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Supplementary Information

Local surface modification via confined electrochemical deposition with FluidFM

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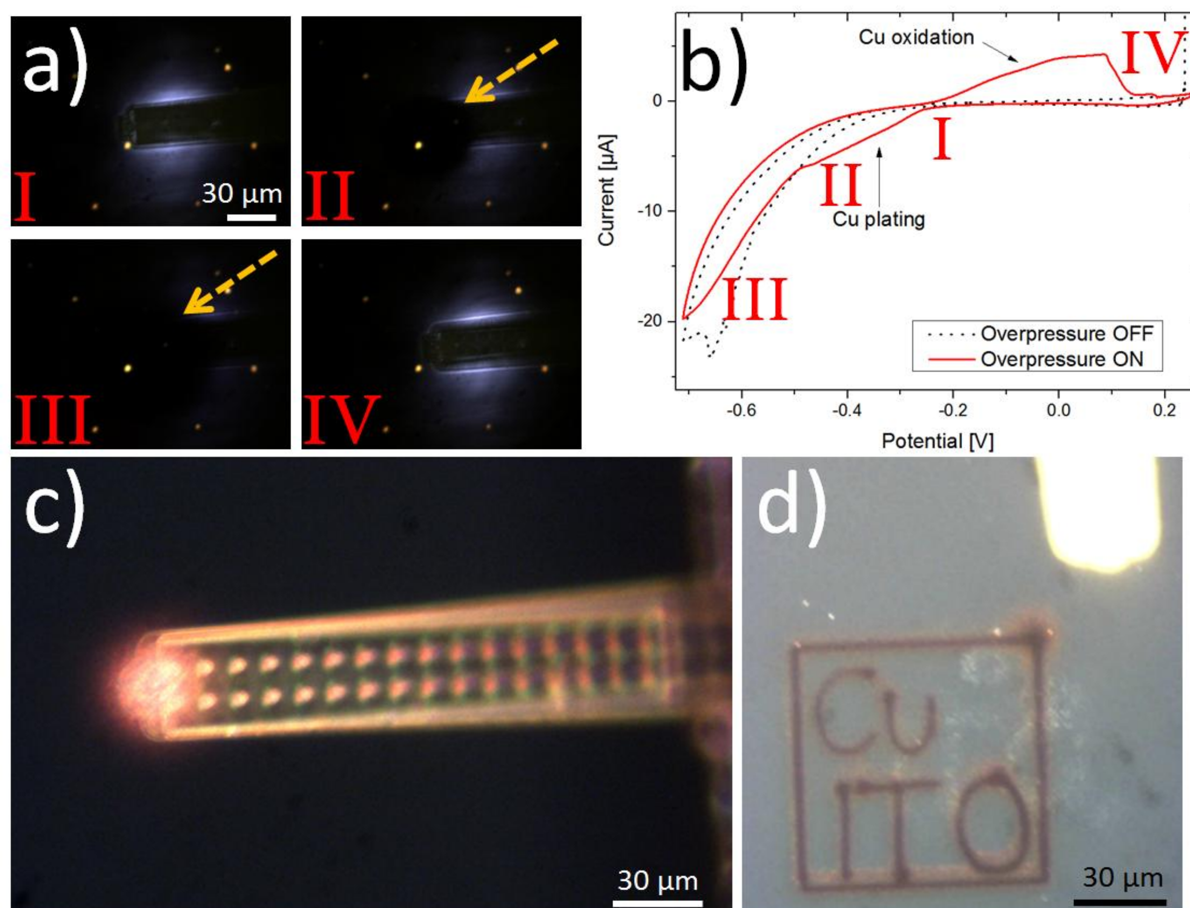

Figure S1: Demonstration of macro-scale localized copper electroplating on gold and ITO substrates under tipless 8 µm aperture FluidFM probes. a) Optical micrographs during a preliminary study of Cu deposition on semi-transparent gold substrates in our system. The potential was ramped from open circuit potential (OCP, 0.23 V) to -0.7 V while a large overpressure was applied by means of a syringe. At potentials below -0.2 V, the formation of a copper deposit (dark spot indicated by orange arrows) could be observed under the microscope, obscuring the cantilever. The deposit dissolved again at more oxidizing potentials during the returning sweep. Roman numerals indicate time point of each frame in b). b) Cyclic voltammogram recorded during the deposition and dissolution. During the first cycle (dashed line), no pressure was applied and no Cu plating could be observed under the microscope nor in the CV. During the second cycle (red line), a large overpressure was applied and the Cu plating

reaction was observed, accompanied by current shoulders for the reduction and the re-oxidation. Sweep rate: 20 mV s^{-1}. The disturbance in the first cycle likely stems from electrode contamination.

c) and d) Preliminary study of metal patterning on ITO electrodes. A reducing potential of -1.8 V vs. a Pt electrode and a high overpressure of 500 mbar were applied, resulting in large spots and lines of copper that could be immediately observed under the microscope.

