Nanodecoding by Dewetting**

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The fragmentation of a continuous liquid film into isolated droplets is a ubiquitous phenomenon, which can be observed in our daily life (in our kitchens and bathrooms) and must be controlled for medical and agricultural applications (e.g., for contact lenses or when applying pesticides on leaves). Such dewetting processes provide a dramatic macroscopic illustration of the importance of weak surface interactions acting on the nanometer scale. Here we show that one may manipulate the short-range part of a surface potential to force a metastable liquid film to rupture into a regular array of ribbons of unexpectedly small width, well below one micrometer. The stability of a liquid film of thickness $h$ depends on the details of an effective interface potential $F(h)$, which results from weak forces such as the van der Waals interaction or hydrogen bonding. Depending on the shape of $F(h)$, a film may rupture by the spontaneous amplification of height fluctuations (unstable films) or by nucleation and growth of holes (metastable films). In both cases the resulting final morphology consists of isolated droplets that range from micrometers to millimeters. In this Communication, we control the dewetting of thin films of polymer fluid on a smaller spatial scale than previously reported. This control is achieved by locally tuning the short-range part of $F(h)$ with chemically nanopatterned surfaces. This technique paves the way for spontaneous fabrication and positioning of soft organic nanowires by the simple decoding of a patterned interface potential, which may be of interest for applications in soft nanoelectronics. By a simple dewetting process, a set of instructions encoded on a medium on the nanometer scale may be read. Here, we focus on the dewetting of a diblock copolymer film on a surface of alternating nanostripes of greater and lesser wettability that vary in width and period.

The block copolymers are central to our attention because they may combine antagonistic characteristics such as a destabilizing block to promote dewetting and an anchoring block to stabilize the dewetted morphology. In addition, block copolymers tend to self-organize into regular nanostructures (cylinders, lamellae, or spheres) through microphase separation, which may provide a supplementary force to stabilize a dewetted morphology. Here, we selected a poly(styrene)-block-poly(ethylene oxide) (PS–PEO) copolymer (Fig. 1) to be deposited on specially designed Si surfaces, which allowed modulation of the metastability of the film. First, a 600 nm layer of thermal oxide was grown on a (100) Si wafer, in order to create a reproducible reference surface. This layer was thicker than those of polymer film that were to be deposited, ensuring that the effects of Si substrate were negligible and could be safely ignored in later analyses. Examination of the Hamaker constants of PS and PEO on SiO$_2$ (see Supporting Information, SI) leads to the conclusion that the long-range part of the effective potential $F(h)$ exhibits a very weak curvature, whose sign cannot be predicted a priori. This implies that an ultrathin film of the block copolymer might be unstable on SiO$_2$. Thicker films will be stable or metastable depending on the short-range part of $F(h)$, which is directly related to the sign of the spreading coefficient of the liquid on the surface, $S$. Therefore, to manipulate $S$ locally, nanostripes of a perfluorinated alkysilane ($\text{CF}_3(\text{CF}_2)_n\text{Si}(\text{Cl})(\text{CH}_3)_2$) were deposited on the thermal oxide, as described previously, and a gamma-aminoethylsilane ($\text{NH}_2(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_2(\text{CH}_3)_2$) was deposited in-between the perfluorinated lines. The wettability of each monolayer by the block copolymer is very different, which allows us to modulate the spreading coefficient $S$, and therefore the metastability of the film. The poorly wettable perfluorinated regions should preferentially promote the nucleation of holes, whereas the amine end groups should increase the stability of the block copolymer film due to their preferential interaction with the PEO block through hydrogen bonding. To quantify this, experiments were performed on homogeneous substrates first. PS–PEO thin films were spin-coated on amine-ended silane substrates from 0.2% w/w benzene solutions. The films were then gradually heated from room temperature (RT) to 170 °C, and were imaged in situ by atomic
force microscopy in intermittent contact mode (IC-AFM) for short dewetting times (hours), or at room temperature after quenching for long dewetting times (days or weeks). Figure 1a–e shows the different dewetting stages of a 14 nm thick PS–PEO film\(^{[23]}\) on a homogeneously amino-silanized SiO\(_2\) substrate. After spin coating, microphase separation was demonstrated by the formation of PEO cylinders with 22 nm diameter and 39 nm period (Fig. 1a). When the film was heated for a short time at 100 °C, close to the glass transition temperature of the PS block (103 °C) and well above the melting temperature of the PEO block (65 °C), the cylindrical structure disappeared and small holes began to appear (Fig. 1b). The formation of holes is indicative of the metastability of the film, while the disappearance of the cylindrical structure is typical for some asymmetric block copolymers confined in films of thickness lower than their period.\(^{[1]}\) The PS block has a lower surface tension, and therefore greater affinity for air, than the PEO ((36.6±0.5) mJ m\(^{-2}\) for PS vs. (44.7±0.3) mJ m\(^{-2}\) for PEO, SI). However, the PEO block has a lower interfacial tension resulting from hydrogen bonding and therefore greater affinity for the amine-ended interface ((0.18±0.2) mJ m\(^{-2}\) vs. (2.4±0.3) mJ m\(^{-2}\) for PS, SI). These two facts resulted in the reorganization of the block copolymer into a layered microstructure, with the PS block at the top and the PEO block at the solid interface. At 100 °C, the holes gradually grew and deepened (Fig. 1c–e) and after a long dewetting time (∼3 h) at 170 °C, droplets finally formed. X-ray reflectometry (XRR) measurements and AFM phase images demonstrate that the

