Supporting Information for

Nanoscale Elastocapillary Effect Induced by Thin-Liquid-Film Instability

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Table of contents:
1. Fabrication of liquid cells with an array of nanopillars.................................................................1
2. Details of \textit{in situ} TEM experimental procedures...........................................................................3
3. TEM imaging and image sequence analysis for collapse characterization.................................4
4. \textit{Ex situ} and \textit{in situ} collapse profiles ..........................................................................................5
5. Estimating the water film thickness during the drying process......................................................6
6. Derivation of the beam-sway model................................................................................................7
7. Supporting video captions .............................................................................................................9
8. Supporting references .....................................................................................................................9
1. Fabrication of liquid cells with an array of nanopillars.

Liquid cells used in our experiments were assembled from two parts: a top chip and a bottom chip (Figure S1).

**Top Chips:** Top chips were fabricated from 100-mm diameter, 300 ± 25 µm thick double-side-polished Si (100) wafers with the dimensions of 6.6 mm × 5.6 mm (Figure S1A). A 25-nm-thick silicon nitride (SiNₓ) film was deposited on both sides of the wafer using a low-pressure chemical vapor deposition (LPCVD) process (Figure S1A). Two loading pockets, central viewing windows, and grooves for cleaving individual chips were patterned on the backside SiNₓ layer using a conventional photolithography process, followed by deep reactive ion etching (DRIE) of the exposed SiNₓ film. After the DRIE, the exposed Si parts were etched from the backside of the wafer using potassium hydroxide (KOH) wet etching process in a beaker containing ~30% (w/v) KOH for ~7.5 hours at a temperature of 70 °C. During the wet etching, the frontside of the wafer was protected to prevent contact with the KOH solution. Lateral dimensions of these electron translucent SiNₓ viewing membrane windows were ~30 µm × 200 µm. A metal spacer (10-nm-thick Cr adhesion layer and 50-nm-thick Au film) was patterned on the front side of the wafer using a lift-off process.

**Bottom Chips:** The bottom chips were microfabricated from 300-mm diameter, 775 ± 10 µm thick Si (100) wafers, with a 30-nm-thick LPCVD SiNₓ film on both sides and had dimensions of 6.15 mm × 5.1 mm (Figure S1B). Arrays of Si nanopillars of different heights were fabricated on top of the frontside SiNₓ film of the wafer using advanced lithography techniques (details are discussed below). The nanopillars (150, 230, 285, and 385 nm in height, 26 – 30 nm in diameter, and 90 nm in pitch) were fabricated from amorphous Si film deposited on top of the SiNₓ film. Again, the viewing windows and cleaving grooves were patterned on the backside SiNₓ film and etched using the same procedure as for the top chips. As the wafer for bottom chips was thicker than for the top chips, the typical KOH etch time for etching the bottom chip wafer was ~18 hours. The frontside of the wafer was protected during the entire microfabrication process and kept out of contact with photoresist, KOH solution, and rinse liquids to avoid contamination and destruction of the fragile Si nanopillars. After the KOH etch, the wafer was rinsed in water, isopropanol, and then dried under ambient conditions.
Figure S1. Liquid cell fabrication. Schematic illustrating the fabrication process for (A) top and (B) bottom chips of liquid cells. (C) The top and bottom chip are aligned and assembled into a liquid cell used for real-time TEM imaging.

Fabrication of nanopillar arrays: Freestanding Si nanopillars were fabricated on top of the SiNₓ film on a 300-mm-diameter Si wafer using the process shown in Figure S1B. A 30-nm-thick LPCVD SiNₓ film was deposited on both sides of a double-side-polished (100) Si wafer, followed by Si deposition at 600 °C on one side of the wafer. The height of the patterned nanopillars is defined by the thickness
of the deposited Si film. An amorphous carbon film was then deposited on top of Si film by a CVD process. Deep ultraviolet (DUV) immersion lithography was used to print 90-nm pitch nano-dots in photoresist through double line exposures.\textsuperscript{2,3} The resist pattern was then transferred into the underlying amorphous carbon layer, which served as a hard mask for the subsequent plasma etching of the Si using CH\textsubscript{2}F\textsubscript{2}/SF\textsubscript{6}/N\textsubscript{2}-based gaseous chemistry.\textsuperscript{3} A soft landing step with high selectivity of Si over SiN\textsubscript{x} was used to ensure straight pillar profiles. At the end of the etching process, the remaining amorphous carbon was removed by O\textsubscript{2} plasma stripping. After the fabrication process, backside KOH etching was performed to remove the bulk Si and release the SiN\textsubscript{x} membrane window with free-standing nanopillars on top.

