Electronic Supplementary Material (ESI) for Soft Matter

Ordered arrays of polymer droplets with triangular, circular, and rod-like shapes: Supplementary Information

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1 Bare Substrates

Figure 1 reports the measurements of patterned oxide surfaces (no overlying PS film).

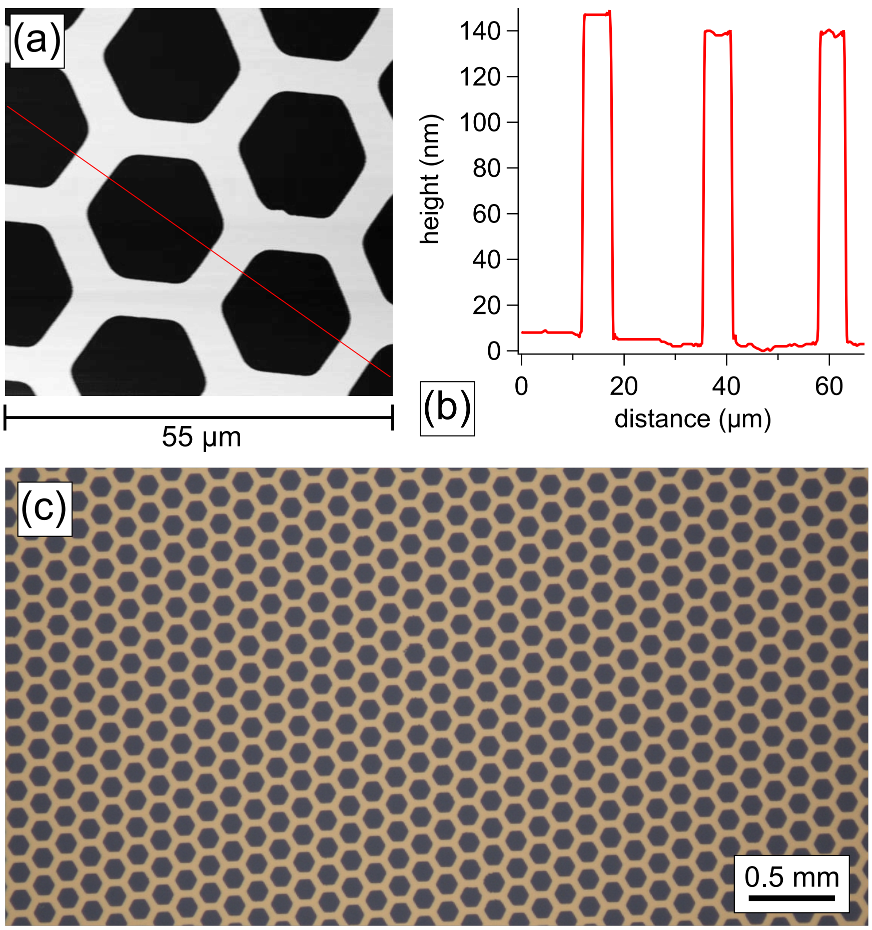

Figure 1: (a) Atomic force microscopy measurement of a patterned oxide surface (no PS film). (b) Line cut from measurements in (a) that illustrates the topography. (c) Optical micrography of a bare patterned surface.

2 Film Thickness on Patterned Surfaces

Film thickness is measured from un-patterned (flat) regions of the sample using spectroscopic ellipsometry. The flat part of the sample is marked by the "star" in Figure 2a, which reports an optical micrograph of a patterned surface after coating with 40 nm of PS. One can see that the apparent film color is continuous from the patterned mesas to flat oxide surfaces. It is well-known that small changes in film thickness will produce large changes in the apparent color, so optical microscopy supports our assertion that films are uniform over these surfaces. The color changes near the edges of the wells due to the sidewall slope (continuous change in thickness of the underlying oxide). From atomic force microscopy in Figure 2b-c, we see that the film on top of the mesas is flat (no "beading").

