AFM STUDIES OF CONFINED DEWETTING ON GRADIENT PATTERNED SURFACES

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Introduction

Thin polymer films having unfavorable polymer-surface interactions on a chemically patterned surface can be expected to spontaneously dewet and self-assemble on the pattern. Our previous studies on phase separation of polymer blend films on patterned substrates have shown that the phase segregation behavior was well correlated to the underlying chemical pattern[1]. AFM studies showed a strong coupling between the film "surface deformation" modes and the phase separation process[2] that depended sensitively on film thickness. In other studies, it was also discovered that ultra-thin films of a homopolymer could break up by a spinodal like mechanism where the thermally induced height fluctuations behaved analogously to composition fluctuations in phase separation processes[3]. By inference from such an analogy, a symmetry-breaking surface energy field imposed by a chemical pattern should likewise influence the spinodal dewetting process of ultra-thin films.

In this study, the topography and morphology of dewetting thin homopolymer films on a chemically heterogeneous self-assembled monolayer (SAM) pattern is investigated by AFM and optical microscopy. The film thickness is an important parameter in the spinodal dewetting process since nucleation and growth of holes dominate the breakup process in relatively thick films. A discrete step-gradient in the width of the periodic chemical pattern across the surface enables simultaneous measurement on a range of pattern dimensions. Such a ''high-throughput'' approach allows for rapidly screening the dewetting behavior of polymers for the entire range of pattern widths, from non-confining to confining dimensions.

Experimental

Materials. The polystyrene (PS) (M_w = 760, T_g below ambient temperature) was purchased from the Aldrich Chemical Company [4] and used as received. Toluene and chloroform solutions were prepared from ACS reagent grade solvents from J.T. Baker Inc [4]. Hexadecanethiol (tech. 90%) and 16-mercaptohexadecanoic acid (90%) were purchased from Aldrich for generating the SAM patterns. Saturated solutions of 16-mercaptohexadecanoic acid in n-hexadecane (Aldrich, 99+% anhydrous) and ethanolic (200 proof) solutions of hexadecanethiol were used as inks for the stamping procedure. Gold substrates were prepared by vapor deposition [100-300 Å Au over 10 Å Cr] on Si Wafers [4" dia., N type, 100, Polishing Corp. of America [4]].

Substrate preparation. The chemical patterns were created by the soft lithographic technique, developed by Whitesides et al. on vapor deposited gold substrates. It consists of transfer of alkane-thiols on to the gold surface by conformal contact of a poly(dimethylsiloxane) stamp previously "inked" with the thiol. The surfaces are then filled with an equivalent chain-length thiol, with a different ω-terminal functional group, to give stable smooth self-assembled mixed monolayer (SAM) with the pattern in surface functionality as defined by the stamp. In this study the gold wafer was stamped with methyl (-CH$_3$) terminated hexadecanethiol and filled with carboxylic acid (-COOH) terminated mercaptohexadecanoic acid. A unique feature of the stamp is a gradient of pattern widths. The pattern as defined by the stamp consists of linear and parallel bands of –COOH terminal groups of widths ranging from 15 µm to 1µm across the surface separated by –CH$_3$ terminal thiols of 3 µm width. Ultra-thin films of low molecular mass poly(styrene) from a dilute solution spontaneously dewets and subsequently coalesces into droplet arrays. Initial film thicknesses were estimated to be of the order of 10 to 20 nm.

Instrumentation. The AFM measurements were conducted on a Digital Instruments Dimension 3100 Nanoscope III[4] in the Tapping mode™. Cantilevers with a spring constant of 30 Nm^{-1} with silicon tips (radius of curvature of 10 nm) were used to study the surface morphologies. The optical images were acquired on a Nikon Optiphot-2 microscope[4] with a Kodak Megaplus CCD Model ES 1.0 camera[4] mounted on the trinocular head.

