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Patterning thin polymer films by surface-directed dewetting and pattern transfer

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Abstract

The pattern evolution processes of thin polystyrene (PS) film on chemically patterned substrates during dewetting have been investigated experimentally. The substrates have patterns of self-assembly monolayers produced by microcontact printing with octadecyltrichlorosilane. Optical microscopy and atomic force microscopy images reveal that ordered micrometer scale pattern can be created by surface direct dewetting. Various pattern sizes and pattern complexities can be achieved by controlling the experimental parameters. The dewetting pattern has been transferred to form PDMS stamp for soft lithography.

Keywords: Polymer film; Dewetting; Pattern

1. Introduction

Morphology evolution during wetting and dewetting of thin liquid film on physically or chemically heterogeneous substrates has increasing promise for fabricating micro- and nanometer pattern in thin film by templating [1–15]. In the past years, much research has been done in this area, both theoretically [1–7] and experientially [7–15]. While dewetting on a homogeneous surface occurs by a randomly distribution of holes and polygon droplets [16,17], deliberately tailored heterogeneous substrates can be used to control the morphological evolution process of dewetting and the morphology of final film structures. With modern experiment technique, it is possible to produce this kind of structured substrate by such as microcontact printing [18, 19], vapor deposition [20] and photolithography [21]. Rehse et al. [8] studied the stability of polystyrene (PS) film on a corrugated substrate. They found that below a critical thickness the PS film would dewet the groove substrate and form nanoscopic polymer channels. Higgins et al. [9] reported an anisotropic spinodal dewetting of polymer film on rough surfaces by simply rubbing the substrate. Preferred orientation morphology of film was observed after dewetting. In another study, Rockford et al. [12] investigated the dewetting behavior of thin polymer films on a periodically rough Si substrate with a regular pattern of Au stripes at the peaks. They showed that the structured substrate could act as a template to control the dewetting behavior of polymer film. Theoretically, the rupture of a thin film on a single heterogeneous patch is now well understood [1–8]. On a chemically patterned substrate, dewetting is induced by the spatial difference of microscale wettability rather than the nonwettability of the substrate itself as in the spinodal dewetting on homogeneous surfaces. Based on the free energy considerations, Lenz et al. [1,2] reported the final equilibrium structures of a thin liquid film on a substrate containing single and multiple stripes. They showed that a wetting layer on structured surface would undergo wetting transition between different morphologies. Using 3-D nonlinear simulations, Kargupta et al. [5–7] investigated the morphological evolution process during dewetting of thin films deposited on chemically patterned substrates. They found that there must be some coupling between the characteristic length scale of dewetting and the substrate surface pattern. They showed that ideal templating occurred only when the period of the substrate pattern was greater than the spinodal wavelength but less than an upper transition length where dewetting was initiated on the stripe

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boundary. Thus using spontaneous dewetting appears to be a simple method to create micrometer and nanometer pattern in soft materials without the conventional lithographic processes. Sehgal et al. [15] recently utilized chemically patterned substrates with arrays of progressively narrower stripes to investigate the influence of pattern size on the morphology of ultrathin (12 nm) dewetting PS films. Using spinodal-dewetting theory, they found that there was a coupling between the dewetting pattern and substrate pattern. Their result confirmed recent numerical simulation by Kargupta and Sharma [5–7].

Motivated by these theoretical work and simulation, we here investigated the dewetting process of thin PS film on octadecyltrichlorosilane (OTS) patterned substrate. From technical point of view, we focus on how to use dewetting to pattern thin (45–47 nm) polymer films by controlling the experiment parameters. Our approach provides a simple, nonlithography method to pattern thin polymer films at a micrometer scale. The resulting dewetting structure can be transferred onto the elastomer mold for future application.

2. Experimental section

2.1. Materials

Polished test grade silicon wafers were purchased from General Research Institute for Nonferrous Metals, China. Octadecyltrichlorosilane (OTS, $CH_3(CH_2)_{17}SiCl_3$, 95%) and PS (The average weight molecular mass (M_w) was 31,600 g/mol and the polydispersity (M_w/M_n) was 1.04.) were purchased from Aldrich. Toluene (99%, anhydrous) was from Beijing Chemical, China and all the regents were used without further purification.