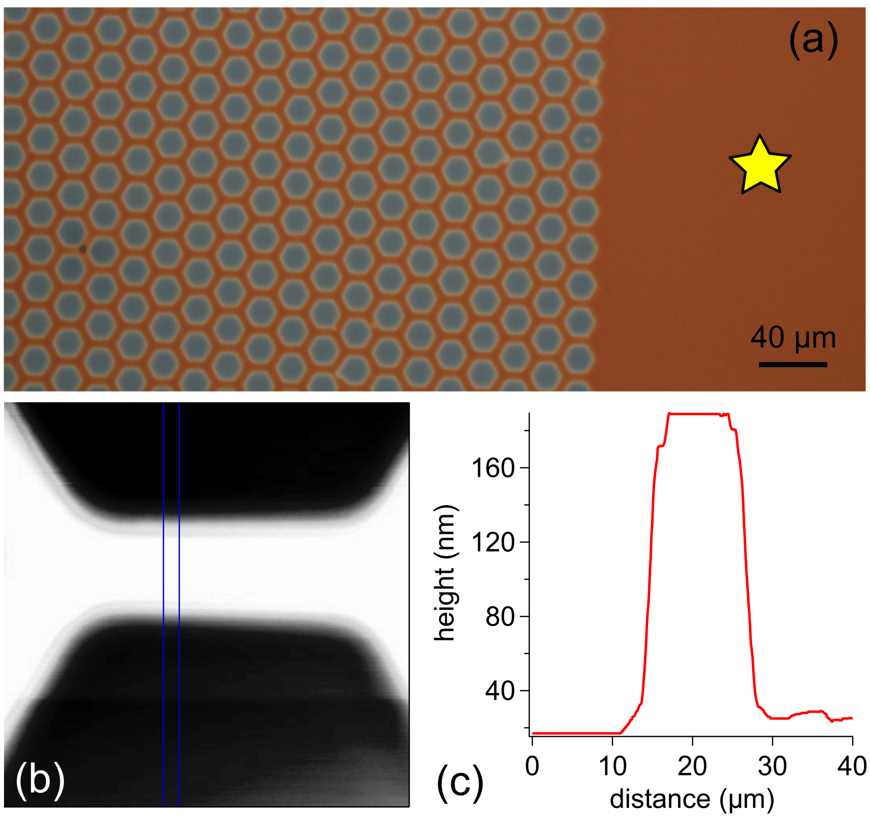

Figure 2: Data for patterned surfaces coated with 40 nm of PS film. (a) Atomic force microscopy measurement of the coated patterns. (b) Line cut from measurements in (a) that illustrates the flat mesa surface. (c) Optical micrography of a coated surface.

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3 Film Profiles on Patterned Surfaces After Thermal Annealing

The data included in Figure 3 demonstrate that PS dewetting is initiated at the edges of the mesas. This behavior is also observed in Figure 2 of the main text. Note that Figure 3b also confirms that the as-cast film thickness on the mesas is approximately 40 nm. (Based on five atomic force microscopy measurements like Figure 3b, we estimate a film thickness of 45 ± 8 nm - although this value depends on the accuracy of the z-deflection calibration.)

