Electronic Supplementary Material (ESI) for Nanoscale Advances.

Supplementary File – Confined Pulsed Diffuse Layer Charging for Nanoscale Electrodeposition with an STM

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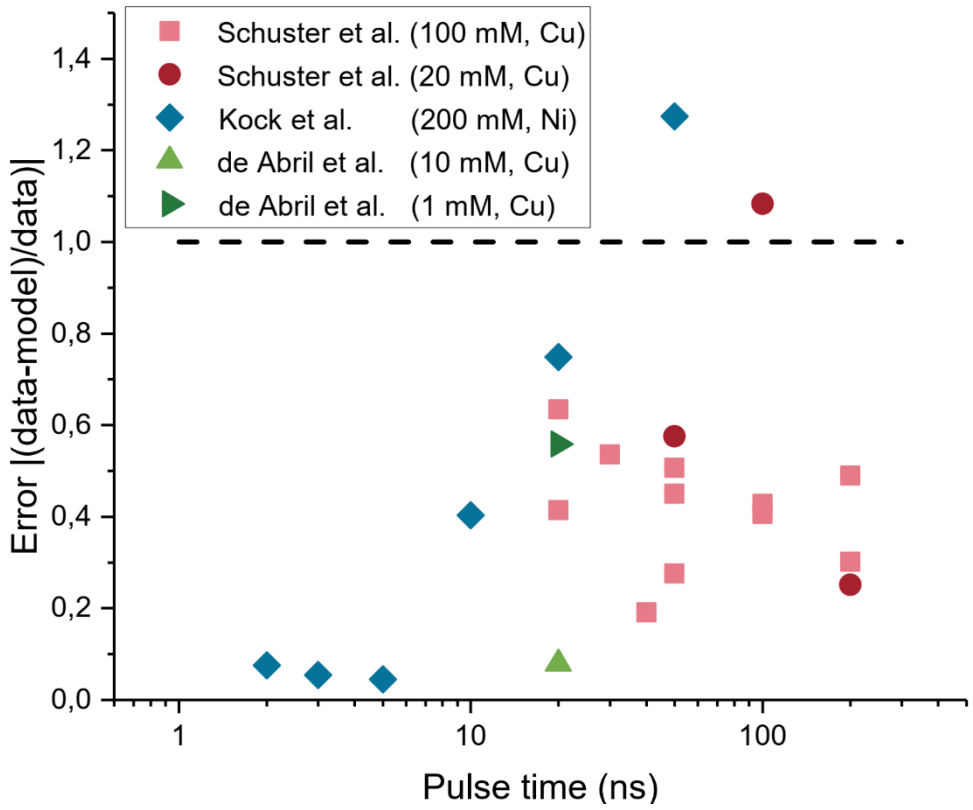
SI-1. Table of experimental parameters from literature.

	Schuster et al.[1]	Kock et al.[2]	De Abril et al.[3]
Material	Cu	Ni	Cu
Charge number	1.1 1.5	1	1 1
Tip/substrate potential (mV)	200/0 vs. Cu^{2+}	-5/-150 vs. Ag/AgCl	100/-100 vs. Cu^{2+}
Pulse Height (V)	1.6	2.2	3.2
pH	1 2	1	2 3
Concentration (M)	0.1 0.02	0.2	0.01 0.001
E_{ox} substrate (mV)	0 vs. Cu^{2+}	-150 vs. Ag/AgCl	0 vs. Cu^{2+}
E_{red} tip (mV)	-400 vs. Cu^{2+} -460 vs. Cu^{2+}	-290 vs. Ag/AgCl	-460 vs. Cu^{2+} -520 vs. Cu^{2+}
Required potential (mV)	600 660	285	660 720
α	0.47 0.53	0.14	0.23 0.255

Parameters used to obtain the predicted extent of the etching reaction as shown in the main text in Fig 3, using Eq. 2 in the main text. Parameters used to calculate α and λ_D are included. As all works considered use (acidic) aqueous electrolytes, a dielectric constant $\varepsilon = 80.1$ and the diffusion constant of protons $D = 1e^{-8}$ m^2/s are used [4].

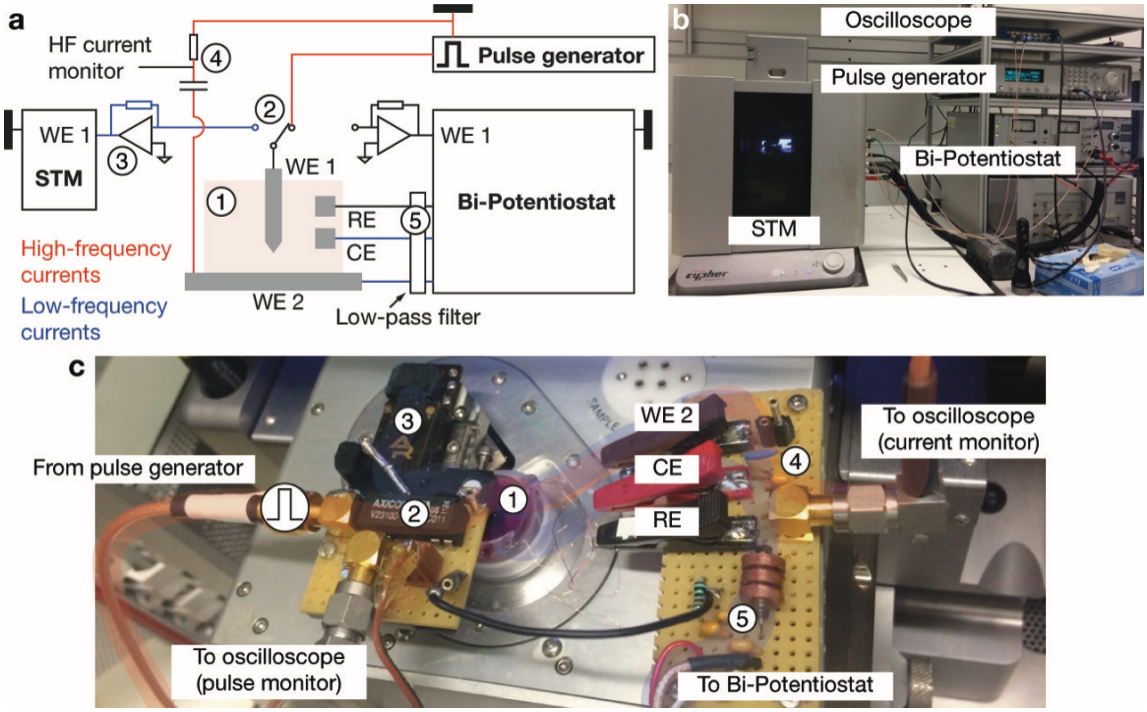
SI-2 Relative error between model prediction and literature etching data