2.2. Microcontact printing of OTS

Silicon wafers were cleaved into pieces approximately 2 cm × 2 cm, and cleaned by immersion in a piranha solution (7/3 (v/v) of 98% H_2SO_4 and 30% H_2O_2) at 90 °C for 30 min and then rinsed with deionized water several times and blown dry with nitrogen. The microcontact printing process was done in a homemade glove box with a nitrogen atmosphere and the humidity was 40 ± 1%. A PDMS stamp was soaped with a 0.2 wt% solution of OTS in toluene and blew dry with nitrogen and kept contact with the pre-cleaned silicon wafers for 30–60 s. Then, the pattern was transferred onto the underlying substrate. Fig. 1 showed the two PDMS stamp geometries used in this study. One is the striped pattern with the width of ridges 10 μm, the height of ridge 1.2 μm and the wave periodicity of 20 μm. Another one is squared pattern with the squares' width 10 μm and the depth 1.1 μm.

2.3. Sample preparation

Thin PS films were deposited onto patterned OTS-covered SiOx substrates by spin coating from a dilute solution (0.8 wt%) of the PS in toluene. The thickness of the polymer film was controlled by the spin-coating speed varying from 2000 to 4000 rpm. The initial thickness of the films was determined by carefully scraping some of the polymer away from the surface with a razor blade and then measured the height difference between the substrate and the surface of the film by the use of AFM topographical image. The average film thickness was 46 ± 2 nm. Cleaning and coating was preformed in an ultra clean workstation and a homemade glove box was used to minimize the influences of dust and particles.

2.4. Dewetting process and morphology characterization

2.4.1. Optical microscopy (OM)

After spin coating, the sample was kept at 60 ± 5 °C for 24 h in vacuum oven to remove any residual solvent. Then, the sample was annealed at 170 °C for various times in a

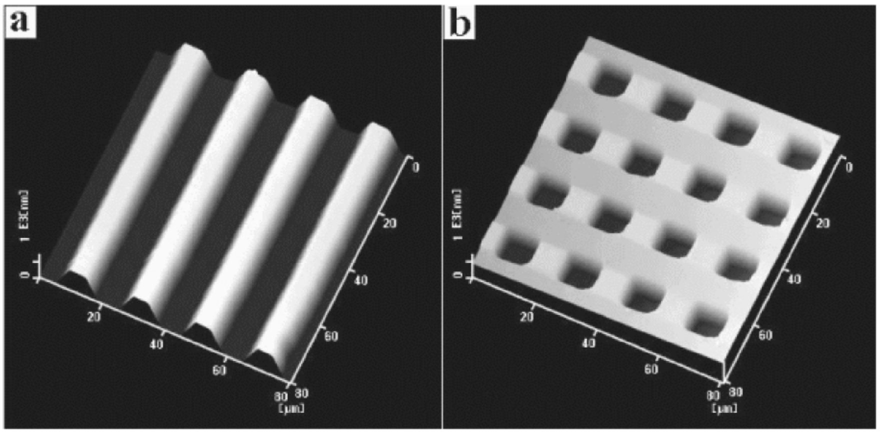


Fig. 1. PDMS stamp geometry: (a) Stripes. The width and the height of the protruded stripe are 10 and 1.2 μm, respectively. The spacing between the two stripes is 20 μm. (b) Square. The hole is 10 × 10 μm in width and 1.1 μm in depth.