2. **Details of *in situ* TEM experimental procedures.**

**Assembly of the static liquid cells for *in situ* TEM imaging:** Wafers containing the top and bottom chips were cleaved along the groove lines to produce individual top and bottom chips. The membrane sides of the chips were plasma cleaned for 45 s using a coating current of 15 mA. Then, a liquid cell was assembled from the top and the bottom chips with their membrane windows aligned and facing each other. The liquid cells were sealed from the sides to prevent the liquid from leaking during the TEM imaging. It should be noted that the spacer thickness (~60 nm) is much smaller than the nanopillar height (150 – 385 nm). However, when the top and bottom chips were assembled together (Figure S1C), the spacer sits on the nanopillars at the edge of the chip and prevents the top chip from crashing the rest of the nanopillars. The nominal thickness between the top and bottom membranes is between 150 nm + 60 nm = 210 nm and 385 nm + 60 nm = 445 nm. To induce the slow drying of water in a liquid cell inside the TEM, we introduced scratch marks at the loading pocket side of a liquid cell using a diamond scriber (2\textsuperscript{nd} panel in Figure S2). The scratches form narrow channels under the gasket through which water evaporates into the column of a TEM. Water was injected into the loading pocket of the liquid cell using a pipette, and this water is pulled by capillary force into the liquid cell. After the water was injected, the loading pockets were sealed with a polydimethylsiloxane (PDMS) gasket inside our custom-built retainer (Figure S2). Finally, the assembled retainer (Figure S2) was attached to a TEM holder and inserted into JEOL2010FEG TEM (JEOL Ltd., Tokyo, Japan).
3. TEM imaging and image sequence analysis for collapse characterization

*In situ* TEM imaging experiments capturing the nanopillar collapse during the drying process were carried out using JEOL 2010FEG TEM operating with an accelerating voltage of 200 kV. Image sequence files were recorded at a rate of 25 – 100 frames per second (fps) using the OneView CMOS camera (Gatan, Inc., Pleasanton, CA, USA). The electron flux was kept below $3 \, \text{e}^+/(\text{Å}^2 \cdot \text{s})$ to minimize electron beam induced effects on the samples.

All image processing algorithms for the analysis of *in situ* sequence files were written in Python-2.7 using the NumPy, SciPy, OpenCV, scikit-image, Cython, and Matplotlib libraries. First, the raw Gatan dm4 files were converted into an 8-bit image sequence in png file format using hyperspy and OpenCV libraries. Second, the image sequence was inverted and blurred using a Gaussian filter with $\sigma = 5$ pixels. Third, the nanopillars were segmented using the Laplacian of Gaussian (blob_log) function implemented in scikit-image library where the parameters $\sigma_{\text{min}}$ and $\sigma_{\text{max}}$ depend on the diameter of the nanopillars, and both of these parameters were set as 11.3 pixels. The threshold parameter in blob_log function was set as 0.15. After the segmentation, the regions with nanopillars were represented with a pixel value of 1 and the background (i.e., area without the nanopillars) was represented with a pixel value of 0. Finally, using these binary images of nanopillars, we tracked and labeled them following the same method described in our previous work. The labelling helps to identify the centroid position of each nanopillar at every frame based on which we performed drift correction by setting the mean displacement of all the nanopillars as zero.
4. **Ex situ and in situ collapse profiles**

To assess the effect of the electron beam of a TEM on the collapse of nanopillars, we compared *in situ* and *ex situ* results of wetting and subsequent drying of different-height nanopillars that were used in our study. As shown in Figure S3, collapse profiles for both cases were very similar. From the similarity between the *ex situ* (Figure S3A) and *in situ* (Figure S3B) results, we concluded that the electron beam does not have a significant effect on the collapse of the nanopillars at the fluxes used in our *in situ* studies (\(< 3 \text{e}^-/(\text{Å}^2 \cdot \text{s})\)). We mention here that the samples used for both *in situ* and *ex situ* studies were plasma cleaned similarly before the wetting to achieve maximal hydrophilicity as validated by contact angle measurements (Figure S4).