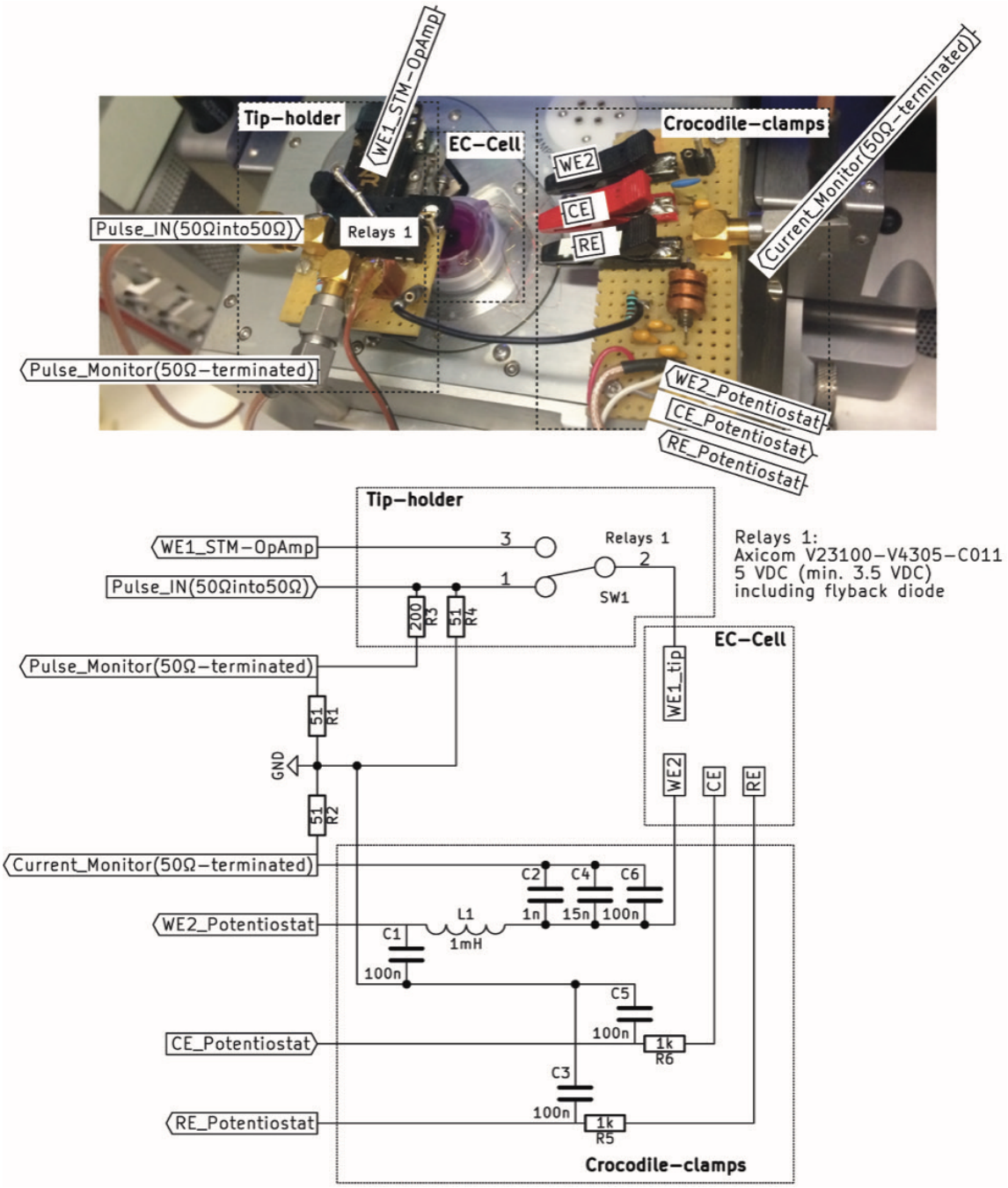
Supplementary figure 2-1: Relative error between the data shown in Figure 3 in the main text, and the model prediction. The relative error is calculated as |(data-model)/data|. The dashed line at 1 indicates a relative error of 1, or a factor 2. The model is within ~< 50% relative error for all data points.

SI-3 Experimental setup for the electrochemical scanning tunneling microscope.

The setup operates in two distinct modes that cannot run simultaneously: the feedback mode and the pulse mode. In feedback mode, the STM tip is connected to the input of the STM current amplifier. This enables monitoring of the tunneling current and hence precise positioning of the tip. The tunneling voltage is equal to the surface potential of the tip (Working electrode 1, WE1) and the surface potential of the substrate (WE2). In pulse mode, the tip is routed to the output of the pulse generator, so that voltage pulses can be applied to the tip. A mechanical relay switch switches the electrical connection of the tip between the STM current input and the pulse generator. In either position of the switch, the potential of the tip is that of measurement ground.
The current circuits for low-, and high-frequency currents (blue and red paths, respectively, in SI 2-1) are separated by appropriate high- and low-pass filters (SI 2-2). The low-frequency currents, representing global faradaic reactions, flow between the counter electrode (CE) and the tip (WE1) or the substrate (WE2). The high-frequency current flows from the pulse generator through the tip into the substrate and subsequently across a capacitance (high-pass filter) to ground. In order to minimize the interference of these two circuits, low-pass filters are connected to RE, CE and WE2 in series (SI 2-2).

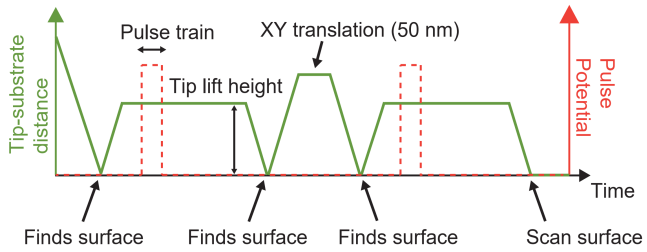


Supplementary figure 3-1: a) Schematic representation of the home-built setup. **b)** Corresponding photographs of the three sub-systems that were joined. **c)** The electrochemical cell with corresponding STM and filter electronics. The STM tip (WE 1) and substrate (WE 2) are immersed in the electrolyte solution contained in the electrochemical cell (1). The surface potentials of WE 1 and 2 are controlled by the bi-potentiostat. The electrical connections are shown in **a)** and **c)**. The tip is either connected to the current input of the STM (3) or the output of the pulse generator and is switched between the two with a mechanical relay (2). A high-pass filter (4) and low-pass filters (5) separate the high-frequency (red) and the low-frequency (blue) current circuits.



