

Supplementary Material

Supplementary discussion

Here we present topography images associated with the current images shown in the manuscript, as well as some secondary ion mass spectroscopy (SIMS) measurements made on SiO_x films following electrical stressing with CAFM. We did not observe significant damage to the probe or sample, other than when we applied high currents (tens of nA, Figure S7). In the context of voltage spiking, such currents are significantly higher than those required to reach the maximum value of S_{ps} (250 pA). Thus, such large features correspond to the device being pushed beyond useful functionality. Otherwise, we observe a small (few nm in height) structural changes, such as small bumps (Figure S6 and Figure S7), and smoothing of the topography (Figure S1 and Figure S5). Topographical smoothing indicates either that the sample has deformed or that the probe has blunted. However, we do not expect the latter of these to have played a significant role in our measurements, as the appearance of the unstressed SiO_x is generally consistent before and after electrical stress has been applied (Figure S3, Figure S6 and Figure S7), i.e. the probe condition is maintained. A possible cause of surface bumps is deposition of platinum from the probe onto the sample. However, we did not detect the presence of platinum on the sample surface or in the SiO_x layer following the application of up to 250 pA (Figure S8). We also note that the appearance of structural changes on the SiO_x surface is quite stochastic. In some cases, a few pA is sufficient to leave a residual feature (Figure S6), whereas in other cases, a current three orders of magnitude greater, 5 nA, causes no apparent change to the sample (Figure S7). Furthermore, these features can disappear over time (Figure S5 and Figure S6). We therefore expect that the observed surface changes indicate deformation of the SiO_x and/or molybdenum as a result of electrical stress, as discussed extensively in the literature, or charging artefacts.