Results and Discussion

The spin cast films on the patterned self-assembled monolayers spontaneously dewet and subsequently coalesced to form droplet arrays. The early stages of dewetting of the films were monitored by optical microscopy (Figure 1). Capillary wave instabilities due to thermal fluctuations in ultra-thin films lead to a "spinodal" instability of the polymer film. Spinodal-dewetting on a chemically patterned substrate results in spatial ordering of the droplet configurations on the underlying pattern. The optical images show the early stages to be strongly influenced by the underlying pattern. These correlations reflect a coupling between the thermally generated surface undulations and the quantized surface modes of a fluid in a channel.
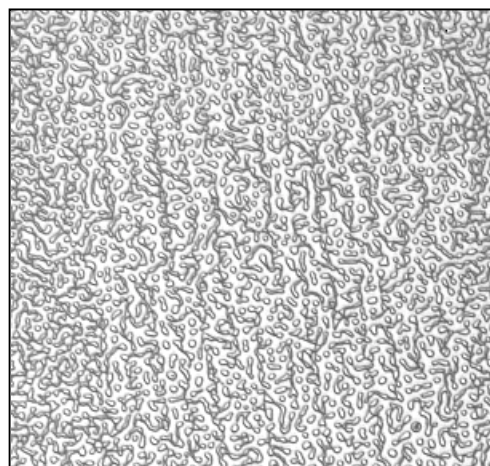

Figure 1. Early stage spinodal-like breakup of a polystyrene film spun from a solution consisting of a mass fraction of 1 % polymer in toluene [M_w = 760[5], Spin coated at 2000 rpm for 60 s]. Outline of the underlying linear chemical pattern may be seen. Image width is 185 µm depicting 9 µm bands separated by 3 µm spacing.

Fourier transformation of the image yielded the characteristic isotropic ring that scales to the pattern of fluctuations associated in this case to a film breakup process (Figure 2). Superimposed on the halo is the anisotropic component comprising of high intensity spots corresponding to the spacing of the SAM pattern. The data shown corresponds to the 9 µm bands as in Figure 1. The radially averaged intensity profiles of the isotropic rings show a transition from a broad maximum for the larger 15 µm and 12 µm bands to more distinctly defined peaks for the 9 µm and 6 µm bands. The position of the maxima was found to shift to higher q (scattering wave vector = $2\pi/x$) with decreasing bandwidth. This provides evidence of coupling between thermally induced capillary waves and the quantized modes of a shallow fluid channel.

The late stage of the dewetting process results in droplet arrays giving a highly structured surface (Figure 3). It shows a relatively monodisperse array of droplets on the 6 µm strips. The droplets are in complete registry with the underlying chemical pattern. Droplet profiles (inset) are used to estimate droplet dimensions and contact angles on different bandwidths. Contact angles are determined to be 4° for the 6 µm band shown and the film thickness is 12 nm. Variation of the bandwidths across the surface shows multiple droplets per band for the 15 µm and the 12 µm widths that coalescence into single droplets for the 9 µm stripes. Further confinement results in a crowding effect for the 6 µm band that changes to complete disorder for the narrowest 1 µm band.
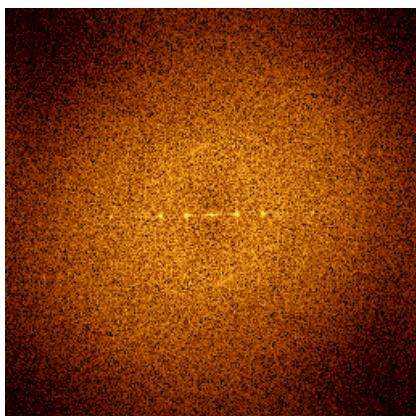
Figure 2. FFT of the early stage of spinodal dewetting on a chemical pattern. Transform corresponds to data in figure 1.
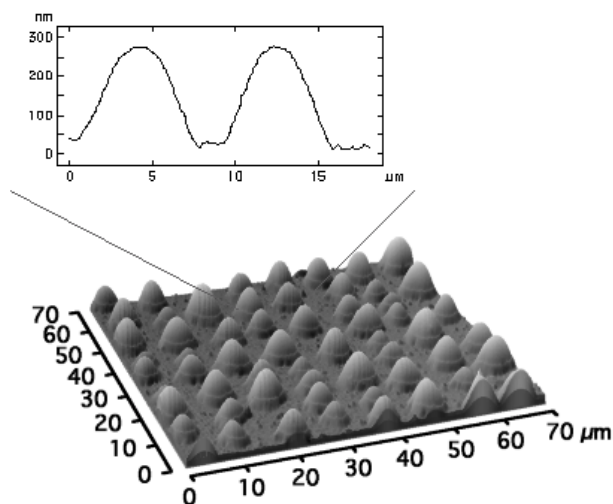