Supplementary figure 3-2: Circuit diagram of the electronic components that couple the nanosecond pulses into the electrochemical cell and separate the high- and low-frequency currents. Main in- and outputs as well as some key components are labelled in the photograph.

SI-4. Illustration for the deposition protocol



Supplementary figure 4-1 : Illustration of the tip position (left axis, green solid) during the deposition protocol as used for pulsed potential (right axis, red dashed) experiments in Figure 6 and 7 in the main text. The STM tip is approached to the surface and then i) lifted by a specified lift height, ii) kept at this height, after which a pulse train is sent, iii) the tip is approached to the surface again, iv) the tip is lifted and moves to the next location (50 nm apart for the experiments conducted here), v) the tip is approached to the sample again, after which the sequence is repeated. The lift height is typically maintained for a period of ~ seconds, i.e. much longer than the duration of the pulse train. The cartoon shows the deposition sequence for 2 locations, for the experiments described in the main text this process is repeated for 10 locations spaced 50 nm apart in a line.

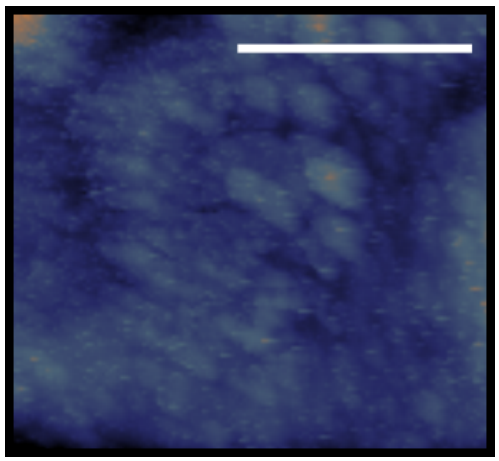
Supplementary table 4-2 : Experimental parameters used for the experiments in Figures 6 and 7 in the main text, and SI-7 and SI-8.

Data	Tip potential vs Au QRE (mV)	Substrate potential vs Au QRE (mV)	Pulse height ON/OFF (V)	Amount of pulses per pulse train
Figure 6, orange circles	-700	-900	2.5/0	10.000
Figure 6, purple diamonds	-850	-1050	2.5/0	10.000
Figure 6, red squares	-700	-900	2.5/0	10.000
Figure 7	-500	-700	5/1	2000
SI-7	-800	-1000	2.5/0	10.000
SI-8	-500	-700	5/1	Varied

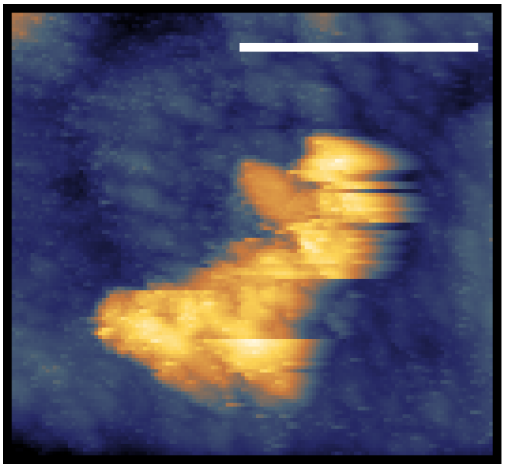
SI-5. STM topography images of deposition sequences.

Images used for the orange circle datapoints in figure 4 in the main text. Scale bar 500 nm.

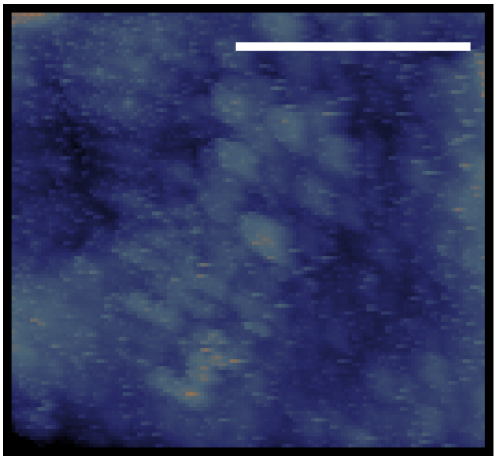
Lift Height (Lift) 10 nm; Pulse width (Pulse) 60 ns