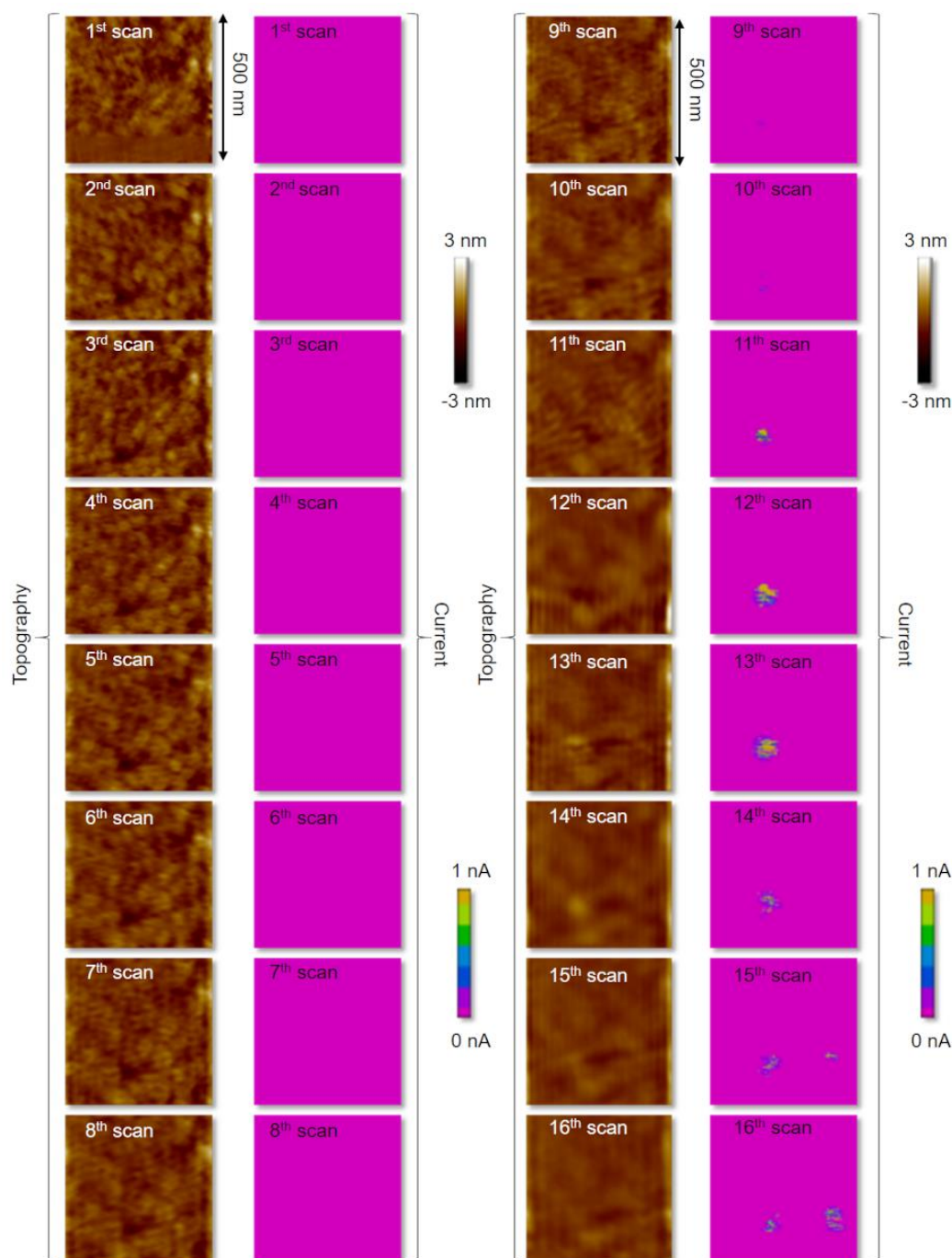


Figure S1. Full set of topography and current maps for the measurement presented in Figure 1 of the manuscript, when scanning at a constant bias of 7.7 V. The topography becomes gradually smoother, indicating either that the probe has become blunt or that the SiO_x surface has deformed under the electrical stress, although the probe condition is maintained (Figure 3) so we do not expect significant blunting to have occurred. The current maps demonstrate the gradual potentiation and depression of the left-hand filament, and the eventual beginning of the potentiation of the right-hand filament.