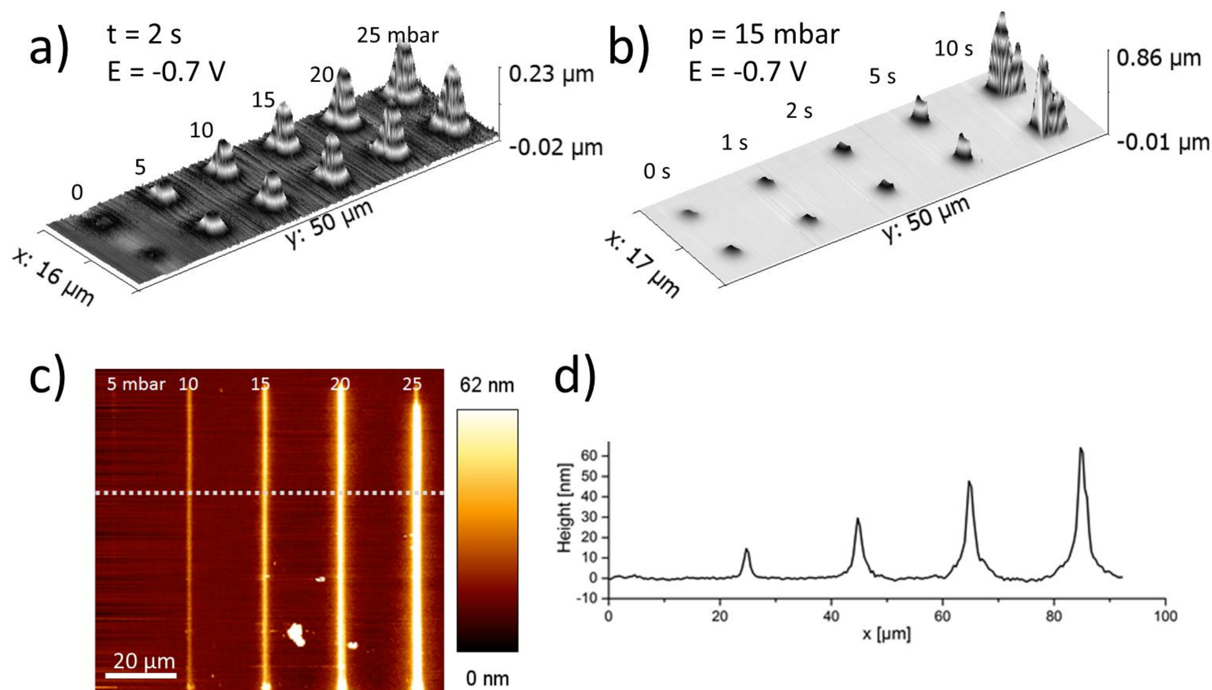

Figure S2: Influence of pressure and deposition time on deposits. a) 3D AFM image demonstrating the influence of applied pressure on copper deposit size. For all spots shown, the probe was approached to the substrate for 2 seconds at -0.7 V vs. Ag QRE while the pressure was increased from 0 mbar to 25 mbar for every additional pair of spots. The spots have a height of up to 230 nm, the spot size growing with the applied pressure. b) 3D AFM image of spots created for various deposition times. Here, the pressure was held constant at 15 mbar and the probe was sequentially approached to the substrate for increasing deposition times between 0 s (immediate retraction) and 10 s. c) AFM image of Cu line patterns on Au generated for different pressures. Probe speed was 5 µm s^{-1}, deposition potential -0.7 V, setpoint 20 nN. d) Height profile for the dashed line in c).

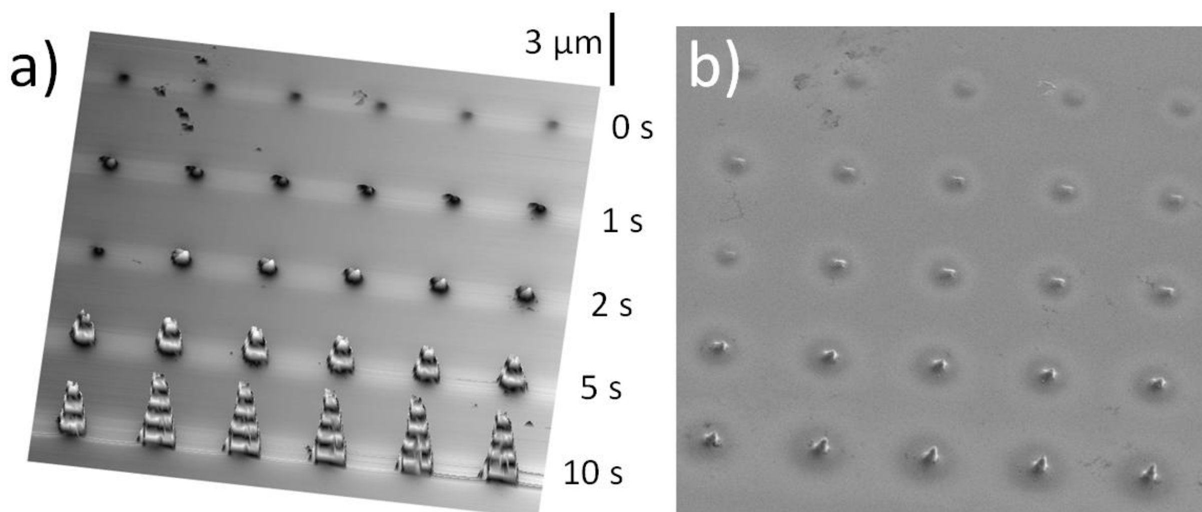

Figure S3: Array of copper metal deposits created for different deposition times with active force feedback switched on during the deposition. The deposition times were 0, 1, 2, 5, 10 s for each line from the top to the bottom, respectively. Deposition parameters: -0.6 V, 15 mbar. a) *In-situ* AFM image of the spots taken immediately after deposition. Image size 100 × 100 μm^2. b) *Ex-situ* SEM image of the dry sample.