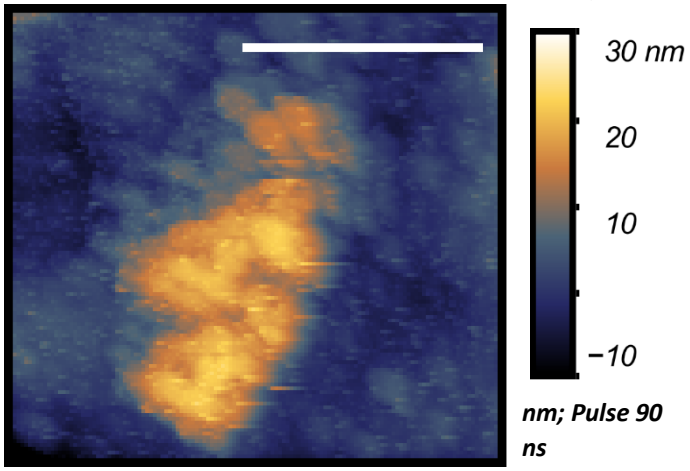
Lift 10 nm; Pulse 70 ns



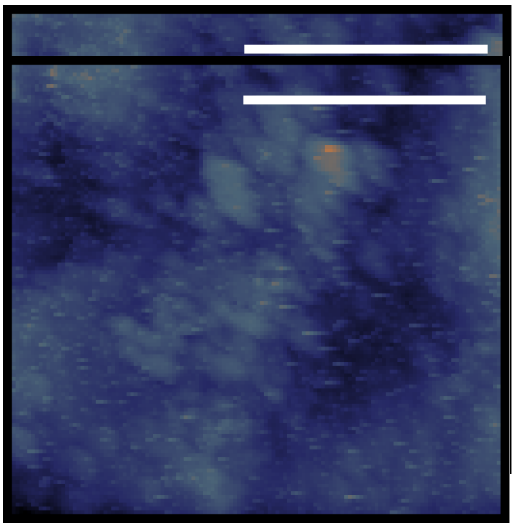
Lift 20 nm; Pulse 80 ns



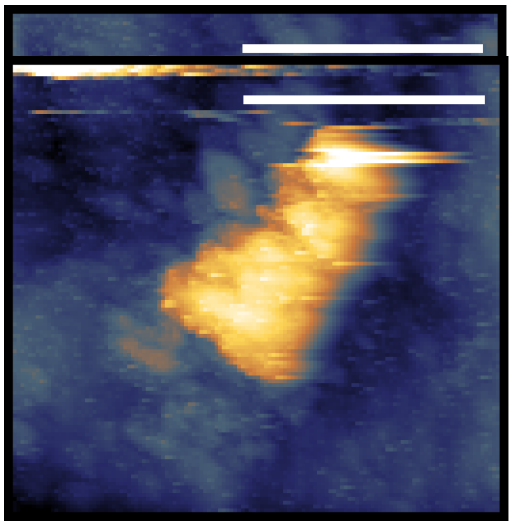
Lift 20 nm; Pulse 90 ns



Lift 30 nm; Pulse 100 ns



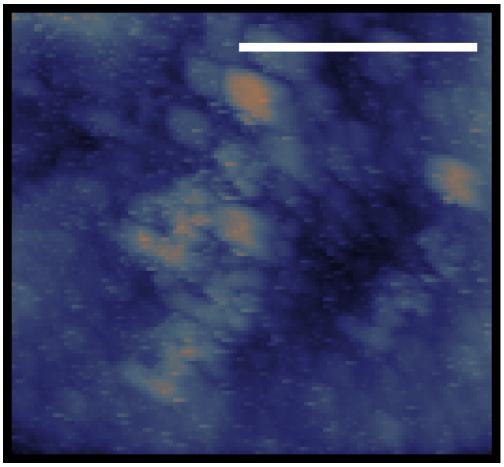
Lift 30 nm; Pulse 110 ns



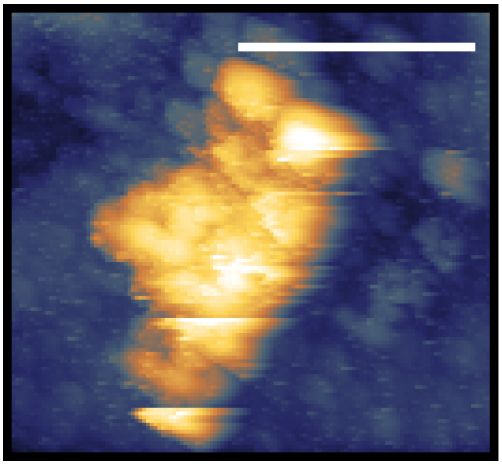
Lift 40 nm; Pulse 110 ns

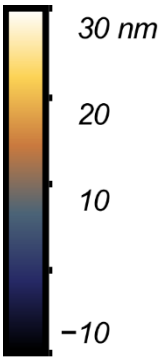
Lift 40 nm; Pulse 120 ns

Lift 50 nm; Pulse 140 ns

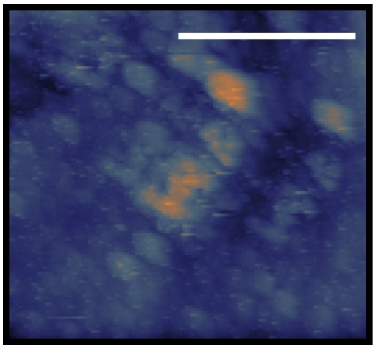


Lift 50 nm; Pulse 150 ns

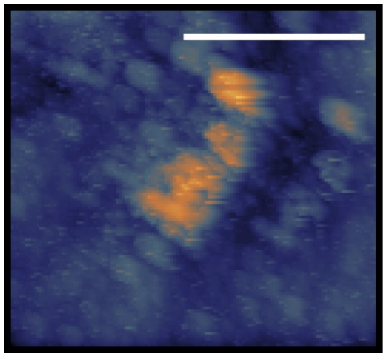




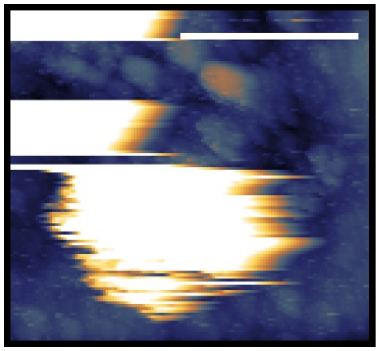
Lift 70 nm; Pulse 170 ns



Lift 70 nm; Pulse 180 ns

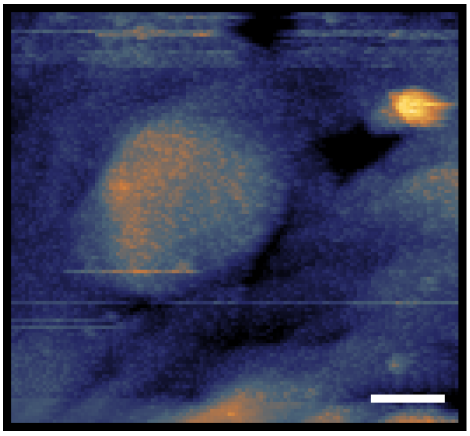


Lift 70 nm; Pulse 190 ns

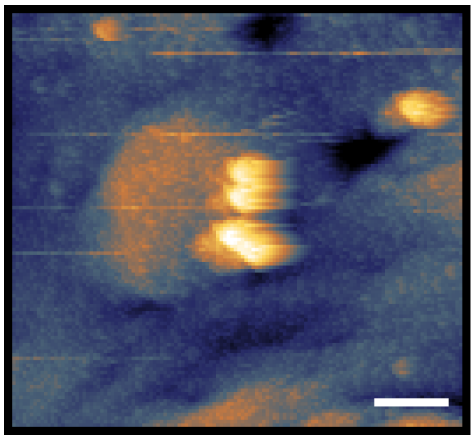


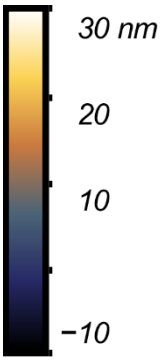
Images used for the purple diamond datapoints in figure 4 in the main text. Scale bar 500 nm.