**Figure S3.** Comparison between *in situ* and *ex situ* collapse profiles of the nanopillars with different heights. Images of 150, 230, 285, and 385 nm nanopillars (A) after the *ex situ* wetting and drying experiments (*i.e.*, benchtop experiments) and (B) after the drying stage in the *in situ* TEM experiments.

**Figure S4.** The contact angle of water on a plasma-treated flat Si wafer was measured to be ~5°.
5. Estimating the water film thickness during the drying process

**Water thickness:** We estimated the thickness of the water film (i.e., wet region) from the average electron counts for the wet ($I$) and dry ($I_0$) regions of the liquid cells with nanopillars by using the single electron scattering approximation:\textsuperscript{13}

$$h = \lambda \ln \left( \frac{I_0}{I} \right) \quad (S1)$$

Here, $\lambda_{\text{water}} \approx 400$ nm is an elastic mean free path of 200 keV electrons in water.\textsuperscript{14}

It should be noted that the pixels which represent the nanopillars in the images were masked in order to prevent the counts associated with the Si affecting our thickness measurement. Following this, the water thickness was calculated for every non-nanopillar pixel of each movie frame using equation S1, and the median thickness was chosen as the representative water film thickness for the given image as plotted in Figure S5.

![Figure S5. Estimating the thickness of water film using electron counts. All the pixels representing nanopillars were masked, and the average electron counts from the remaining pixels were plotted as a function of time (red curve) for the drying process shown in Figure 3D. Between $t - t_0 = 0$ to 10 s, the nanopillars were fully wet, after which they started to dry ($t - t_0 = 10$ to 27 s). Finally, the nanopillars dried completely ($t - t_0 = 40$ s), and the electron count detected by the camera was at its maximum. This maximum count was chosen as $I_0$ (dashed black curve) for all the frames. Water thickness at each non-nanopillar pixel was calculated using equation S1, and the median thickness of the water was plotted as a blue curve.](image)

**Testing the validity of the single scattering approximation for thickness estimation:** To test the reliability of equation S1 in estimating the thickness of the water in drying liquid films, we compared the estimated height of Si nanopillars from their top-down TEM images (Figure 1C) against their actual known heights from SEM images (Figure 1B). From TEM images, we first identified the location of
each nanopillar using the blob detection method\textsuperscript{15} implemented in Python library scikit-image.\textsuperscript{8} After detecting 3000 nanopillars for each height category (150, 230, and 285 nm), we apply Otsu’s thresholding method\textsuperscript{16} on these images to obtain binary images where the pixels containing the nanopillars are represented as 1, and the regions without the nanopillars are represented with 0. Afterward, we calculated the average electron counts ($I$) for each of the nanopillar regions. We also estimated the average electron counts outside the nanopillar regions ($I_0$), which represent pixels from SiNx membranes. Using the mean free path of Si as 250 nm (ref. 17) for 200-keV electron beam, we obtained the estimated heights of the Si nanopillars ($\hat{L}$) from equation S1, which was within 5\% of the actual height ($L$) for the nanopillars whose height is less than the mean free path. In the case of the 285-nm pillars, the estimated height was off by 20\% because of multiple electron scattering (\textit{i.e.}, single scattering approximation in equation S1 does not work for materials whose thickness exceeds the mean free path of the electrons). These results are summarized in Figure S6. For the case of water ($\lambda_{\text{water}} \approx 400$ nm),\textsuperscript{14} we expect reliable thickness estimates because the maximum thickness of a thin water film is slightly less than the pillar height, and the tallest nanopillars used in our study were 385-nm-tall, which is less than the mean free path of 200-keV electrons.