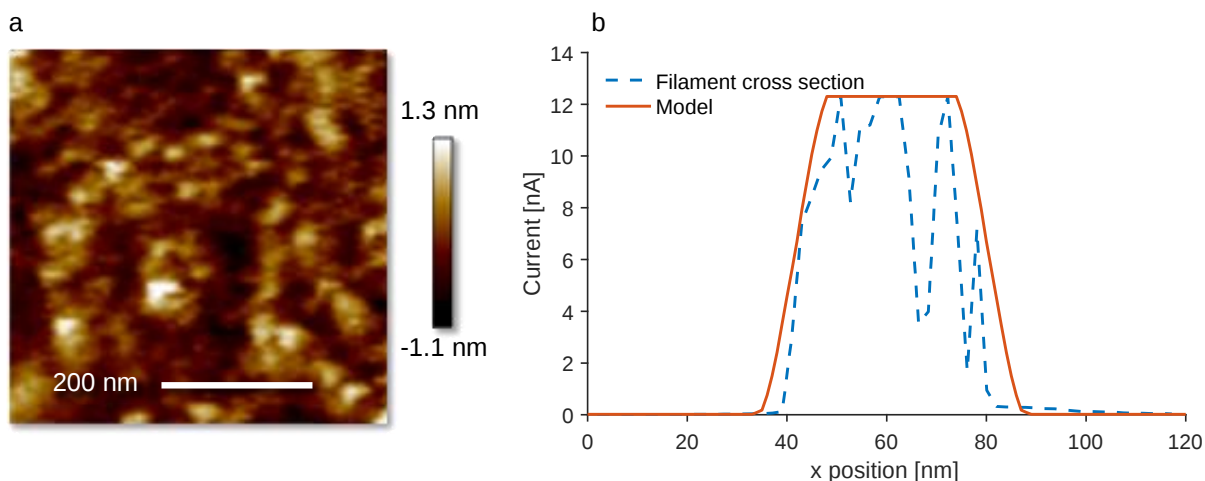


Figure S2. The methodology of estimating the filament width. a) Topography image of SiO_x taken following the measurements shown in Figure 1 of the manuscript. This image was used to estimate the width of the probe to be 40 nm, using Nanoscope Analysis. b) A cross section was taken from the 13th scan (as shown in Figure S1), through the left-hand filament, at its widest point, so as to avoid underestimating the width. A 1D overlap addition was then performed between a probe 40 nm in length and of magnitude 1, and a conductive feature, modeled as a line of length l and magnitude 1, to produce a convoluted trace. l was then varied and found to best fit the cross-sectional data when set to 14 nm. The fitted data were then scaled to the maximum current measured in the filament. We stress that this is an estimate, to give a rough idea of how wide a feature might be if we assume a linear edge convolution. Notably, the real convolution would not be linear due to the geometry of the probe apex and the nonlinearity of the dependence of the current on the contact area. We might therefore expect the real filament to be narrower than 14 nm, or to be composed of multiple narrower filaments. Additionally, the current reached saturation, so the feature plateaus, which likely further convolutes its width. The image in a) also serves as validation that the CAFM probe was still in good condition (i.e. not significantly blunted) following the measurements made in Figure 1 of the manuscript. This is because we are able to resolve features of a few tens of nm diameter, a similar size to the apex of a fresh the CAFM. However, we note that there may be a small tip artefact present, given the shape of the surface features of the SiO_x.

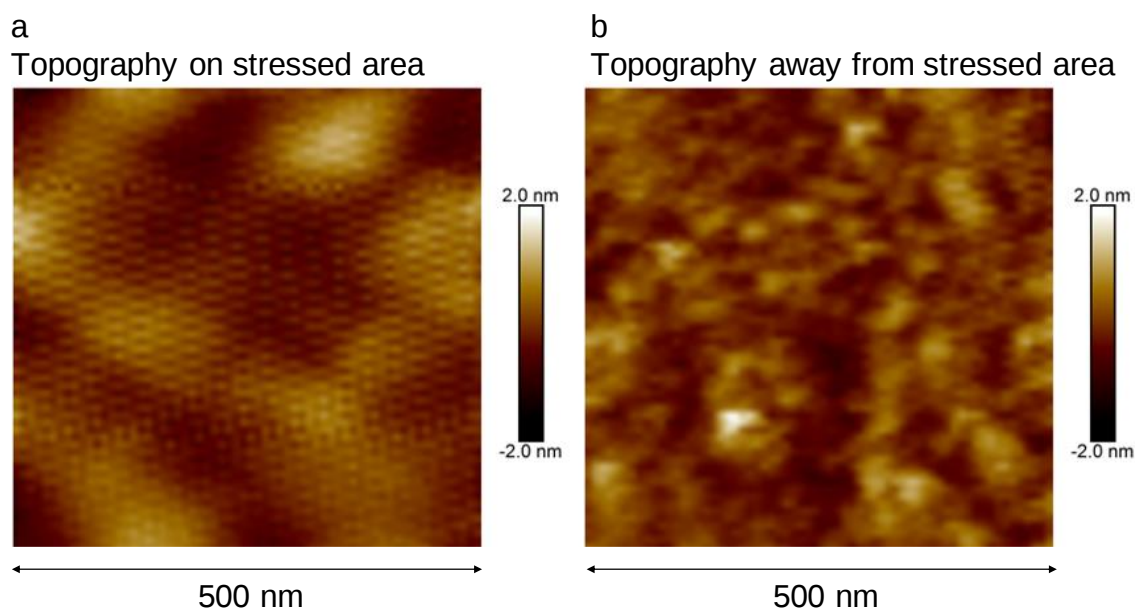


Figure S3. Topography scans demonstrating that the changing surface topography likely results from deformation of the SiO_x and/or molybdenum, rather than changes to the probe, such as blunting. a) Topography of the area scanned in Figure 1, Figure 2 and Figure 3 of the manuscript, showing that the sample surface is rather distorted. b) Topography scan of an unstressed region of SiO_x , using the same probe as in a, immediately after the stressing was completed (i.e. after image a was taken). The surface appears similar to other pristine areas shown in the Supplementary Information, for example in Figure S4 and Figure S5. Thus, we do not expect the probe to have become significantly blunted during electrical stressing, and so do not expect that deposition of platinum has played a significant role in our observations, although we cannot rule this out. More likely, we suppose that the SiO_x or molybdenum have deformed under electrical stress.