Lift 20 nm; Pulse 200 ns

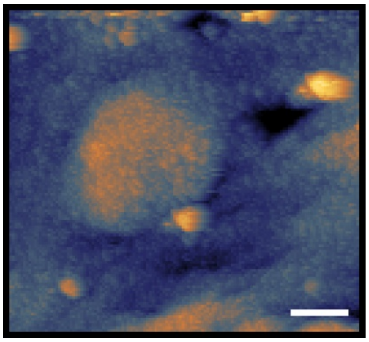


Lift 20 nm; Pulse 250 ns

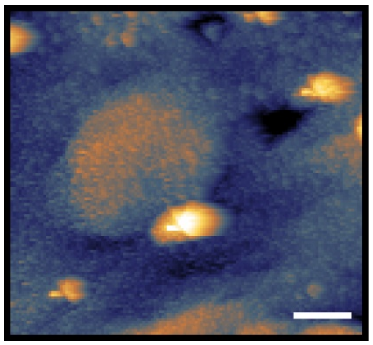




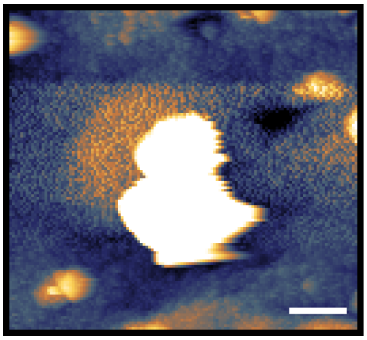
Lift 50 nm; Pulse 300 ns



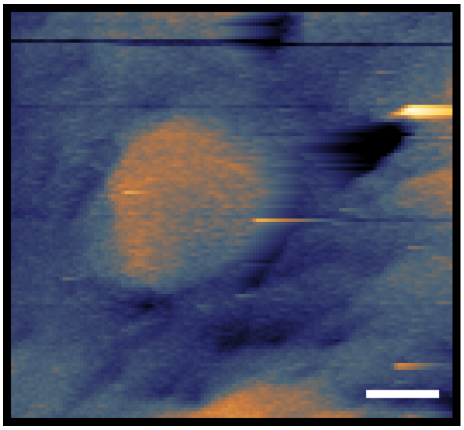
Lift 50 nm; Pulse 350 ns



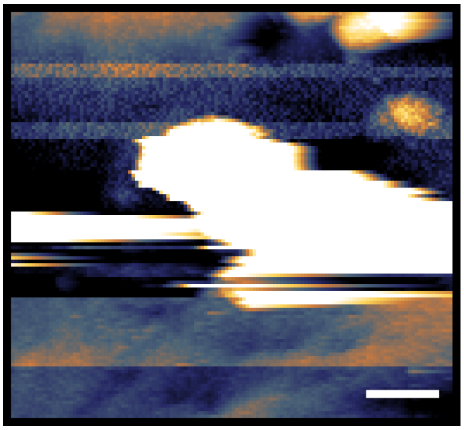
Lift 50 nm; Pulse 400 ns



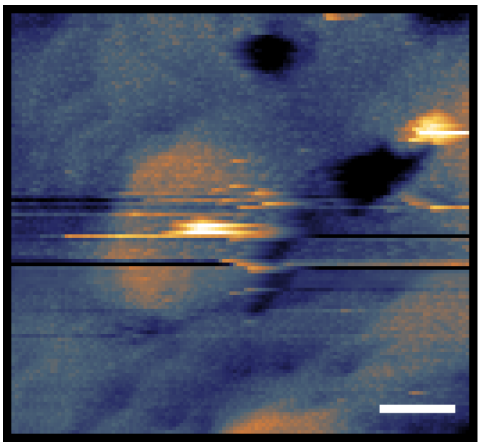
Lift 100 nm; Pulse 650 ns



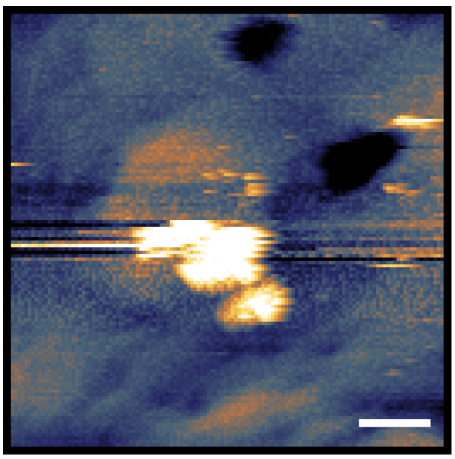
Lift 100 nm; Pulse 700 ns



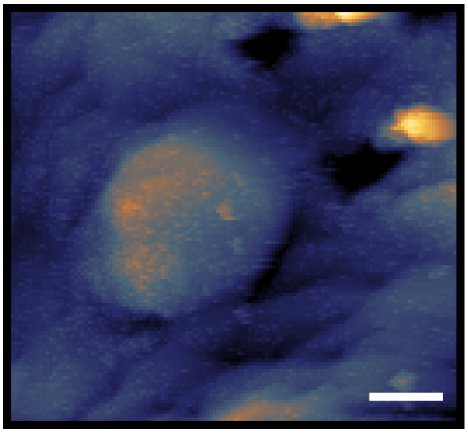
Lift 150 nm; Pulse 950 ns



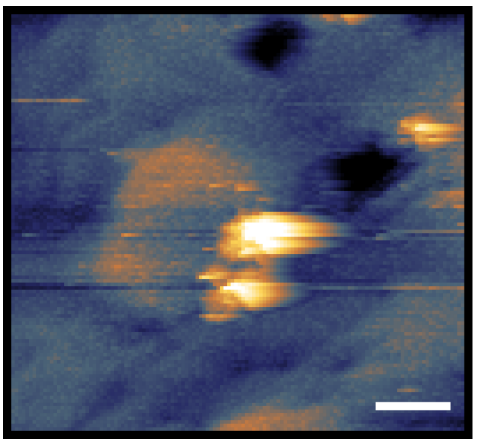
Lift 150 nm; Pulse 1000 ns



Lift 200 nm; Pulse 1150 ns

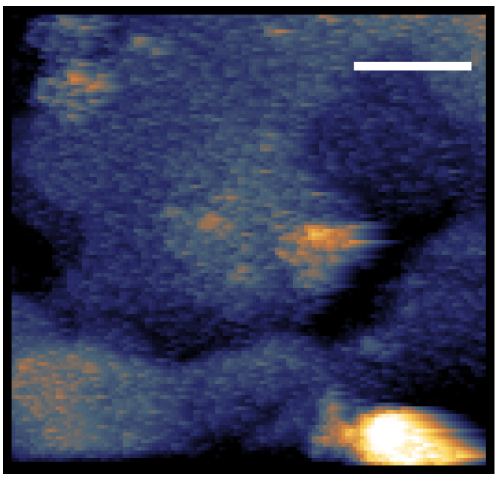


Lift 200 nm; Pulse 1200 ns

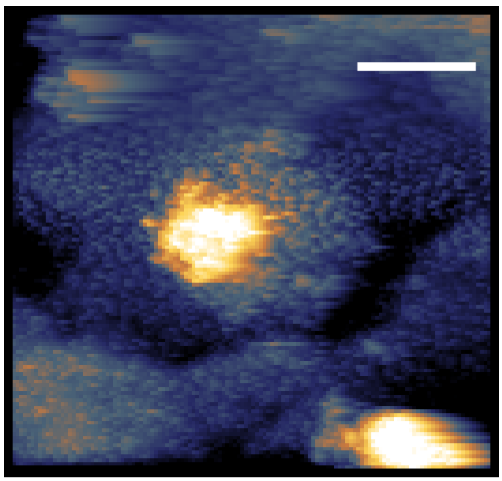


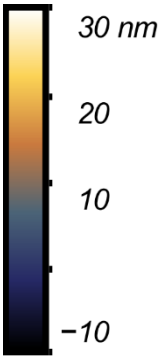
Images used for the red square datapoints in figure 4 in the main text. Scale bar 500 nm.