Figure 1. IC-AFM (topography) images of 14 nm thick PS–PEO films dewetting on homogeneously silanized silicon wafers. a–e) amine-ended silane; f) perfluorinated silane. The images were acquired in situ. a) Just after spin-coating at RT. b) After 10 min at 100 °C. c) After 10 additional minutes at 150 °C. d) After 10 additional minutes at 170 °C. e) After 3 additional hours at 170 °C. f) After 1 min heating at 170 °C (perfluorinated silane substrate). The inset in (a) shows the chemical structure of the polymer.
regions between the droplets are essentially dry (see SI). The AFM-determined contact angle of the droplets, \( \theta = 3.9 \pm 0.4^\circ \), confirmed that the 14 nm PS–PEO film is slightly metastable on the amine-ended SiO\(_2\) substrate, with \( S \) close to zero but nevertheless negative (\( S = \gamma(\cos \theta - 1) < 0 \), where \( \gamma \) is the polymer surface tension). Experiments were also performed on PS–PEO films that had been drop-cast on homogeneously perfluorinated substrates (spin-coating was impossible in this case). Figure 1f shows one of these drop-cast films after one minute heating at 170 °C. In this case, the film ruptured extremely rapidly, leaving droplets of contact angle \( \theta = 64.1^\circ \pm 0.7^\circ \). Once again, the spreading coefficient was negative, but the larger contact angle indicated a much stronger metastability of the film on the fluorinated surface than on the amine-ended surface. These experimental observations are essentially in agreement with theoretical expectations (see SI).