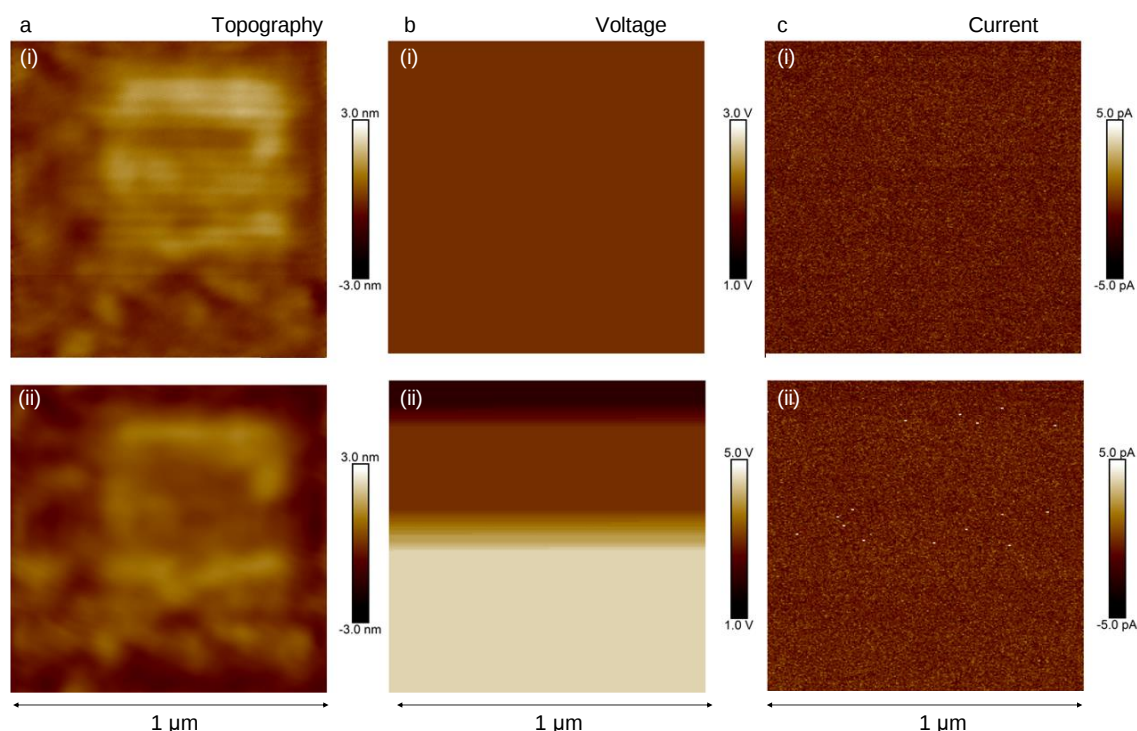


Figure S4. Two sets (i and ii) of topography (a), voltage (b) and current (c) scans taken on the region stressed in Figure 1, Figure 2 and Figure 3 of the manuscript, as well as Figure S5, demonstrating that voltages up to 5 V did not produce any measurable current. Note that there are some bright points in c (ii), corresponding to instrumental artefacts occurring when the applied voltage was changed.

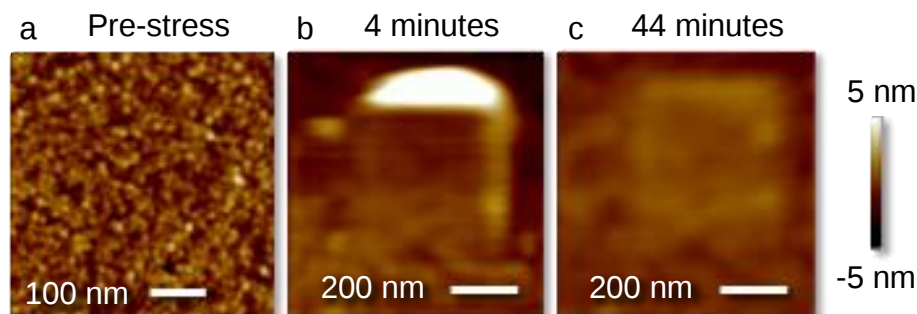


Figure S5. Topography of region scanned in Figure 1, Figure 2 and Figure 3 of the manuscript. a) Topography before any stress was applied, demonstrating the intrinsic structure of the SiO_x and sharpness of the CAFM probe. b) A wider view of the same region, following 16 scans at 7.7 V, with the bias reduced to 5.5 V. It is clear that the either the surface has become smoother, or the probe has become blunter. Given the observations made in Figure S3, it is more likely that the surface has changed.. There is also a tall (around 5 nm) feature in the upper portion of the scan area. This might be a charging artefact, or surface deformation resulting from the repeated passage of the probe over the scan area. c) The same region as in b, following 40 minutes of scanning at 5.5 V. The topography does not appear to have changed significantly, although the raised feature in the upper portion of the scan area has disappeared.