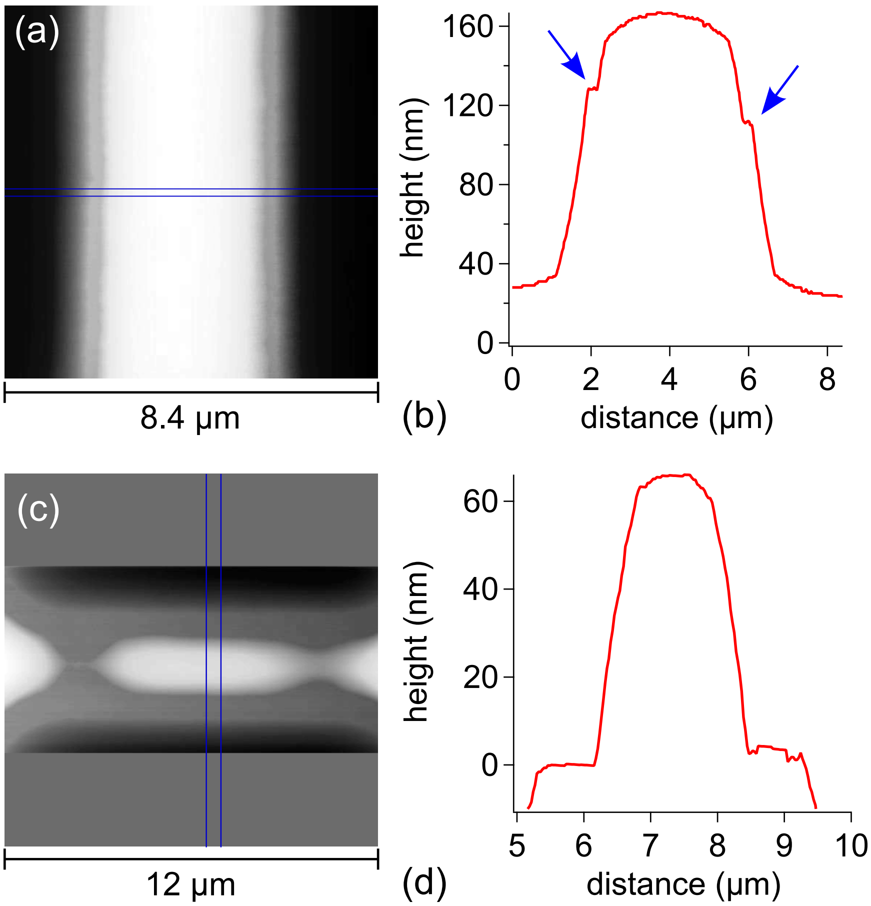

Figure 3: Data for patterned surfaces coated with 40 nm of PS film and annealed at 160°C. (a,b) Atomic force microscopy measurement after annealing for approximately 2 minutes; (c-d) After annealing for 45 minutes.

4 Equilibrium Droplet Shapes

Most of the droplets are circular after 24 hours of annealing at 160°C (vacuum). The degree of circularity is coupled to the mesa length a. When $a < \lambda_f$, the film breaks apart at the midpoint of the mesa and the polymer diffuses to the vertices to form droplets. Therefore, circular droplets are first seen on the shortest mesas (smallest diffusion distance). When the mesa is long enough to support a fingering instability, the rim pinches off near the vertices rather than the midpoint of the mesa. In these cases, circular droplets are quickly formed at the vertices because the polymer does not diffuse over a very large distance. The data in Figure 4 support this view of the transient and equilibrium structures.