![Figure S6. Plot of nanopillar heights ($\hat{L}$) estimated from equation S1 against the actual heights ($L$) measured from the SEM images (Figure 1B). Black markers with error bars represent the average estimate and the standard deviation for 3000 nanopillars. Dotted red line represents $\hat{L} = L$.](image)

6. Derivation of the beam-sway model

The capillary force resulting from lateral meniscus interaction between two cylindrical pillars that are partially immersed in a liquid, as derived by Kralchevsky, is:\textsuperscript{18,19}
\[ F_C = \frac{-\pi \gamma d^2 \cos \theta^2}{2 \sqrt{(p-2\delta)^2 - d^2}} \]  

(S2)

Here, \( \gamma \) – surface tension of water, \( d \) – pillar diameter, \( \theta \) – intrinsic contact angle, \( p \) – interpillar spacing (pitch), and \( \delta \) – pillar deflection (for straight, fully immersed pillars \( \delta = 0 \)). The pillar of length \( L \) will remain freestanding if the elastic restoring force, given by

\[ F_E(\delta) = \frac{3EI}{L^3} \delta, \]  

(S3)

is sufficiently strong to counterbalance the capillary forces (i.e., \( F_C < F_E \)). The pillar will bend and come into contact with the other bending pillar if \( F_C > F_E \). Hence, there is a critical pillar length and deflection for which \( F_C = F_E \). The critical deflection of the pillar \( \delta_{cr} \) for which \( F_C = F_E \) can be obtained by noting that the force curve for \( F_C \) must be tangential to the force curve for \( F_E \):

\[ \frac{\partial F_C}{\partial \delta} = \frac{F_C}{\delta} \]  

(S4)

After solving the equation S4 in terms of \( \delta \), the resulting critical deflection is:

\[ \delta_{cr} = \frac{3}{8} p \pm \frac{1}{4} \sqrt{\frac{p^2}{4} + 2d^2} \]  

(S5)

Next, we equate the capillary (equation S2) and elastic (equation S3) forces at \( \delta_{cr} \) (equation S5):

\[ F_C(\delta_{cr}) = F_E(\delta_{cr}), \]  

(S6)

and obtain an expression for the critical pillar length:

\[ L_{lateral}^3 = \frac{3EI}{16 \pi \gamma d^2 \cos^2 \theta} \left( 3p - \sqrt{p^2 + 8d^2} \right) \left( \sqrt{\left( p + \sqrt{p^2 + 8d^2} \right)^2 - 16d^2} \right) \]  

(S7)

We can then rewrite the equation S7 in terms of the elastocapillary length, \( L_{EC} = \sqrt{EI/\gamma d} \), and dimensionless geometrical prefactor, \( f(p, d) \):

\[ L_{lateral} = \frac{3}{\sqrt{d}} \frac{L_{EC}^2 f(p, d)}{d} \]  

(S8)

\[ f(p, d) = \frac{3}{16\pi \cos^2 \theta} \left( \frac{3p}{d} - \sqrt{\left( \frac{p}{d} \right)^2 + 8} \right) \left( \sqrt{\left( \frac{p}{d} \right)^2 + \left( \frac{p}{d} \right)^2 + 8} \right) - 16 \]  

(S9)
7. **Supporting video captions**

**Video 1.** Drying process which induces the collapse of 385-nm-tall nanopillars (AR = 13) shown in Figure 2A.

**Video 2.** Drying of a flat SiNx membrane showing how liquid recedes until the membrane is fully dry, as shown in Figure 3A.

**Video 3.** Drying process which induces the collapse of 150-nm-tall nanopillars (AR = 6) shown in Figure 3B.

**Video 4.** Drying process which induces the collapse of 230-nm-tall nanopillars (AR = 8) shown in Figure 3C.

**Video 5.** Drying process which induces the collapse of 285-nm-tall nanopillars (AR = 11) shown in Figure 3D.

**Video 6.** Drying process which induces the collapse of 385-nm-tall nanopillars (AR = 13) shown in Figure 3E.

8. **Supporting references**


