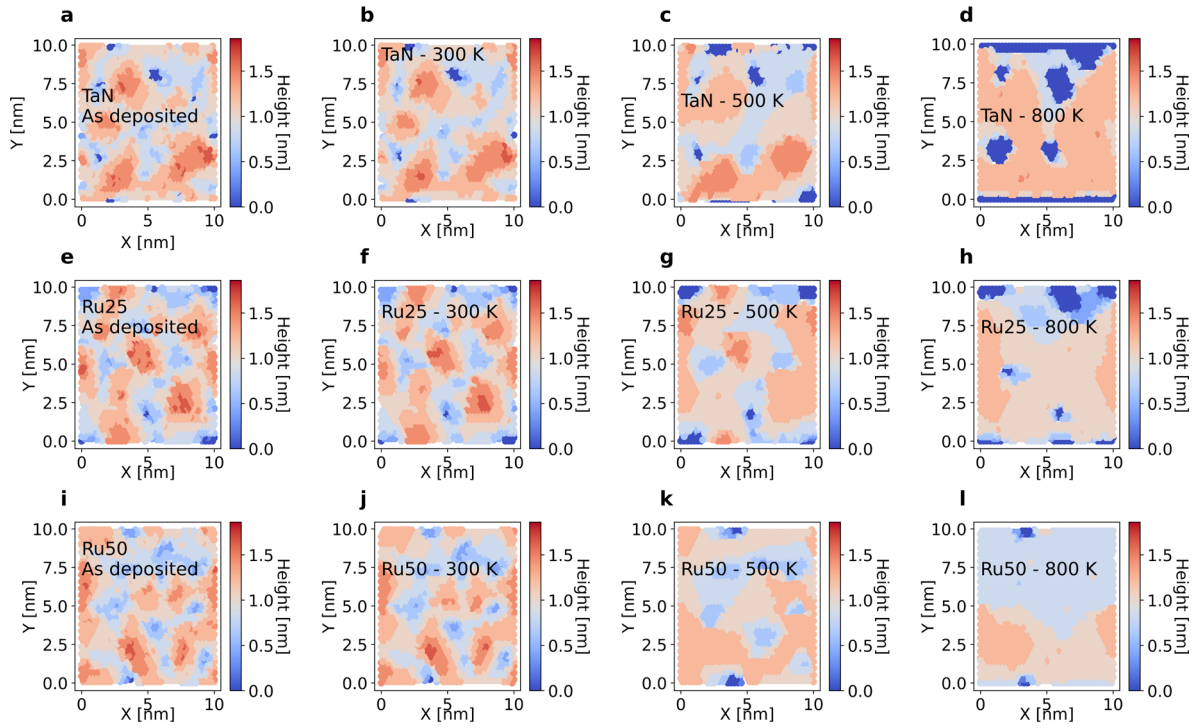

Figure S16: Height color maps of deposited Cu employing a partial pressure of P=0.5 Pa. Rows are different substrates: TaN (a, b, c, d), Ru25 (e, f, g, h) and Ru50 (i, j, k, l). First column represent the film deposited at 500 K for the different substrates, while the other columns are the layer surfaces annealed at varying temperature: 300 K (b, f, j), 500 K (c, g, k) and 800 K (d, h, l).

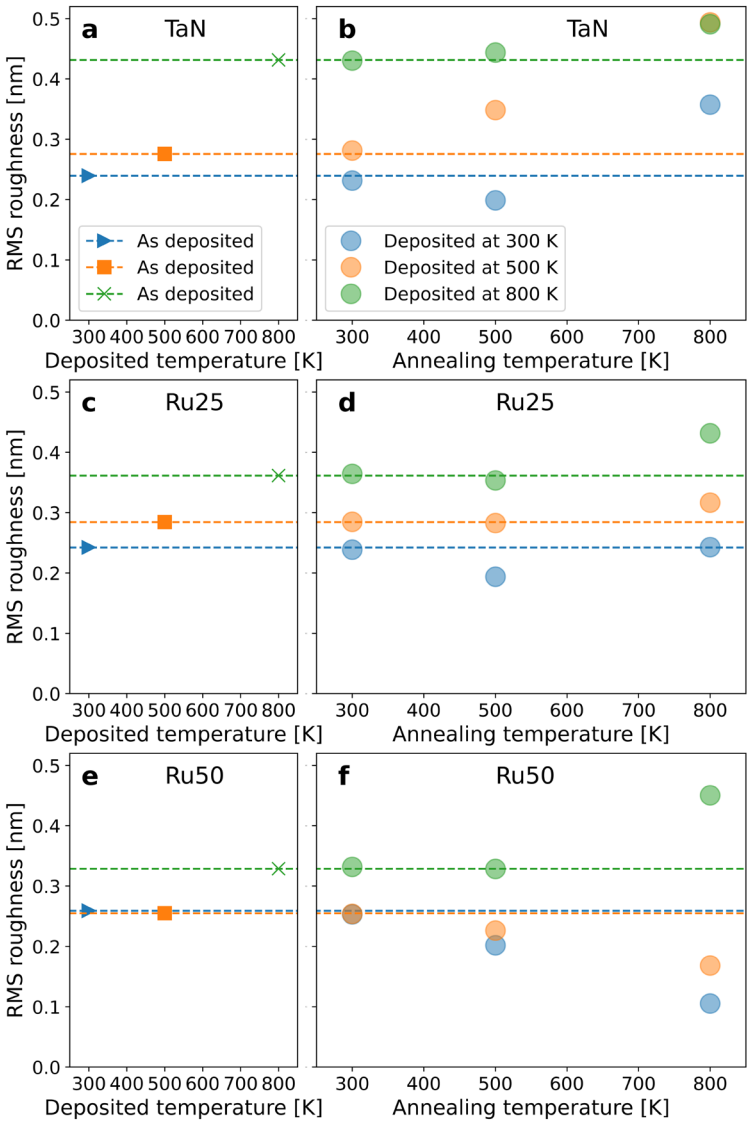

Figure S17: RMS roughness of Cu films deposited at a partial pressure of P=0.5 Pa, with deposition (a, c, e) and annealing temperatures (b, d, f) of 300 K, 500 K and 800 K. The roughness of Cu films on TaN as deposited (a) and after annealing (b). The roughness of Cu films on Ru25 as deposited (c) and after annealing (d). The roughness of Cu films on Ru50 as deposited (e) and after annealing (f). Orange symbols correspond to the simulations in Figure S14 and S15. Horizontal dashed lines indicate reference values for the as-deposited films. Y-axes in the same row have the same scale and labels.

References

(1) Nies, C.-L.; Natarajan, S. K.; Nolan, M. Control of the Cu Morphology on Ru-Passivated and Ru-Doped TaN Surfaces – Promoting Growth of 2D Conducting Copper for CMOS Interconnects. *Chem. Sci.* **2022**, *13* (3), 713–725. https://doi.org/10.1039/D1SC04708F.

(2) Kim, S. Y.; Lee, I.-H.; Jun, S. Transition-Pathway Models of Atomic Diffusion on Fcc Metal Surfaces. II. Stepped Surfaces. *Phys. Rev. B* **2007**, *76* (24), 245408. https://doi.org/10.1103/PhysRevB.76.245408.