If we now consider a copolymer film, of similar thickness to the previous film, resting on a perfluoro–amine nanopatterned surface, the short-range part of the interface potential \( \Phi(h) \) will be locally modulated according to the specific patterning of the silane monolayer. On both types of silane, the film is metastable and should dewet by nucleation and hole growth. However, since the velocity of hole growth is proportional to the third power of the contact angle,[1] one expects holes to grow at least 4000 times faster on perfluorinated regions than on amine-ended ones. Obviously, the overall dewetting velocity will also depend on the nucleation rates, which are determined by temperature and the size of the patterned regions. Figure 2 presents IC-AFM images of PS–PEO spin-coated, under the same conditions as described for the homogeneous substrates, onto perfluorinated nanostripes drawn in an amine-ended background (250 nm wide, 1 \( \mu \)m period). Just after spin-coating (Fig. 2a), the morphology was identical to the one found on homogeneous amine-ended surfaces, except for the presence of shallow grooves of 1.3 nm depth and 250 nm width located above the perfluorinated nanostripes. These are probably due to the higher interfacial surface tension of the solution on these regions. These areas of reduced height may ease the nucleation of holes on fluorinated stripes, which would reinforce the difference in dewetting rates between perfluorinated and amine-ended regions. After 10 min at 100 °C, a few linear holes appeared on the perfluorinated stripes, with an average height difference of \( 14.5 \pm 0.5 \) nm between the film and the bottom of the holes. Since the starting film thickness was close to 14 nm, this indicated that dry holes were formed in the perfluorinated regions. This can be confirmed by XPS at the end of the dewetting process (see SI). Remarkably, a close-up image of a growing hole showed that the liquid was essentially displaced laterally, whereas the hole grew longitudinally (Fig. 2b, inset). This is different from classic dewetting processes in which liquid is displaced radially, that is along the growth direction of the hole. Here, the liquid was displaced perpendicular to the growth direction, like the wave generated by a ship moving through an ocean. The width of the hole was \( \sim 250 \) nm at its top, equal to the initial width of the perfluorinated stripes. Therefore, the hole growth almost stopped at the borders of the stripe as the hole propagation was slower in the amine-ended regions. When the film was heated for a further 5 min at 130 °C, an increasing number of trenches were opened above the perfluorinated stripes. The longitudinal growth rate varied from hole to hole, as shown by comparing the propagation of holes 2 and 3b, as labeled in Figure 2b–c. This was confirmed by the spectacular pinning of hole 4 in the next image (Fig. 2d) after the film was held for 2 h at the same temperature, 130 °C. The unpinning of this hole only occurs after 6 more hours of annealing at 170 °C (Fig. 2e). Line profiles in Figure 2c–e indicate that the fluid level is 2–4 nm higher between two neighboring fully dewetted lines than in unperforated regions, due to the lateral accumulation of the liquid as expected from the mode of hole growth described above. It should be noted, however, that the AFM-determined depth of the holes in Figure 2c–e was 20 nm, an unrealistic value, suggesting that the absolute values of height may be incorrect. This is probably due to a contamination of the tip during scanning. Figure 2f shows the final topography image of the film after quenching at RT and using a cleaned tip. The line profile indicates a difference in height of 18.5 nm between the top and the bottom of the resulting fluid ribbons that corresponds quantitatively to the initial film thickness (14 nm) plus the 14/3 nm of liquid displaced from the 250 nm wide perfluorinated stripes onto the adjacent 750 nm wide amine-ended regions.

It is noteworthy that dewetting did not continue on the amine-ended background, as the copolymer film was shown to be slightly metastable on amino-silanized SiO\(_2\). This shows that an additional force stabilizes the copolymer in these regions; we ascribe this to the structural forces associated with block connectivity that relate to the ordering of the copolymer. These forces need time to develop as they require chain diffusion and ordering near the newly created interfaces. To check this hypothesis, we performed an experiment in which the copolymer was directly heated to 130 °C (Fig. 2g–h), a temperature at which dewetting occurs much faster than at 100 °C. In this case, the polymer ribbons broke into elongated droplets lying along the amine-ended stripes. This probably happens as the characteristic dewetting time was smaller than the time required to order the copolymer at the freshly created interfaces. This result indicates that the success of the decoding of the modulation of the interface potential depends on kinetic aspects and that the ordering of the copolymer plays an important role in the stabilization of the dewetted morphology.

Could a similar differential dewetting behavior be obtained for even smaller stripe widths? Figure 3a shows a 16.3 nm thick copolymer film on an identical binary chemical nanopattern, where the perfluorinated line width was \( \sim 70 \) nm and the period \( \sim 400 \) nm. After 100 min heating at 100 °C (Fig. 3b), the cylindrical structure was lost and a few holes appeared on the perfluorinated stripes. This was identical to case of the larger stripes, except that the nucleation rate was severely reduced. Although Figures 2b and 3b look similar, they were acquired after 10 and 100 min, respectively. This decrease in
the nucleation rate results from the random nature of the hole nucleation process, which reduces the nucleation probability in smaller regions. The shape of the holes at the start also differed from that seen with larger stripes. They were more ellipsoidal, looking like buttonholes. In addition, they were significantly wider than the fluorinated stripes (∼250 nm vs. ∼70 nm), especially in the middle part of the hole. Significantly reduced longitudinal growth rates of the holes, which allowed partial lateral spreading of the holes on the amine-ended background, must have been responsible for this. However, matter was still pushed to the sides, rather than to the front of the propagated holes, as was seen from the shape of the rim surrounding the hole. The height difference between the top of the fluid and the bottom of the hole was 17–18 nm, in agreement with the starting film thickness. After further heating for 160 min at 130 °C (Fig. 3c), the film consisted of a set of completely dewetted stripes, separated by fluid ribbons containing variable numbers of undewetted stripes. The height of the separating fluid ribbons depended on their width (see inset line profiles), since the fluid level was raised by the liquid rejected from the nearest dewetted stripes. After 240 min at 150 °C, dewetting was complete (Fig. 3d). Different fluid ribbons then had different heights (from 23 to 29 nm), reflecting the sequence of events leading to the dewetting of