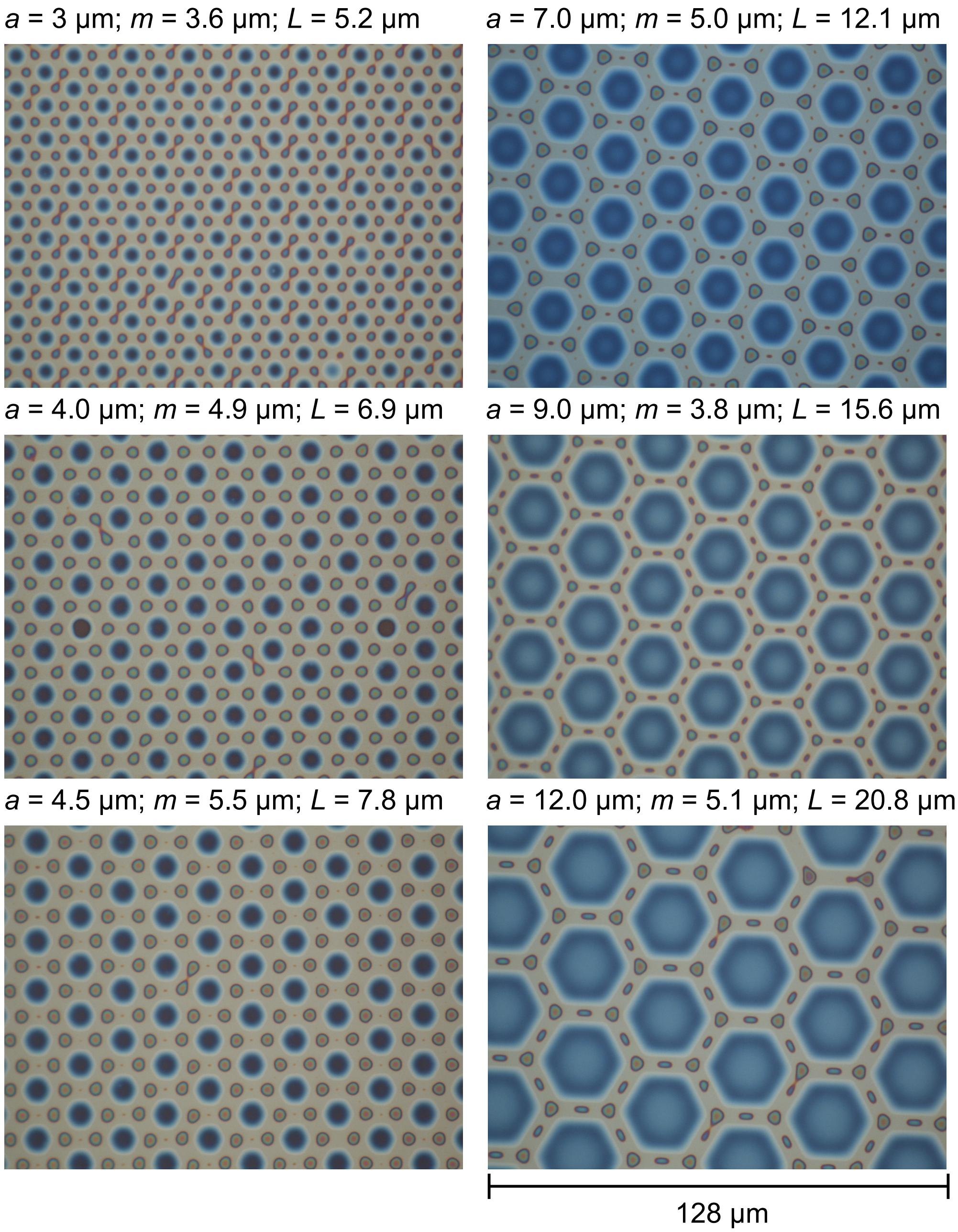

Figure 4: Droplet shapes as a function of pattern dimension.

5 Rim Break-Up

On very long mesas ($a \gtrsim 30$ μm), the PS rim is unstable and will break-up into smaller droplets. An example of this behavior is included in Figure 5 for a 40 nm PS film annealed at 160°C for 85 minutes (vacuum).