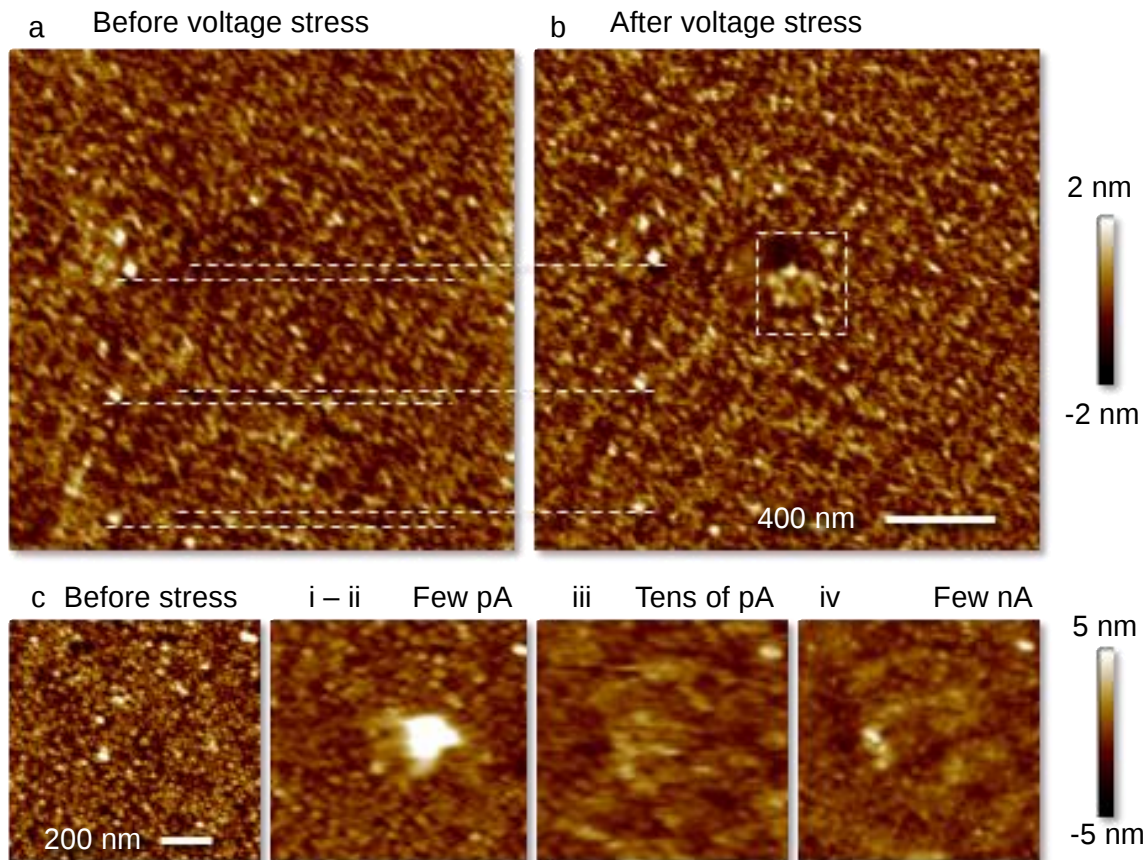


Figure S6. Topography of regions stressed in Figure 4 of the manuscript. a) and b) Topography before and after, respectively, the application of 4 V for around 1400 seconds, as shown in Figure 4a of the manuscript. We can see here that around 50 nm of drift has occurred during the scan, as indicated by the dashed white lines. This might have been a gradual process, due to the long duration of the measurement, in which case the time taken for the current to increase might be overestimated, as the contact location was constantly changing. Indeed, the current might only have begun to change more rapidly once a preferential filament formation location was reached. It is also possible that this occurred when the current sensitivity was changed at the end of the 1400 seconds, before imaging the stressed spot. Notably, when we changed the current sensitivity after the scan size was set to 0 nm, we observed jumps in the height and friction signals, indicating that the probe moved both vertically and laterally. Thus, the drift may have occurred before or after the electrical stress was applied, as the sensitivity was kept constant. There is also a slight surface deformation at the probe contact point, as indicated by the dashed white box, resulting from the electrical stress of 4 V and up to 12.3 nA. c) Topography images from the current maps shown in Figure 4b to d of the manuscript. The largest structural change is noted following a few pA of electrical stress. Subsequently, this feature disappears and there are no further large features present following a few nA of stress. The appearance of this feature on the SiO_x surface during these measurements likely indicates either a transient charging artefact surface deformation that relaxes over the course of the measurement. We do not expect them to correlate with material deposition from the probe, as the diameter of features that we are able to resolve around the contact point before and after the measurements is quite consistent, at a few tens of nm (i.e. a similar size to the apex of the CAFM probe).