Figure 2. IC-AFM (topography) images of a 14 nm thick PS–PEO film dewetting on striped amino−perfluoro nanopatterns of 1 μm period and 250 nm fluorinated stripe width. a) After spin coating and before annealing; the inset is a magnified image (×4) with an averaged height profile. b) After 5 min at 100 °C; the inset is a 3D representation of the hole located between arrows 3a and 3b. c) After 5 additional minutes at 130 °C. d) After 2 additional hours at 130 °C. e) After 6 additional hours at 170 °C. f) After quenching at RT. g) Topography of film heated directly to 130 °C. h) the phase image of (g). b–f) Height profiles corresponding to the white lines drawn in the images.
neighboring perfluorinated stripes, and the progressive accumulation of matter in regions separating two dewetted lines. Note that the heights were not homogeneous along the ribbons themselves due to the randomness in the nucleation events along the longitudinal direction. In addition, the ribbons were not sharp, and the width of dewetted stripes (∼250 nm) was well above the width of perfluorinated stripes (∼70 nm). The waviness of the fluid ribbon may have resulted from slow dewetting over amine-ended regions, or from a Rayleigh-like instability.\[1\] Since the ribbon interfaces have different total annealing times depending on when they were created, the degree of waviness of the interfaces varies from place to place. This can be clearly seen in the image in Figure 3, obtained after quenching at room temperature, where every third line (marked by arrows) is less wavy than the others.

To check whether the waviness of the fluid ribbons would increase with time and finally destroy the pattern, the sample was annealed further for approximately 700 h at 170 °C and then imaged at RT (Fig. 4b). The pattern was not found to be significantly damaged, indicating that dewetting did not continue in the amine-ended regions, again suggesting a stabilization force. In agreement with this view, a new ordered hierarchical is seen to develop in Fig. 4b, indicating a reorganization of the structure of the block copolymer within the liquid ribbons. This reorganization results in the formation
within the liquid ribbons of a set of continuous regions of higher level ((6.12±0.4) nm, average value) running parallel to the newly created interfaces. This parallelism confirmed that the reorganization was driven by the vertical interfaces created during the dewetting process. From Fourier analysis of the image a repeat period of 150 nm for the height fluctuation was calculated (Fig. 4b, bottom); this was much larger than the repeat period of the copolymer (∼40 nm). This repeat period, internal to the ribbons, is superimposed on the 400 nm period fluctuation due to the patterning of the substrate. A similar experiment was performed for a pattern of 600 nm period and 70 nm perfluorinated stripe width (Fig. 4a), this also led to liquid ribbons of 600 nm periodicity bearing a height fluctuation of 150 nm periodicity (Fig. 4a, bottom). When this experiment was attempted for a pattern of 200 nm period and 70 nm perfluorinated stripe width, the reproduction of the underlying pattern was very poor, showing the limit of the decoding by dewetting (Fig. 4c).

It is difficult to elucidate the internal structure of the reorganized block copolymer ribbons. However, it was interesting to note that, for the pattern of 400 nm period, the regions of higher level were either located at the vertical interfaces, in which case three such regions were formed per ribbon, or away from them, in which case there were only two such regions per ribbon. It is also noteworthy that ribbons containing only two regions of higher level were repeated every third ribbon (Fig. 4b). This three-ribbon period was equal to the one in Figure 3e, suggesting that reorganization depended critically on details such as the average height of the ribbon and therefore the time at which it was generated. Clearly, the copolymer confined in narrow ribbons adopted a regular microstructure, most probably driven by the preferential segregation of the PS block at air interfaces and of the PEO at amine-ended surfaces. This segregation provided a stabilizing force against further dewetting. After dewetting, the block-copolymer was physically confined and reorganized according to the set of constraints imposed upon it by the underlying stripe and the vertical and horizontal air interfaces. This has been demonstrated before for copolymers on physical or chemical nanopatterns. Asymmetric block copolymers only showed homogeneous coverage if the film thickness was commensurate with the intrinsic polymer length scale (defined as the distance between the cylinder rows). Furthermore, copolymers showed domain compression or dilatation if the size of the confining template was not commensurate with the period of the copolymer. In our case, the PS–PEO copolymer period could then scale with the size of the amine lines. Depending on the exact height and width of a ribbon, the available material then reorganized into a different configuration. Although this configuration was not known in detail, it provided the force required to avoid further dewetting.