Lift 10 nm; Pulse 250 ns

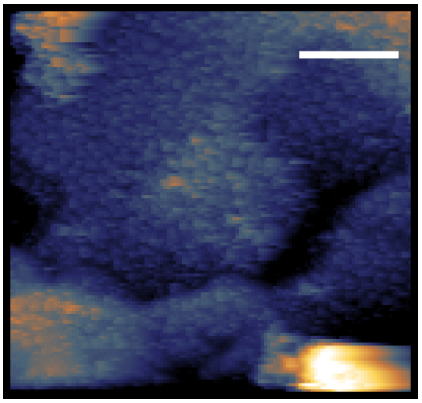


Lift 10 nm; Pulse 300 ns

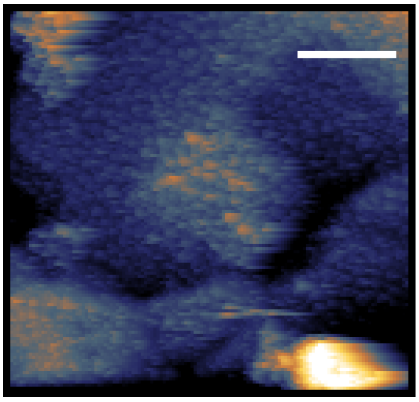




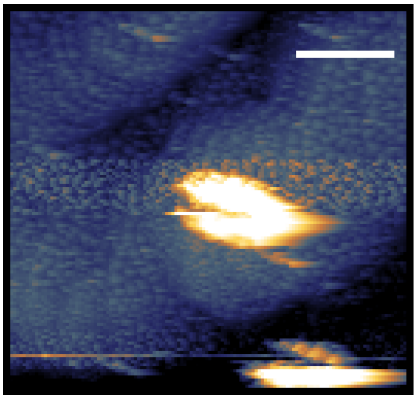
Lift 20 nm; Pulse 300 ns



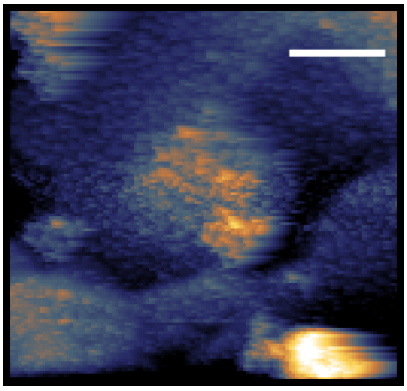
Lift 20 nm; Pulse 350 ns



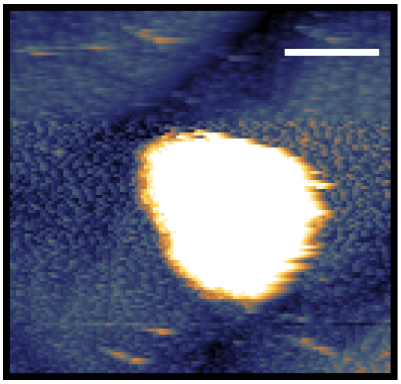
Lift 20 nm; Pulse 350 ns



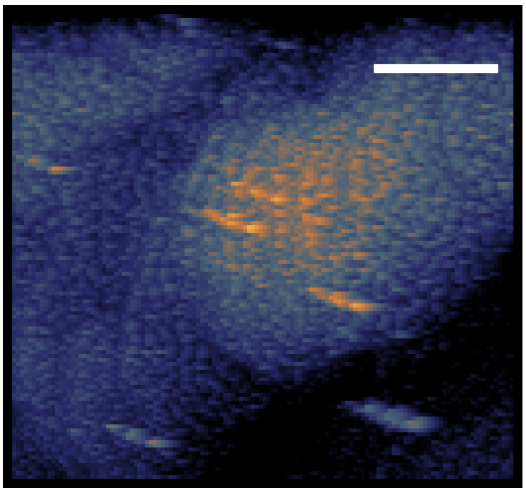
Lift 20 nm; Pulse 400 ns



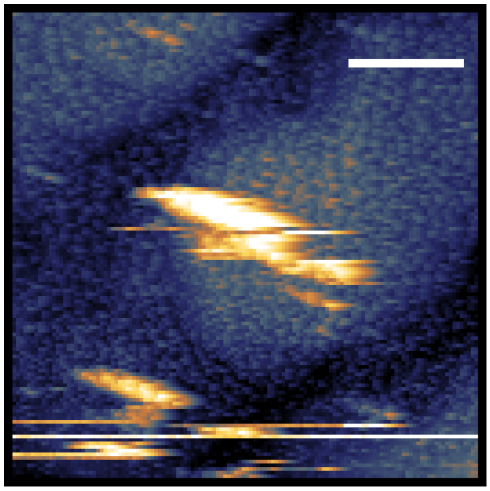
Lift 20 nm; Pulse 400 ns