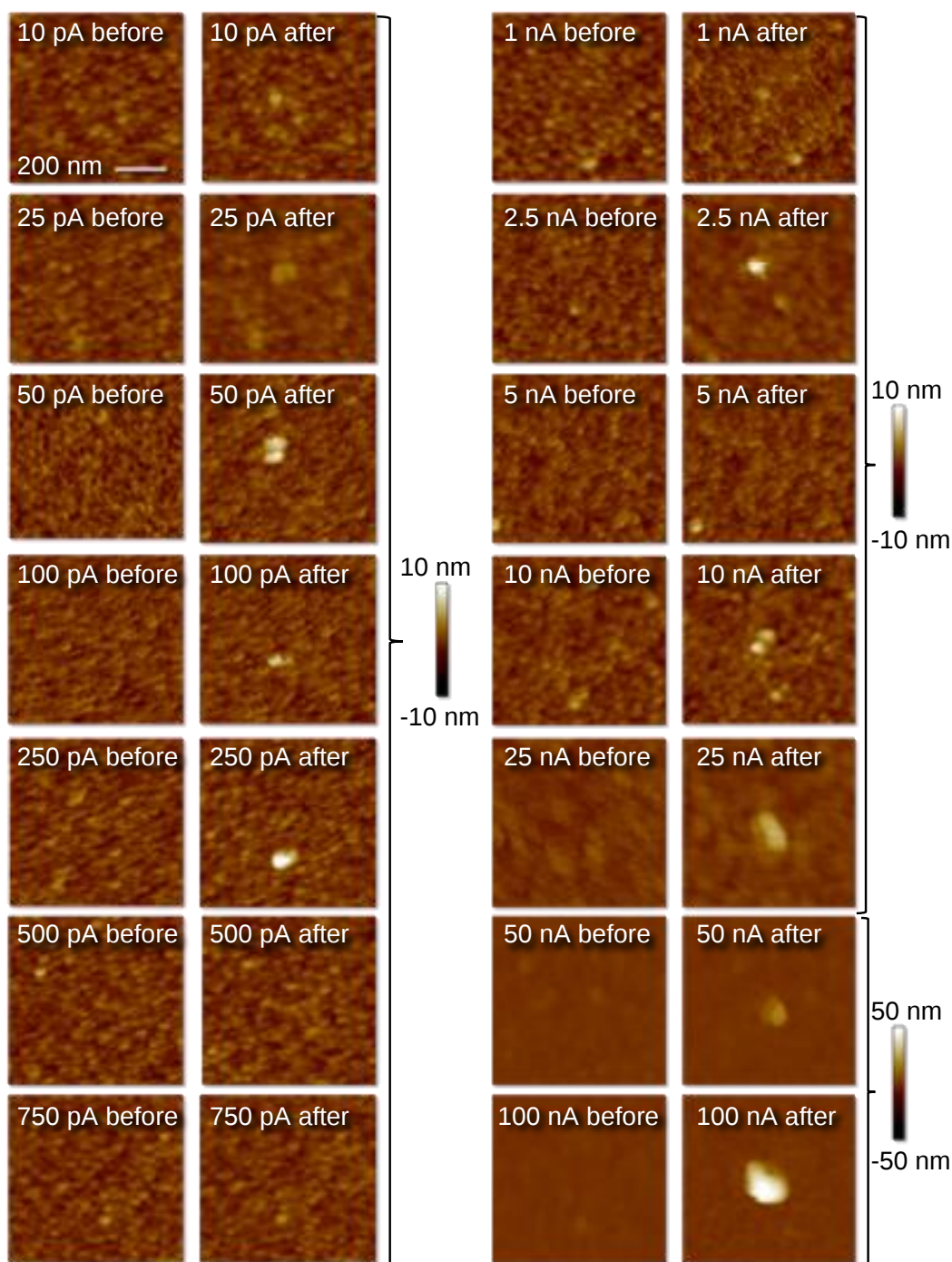


Figure S7. Topography images taken before and after the constant current measurements shown in Figure 5 and Figure 6 of the manuscript. We note that surface deformations appear as a result of current stress, although this seems to be a stochastic process, as not all stresses produce a deformation. Up to 25 nA, these features are at most a few nm in height. Above this, the features are tens of nm in height. However, as noted in Figure 6, S_{pS} reaches a maximum from around 250 pA, and the topography data shown here indicates that significant structural deformation should only occur following the application of tens of nA.

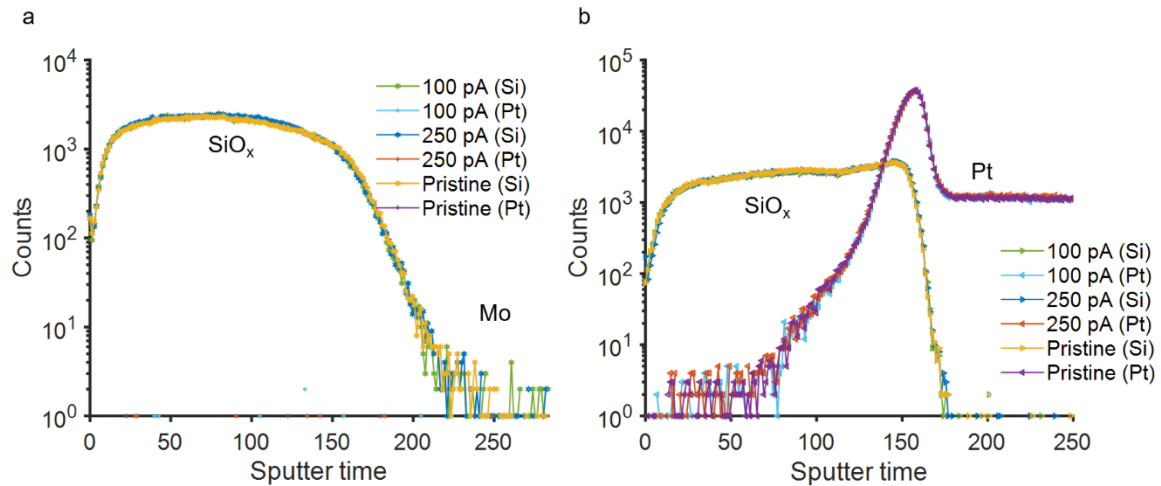


Figure S8. SIMS depth profiles for electrically stressed SiO_x films on molybdenum and platinum bottom electrodes. CAFM stressing at 100 pA and 250 pA was performed with a constant current while the tip scanned a $500 \mu\text{m}^2$ sample region (i.e. two stressed regions were produced for each sample). SIMS measurements were carried out using an ION-TOF TOF-SIMS V instrument. Samples were sputtered with a 1 keV, 70 nA Cs^+ beam for depth profiling and a 25 keV Bi^+ analytical ion beam for secondary ion generation. Charge compensation was performed using a low energy electron gun. Each trace in a) and b) corresponds to the silicon or platinum signal from a different sample region, either pristine or following 100 pA or 250 pA constant current writing. All regions for each sample were adjacent in order for them to be captured under consistent sampling conditions in a single SIMS measurement per sample. a) For the SiO_x film on a molybdenum bottom electrode (i.e. the same configuration as in the CAFM measurements of the manuscript), no platinum is detected on the sample surface or in the film following the application of 100 pA or 250 pA. Indeed, there is no platinum signal at all from this sample, with only a few data points of noise present at low counts. This suggests that the application of up to 250 pA does not cause platinum deposition from the CAFM probe, or at least not to a detectable level. To confirm that platinum should be detected if present, b) shows the same data for an SiO_x film on a platinum bottom electrode. Here, the signal for platinum is clear in each region, initially at a trace level in the SiO_x layer and subsequently as a strong signal as the bottom electrode is reached. These data indicate that platinum would be detected even if present at a trace level, below what we would expect if the CAFM probe had deposited platinum during electrical stressing.