The three-ribbon period detected at various stages of the process (Figs. 3e and 4b) suggested that a longer-range organization mechanism may also contribute to dewetting. This mechanism could not be identified; it may be directly related to the specific nucleation mechanism governing the system. Different nucleation mechanisms can be considered, depending on film thickness and pattern size. Some of them involve periodic fluctuations in the thickness, with micrometer-scale wavelengths. A complete investigation of parameters governing structure formation would therefore require the sampling of a large range of fluctuation wavelengths, which depend on the curvature of the surface potential at the thick-
ness of the film; block copolymer periods, which may vary depending on confinement; block copolymer architectures; film thicknesses; surface or polymer specific interactions; polymer viscosities and hence, temperatures; and pattern sizes and periods. The determination of the role of each of these parameters is required before this method of decoding may be implemented using other polymers of interest. This kind of extensive study is beyond the scope of this Communication, in which the main aim was to demonstrate the possibility of fabricating arrays of nanowires by templated dewetting of block copolymers.

In summary, we have shown that the short range part of the effective interface potential of a surface can be tuned locally to generate a nanopattern of metastability for a thin polymer film. The higher dewetting rate of regions of higher metastability (more negative spreading coefficient) results in preferential dewetting of these regions. Here, dewetting can be controlled along stripes as narrow as 70 nm, resulting in the formation of liquid ribbons of ~20 nm height and 300–800 nm width. These liquid ribbons are stabilized using an asymmetric block copolymer. The ordering of the block copolymer at the newly created interfaces provides the force required to prevent further dewetting. Under specific circumstances, the ordering even results in the formation of regular arrays of higher regions running parallel to the fluid ribbons. This work illustrates that rational design of surfaces and of a complementary chain fluid can be used to generate rapidly new 3D nanostructures by controlled dewetting on a smaller scale than has previously been reported.

**Experimental**

The block-copolymer used in our experiments was PS–PEO (Fig. 1, inset) ($M_n = 80000 \text{ g mol}^{-1}$; $M_w = 84800 \text{ g mol}^{-1}$; PS volume fraction: 65 %, from Polymer Source). The silanes, (CF$_3$(CF$_2$)$_5$Si(Cl)(CH$_3$)$_2$) and (NH$_2$(CH$_2$)$_3$Si(OCH$_3$)(CH$_3$)$_2$) were obtained from Gelest (Germany). The surfaces were prepared by thermal oxidation of (100) Si wafers (ACM, France) at 1000°C in a Tempress (USA) oven. The preparation of homogeneously silanized wafers was performed by gas phase silanation as described previously.[17] The nanopatterned wafers were prepared by combining electron-beam lithography with gas-phase silanation, as described elsewhere.[17,27] Contact angle measurements were performed using a Digidrop goniometer (GBX, France, SI).

X-ray photoelectron spectra were recorded on a SSX-100/206 spectrometer (Surface Science Instruments). The spectra, recorded at normal ($\theta = 55^\circ$, defined as the angle between the surface normal and the analyzer line of view) and grazing incidence ($\theta = 75^\circ$), with a 150 eV pass energy, were referenced to C 1s at 284.8 eV. Intensity ratios were converted into atomic ratios using the sensitivity factors proposed by the manufacturer (Sofield photoemission cross sections, variation of the electron mean free path according to the 0.7th power of the kinetic energy, and a constant transmission function).

X-ray reflectometry (XRR) was used to determine the film thickness, as described elsewhere.[29]

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[23] The thickness of the organic film was obtained by X-ray reflectometry, from which the thickness of the block copolymer film was obtained by subtracting the thickness of the silane monolayer (0.7 nm).