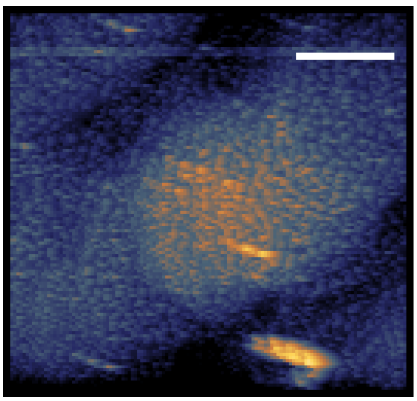
Lift 50 nm; Pulse 550 ns



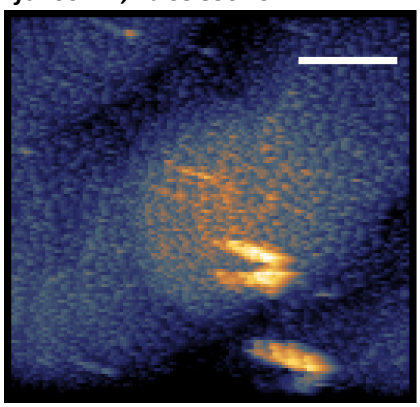
Lift 50 nm; Pulse 600 ns



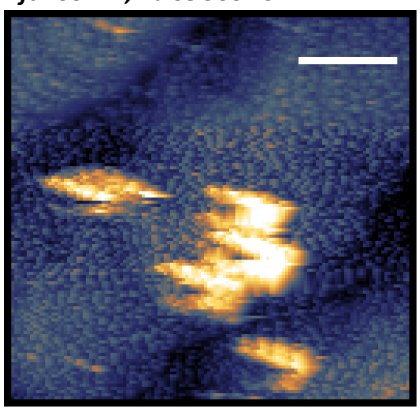
Lift 100 nm; Pulse 800 ns



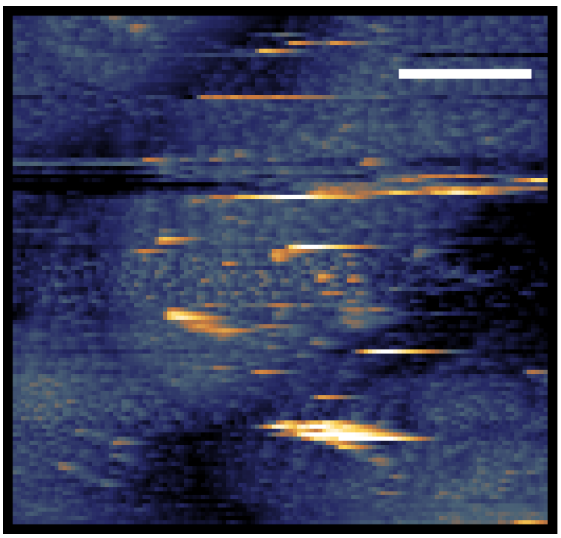
Lift 100 nm; Pulse 850 ns



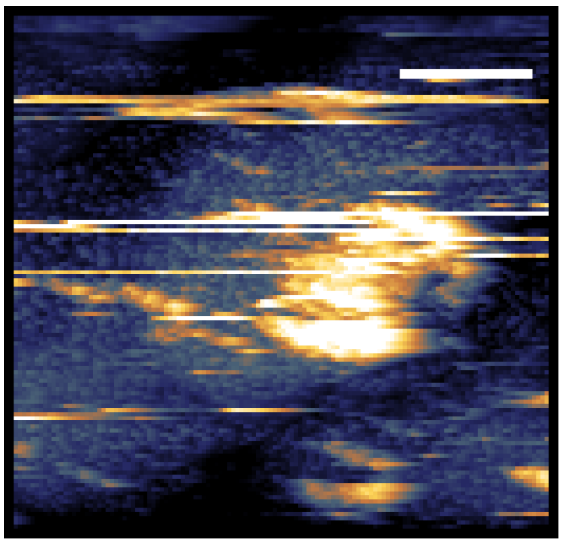
Lift 100 nm; Pulse 900 ns



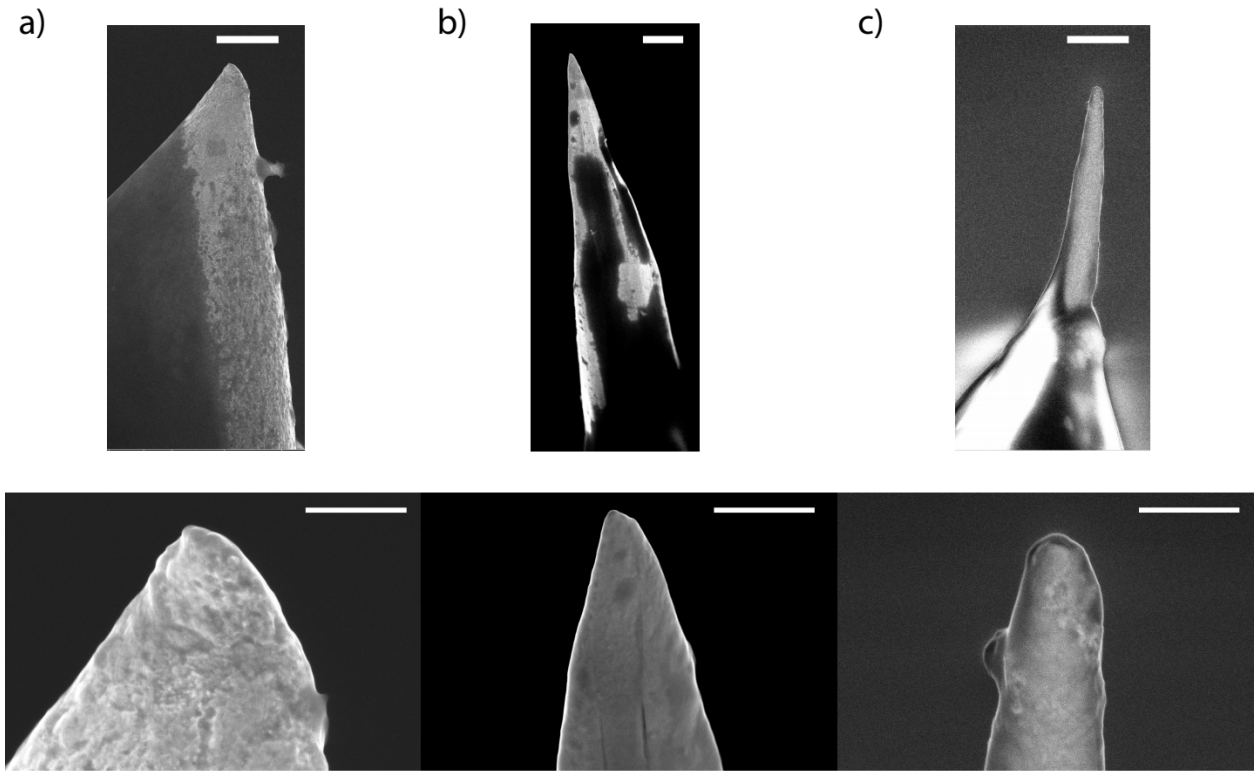
Lift 150 nm; Pulse 1350 ns



Lift 150 nm; Pulse 1400 ns



SI-6. SEM images of STM tips.