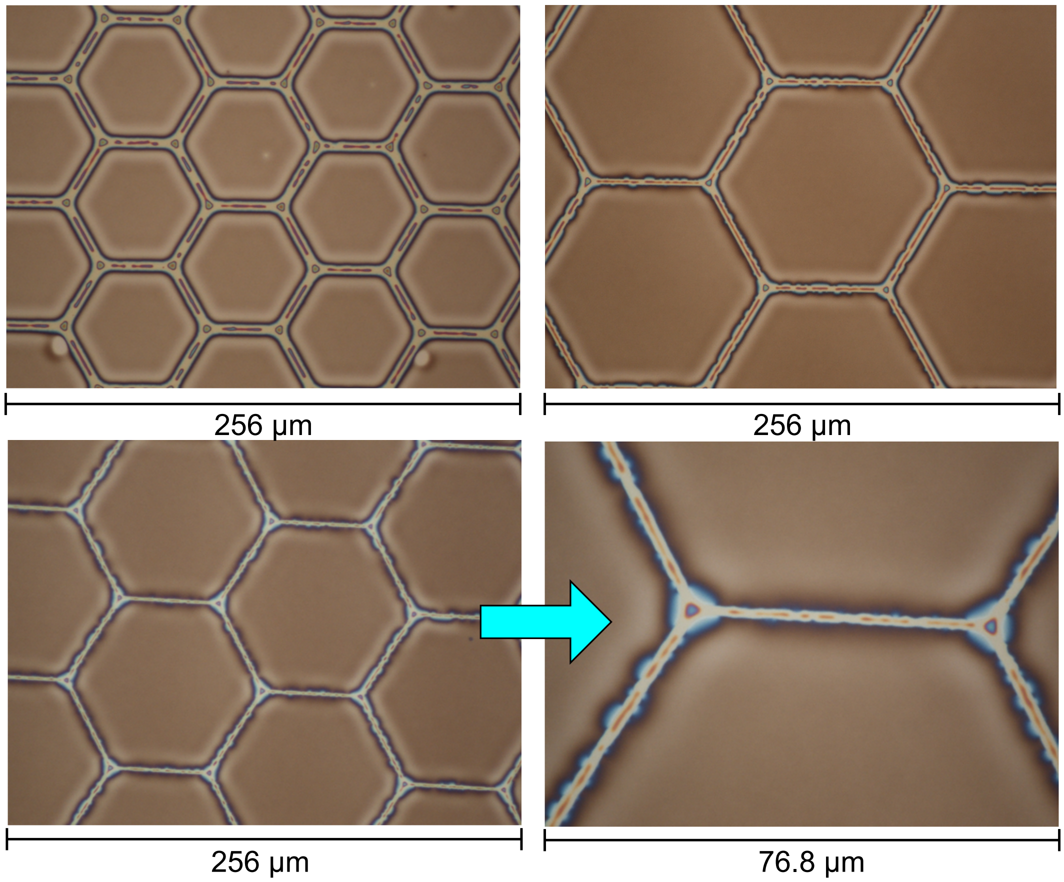

Figure 5: Break-up of cylindrical PS rim on long mesas.

6 Square Patterns

A similar dewetting mechanism is observed with square pre-patterns (Figure 6), although our data are very limited for these cases.

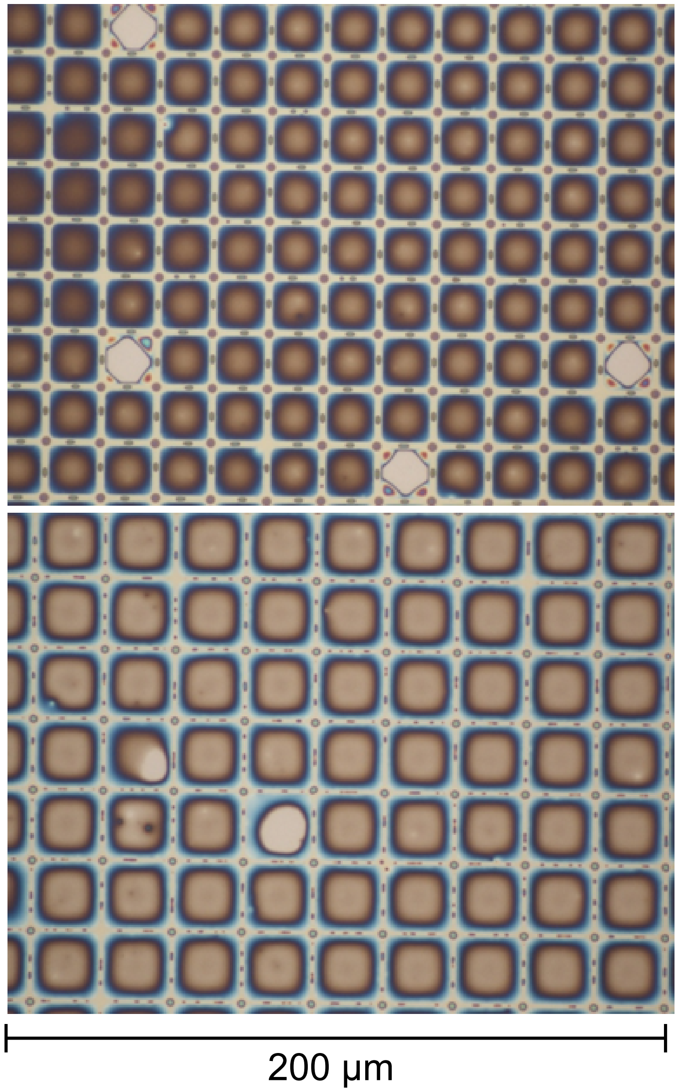

Figure 6: PS droplets on square-grid oxide patterns (after annealing at 160°C for more than 24 hours).