Figure 3. AFM height image of late stage dewetting on a chemical pattern. The droplet size is governed by the confining bandwidth.

Lenz et al.[6] in their theoretical treatment have defined a "channel state", for simple liquids dewetting on a chemically patterned surface, where the dimensions and the contact angle of the fluid are dictated by the confining geometry. It is important to note that Young's law is no longer valid in this confining regime. Figure 4 shows an AFM surface topography in 3-D for a slightly thicker film (18 nm) cast from a chloroform solution. It exhibits droplets with a higher contact angle of 8.5° on the 6 μm bandwidth. Further confinement results in a crossover into an "intermediate stage" where the droplets are no longer confined by the pattern, but span multiple stripes. The droplet size distribution evolves from a bimodal distribution for the larger bandwidths to a unimodal distribution with confinement and coalescence. By comparison, the droplets are completely disordered on the unpatterned surfaces.
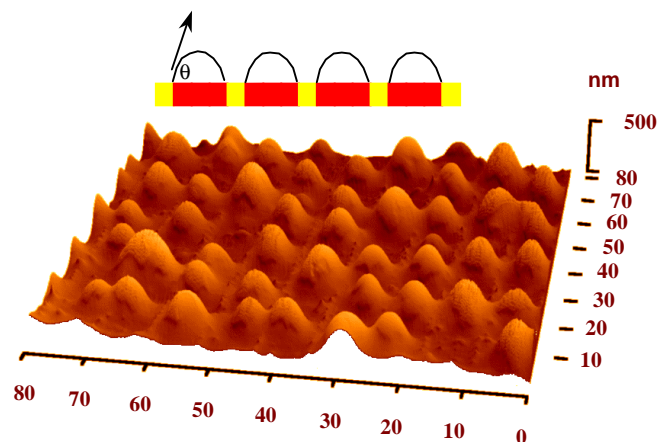

Figure 4. The channel state (top)[6] where 'θ' is larger than that predicted by Young's law. AFM image of droplets for a thicker film (18 nm) on the 6 μm bands with a higher contact angle of 8.5°.

The data suggests that a critical contact angle defines the crossover from the confinement regime or channel state to the multiple band intermediate states. The onset of the crossover on a specific bandwidth is governed by the film thickness relative to the pattern bandwidth.

Summary and Conclusions

Topographic scanning force microscopy (SFM) was used to probe dewetting of polymer films on chemically patterned substrates. Sections of these images were used to characterize droplet shapes and contact angles. A correlation was observed between the spinodal breakup and the underlying pattern. Confinement of the fluid to a stripe disturbs the natural droplet dimensions leading to an increase in contact angle with constraint. The study illustrates the large degree of dimensional and spatial control of droplet arrays possible on chemically patterned substrates with varying pattern bandwidth.

References

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(4) Certain equipment and instruments or materials ar identified in the paper in order to adequately specify experimental details. Such identification does not imply reccommendation by the National Institute of Standards and Technology, nor does it imply that the materials are necessarily the best available for the purpose.
(5) According to ISO 31-8, the term "molecular weight" has been replaced with "relative molecular mass," symbol M_r. The conventional notation rather than the ISO notation has been employed for this publication.
(6) Lenz, P.; Lipowski, R. *Physical Review Letters* **1998**, *80*, 1920-1923.