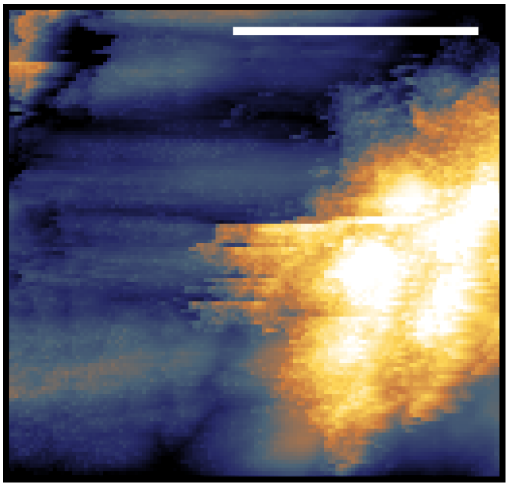


Supplementary figure 6-1: SEM images of the STM tips used for Fig. 5 in the main text. Used for data **a)** orange circles **b)** purple diamonds **c)** red squares. The scale bar is 2 µm in the top images, and 500 nm in the bottom images.

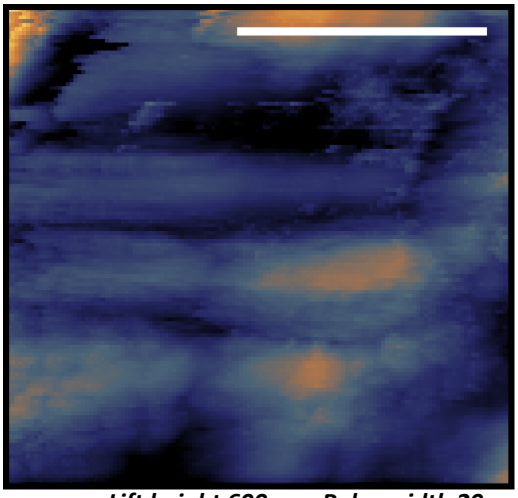
SI-7. Deposition from aqueous electrolyte (50 mM $CoSO_4$)

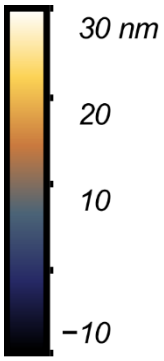
Deposition sequence done in an aqueous solution (50 mM $CoSO_4$). The tip/substrate rest potentials were -800/1000 mV vs. Au quasi reference electrode. The pulse train consisted of 10^4, 2.5 V pulses (OFF value 0 V), with period 10 µs. The scale bar is 500 nm in all images.

Lift height 200 nm; Pulse width 10 ns

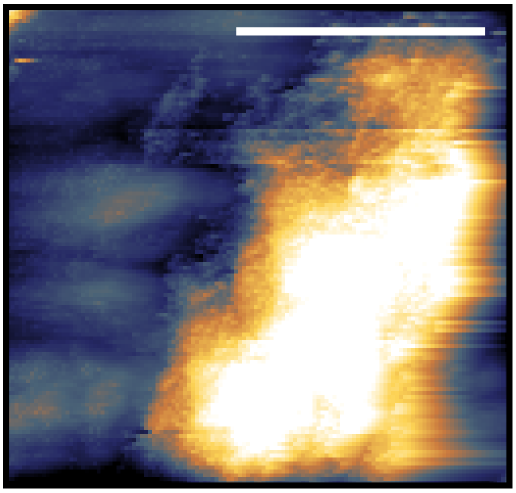


Lift height 400 nm; Pulse width 10 ns

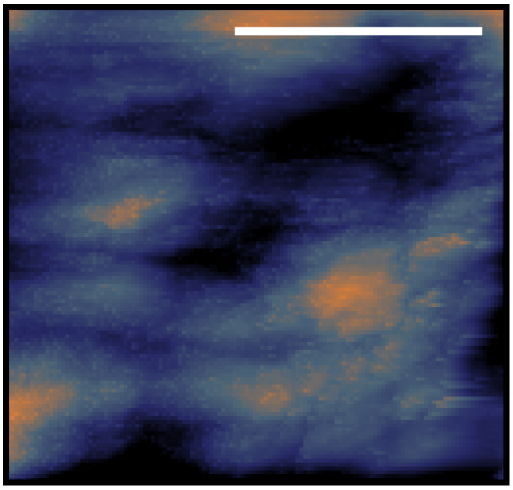




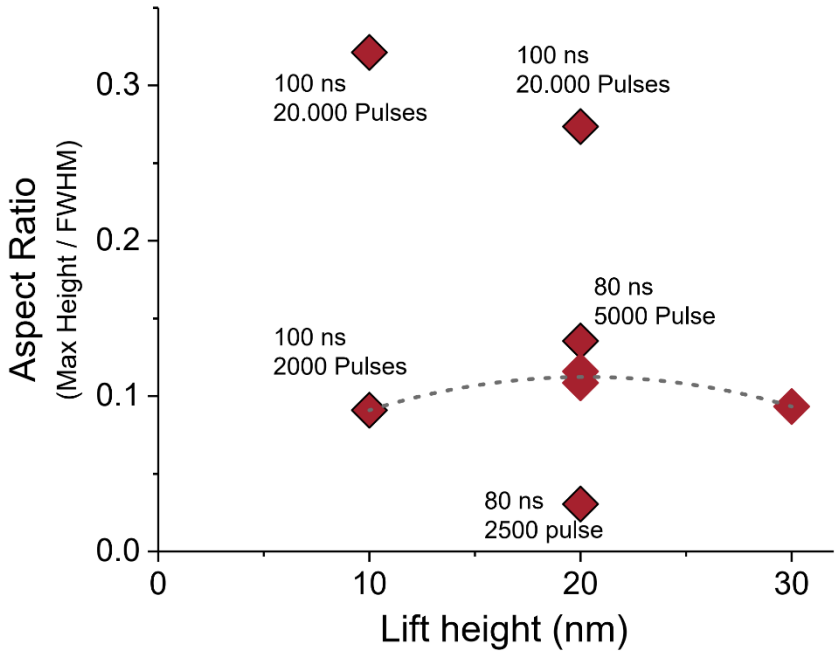
Lift height 500 nm; Pulse width 20 ns



Lift height 600 nm; Pulse width 20 ns



SI-8. Aspect ratio of written lines for various conditions



Supplementary figure 8-1: Changing aspect ratio of written lines taken as the maximum height divided by the full width at half maximum (FWHM) for different conditions. The 4 datapoints connected by the grey dashed curve have the same pulse parameters (100 ns, 2000 pulses). The writing routine and all other parameters are the same as for the lines shown in Figure 6a in the main text (5 V pulses, OFF 1 V, 10 µs period, tip/sample potential -500/-700 mV vs. Au QRE).

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