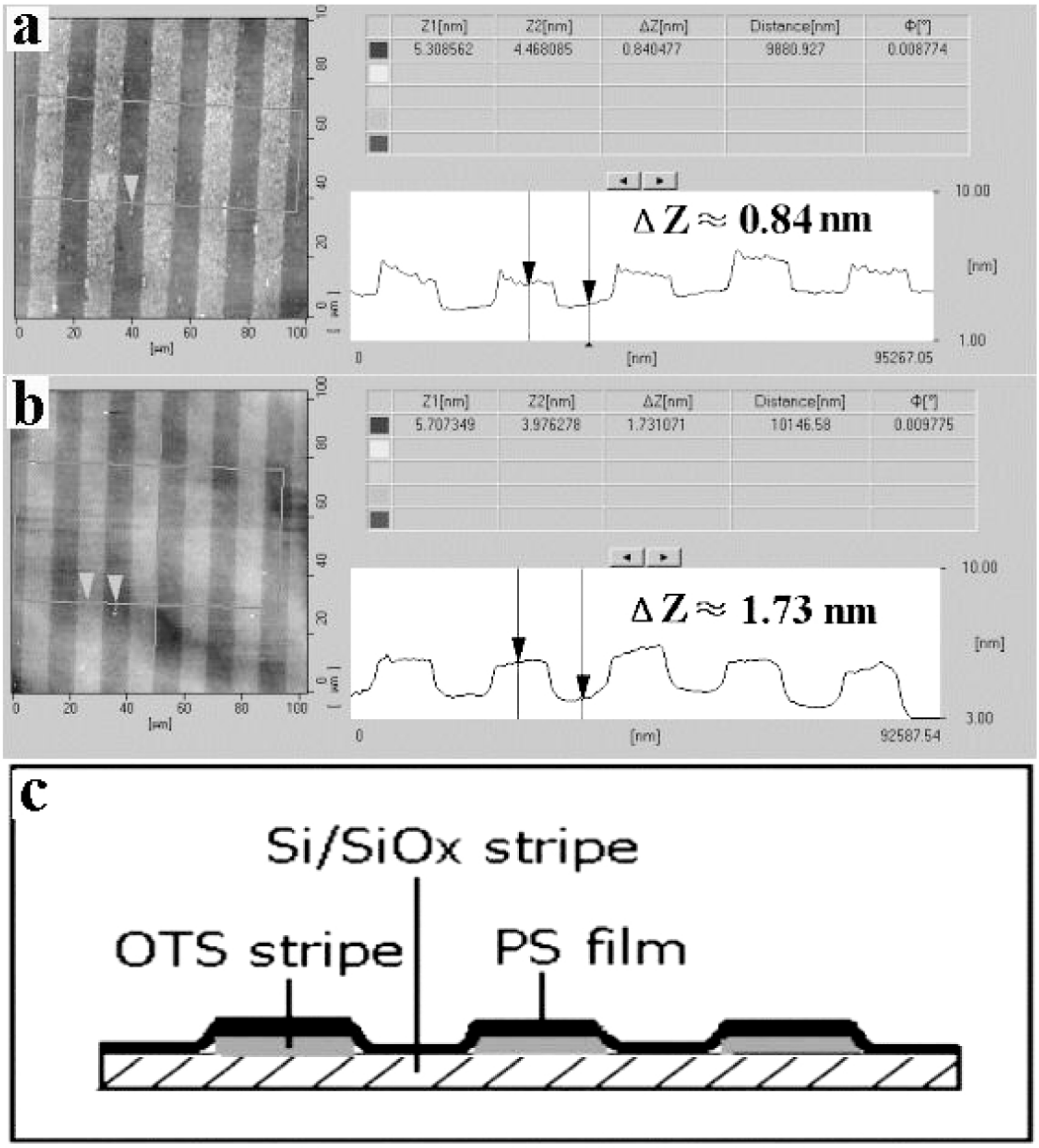
Linkman hot stage and was imaged simultaneously by the use of Leica optical microscopy in reflection mode with a CCD camera attachment. The annealing times range from 0.5 min to 1 h and longer time annealing was done in vacuum oven. Rim and hole topography showed a high contrast due to differences in height. Holes appear as lighter areas, and rims appear as darker areas in the optical micrographs.

2.4.2. *Atomic force microscopy (AFM)*

The PDMS stamp and dewetting morphology were imaged by SPI3800N AFM (Seiko Instruments Inc., Japan) in contact mode. A triangular cantilever with a standard pyramidal Si_3N_4 tip was used.

2.5. *Patterns transfer*

The final dewetting pattern can be transferred onto the PDMS elastomer. The details of how to make a PDMS elastomer mold have been described elsewhere [23]. Casting prepolymer, Sylgard 184 on the dewetting pattern and curing at 65 °C for 4 h, after peeled off, the PDMS molds with relief structures as negative replicas of the dewetting structures are formed.



	Z1[nm]	Z2[nm]	ΔZ[nm]	Distance[nm]	Φ[°]
■	5.308562	4.468085	0.840477	9880.927	0.008774

	Z1[nm]	Z2[nm]	ΔZ[nm]	Distance[nm]	Φ[°]
■	5.707349	3.976278	1.731071	10146.58	0.009775

Fig. 2. AFM cross-section analysis (average line profile) of (a) OTS SAM/SiOx stripes pattern, (b) PS film on OTS/SiOx stripes pattern before dewetting, (c) schematic diagram of the thin polymer film on an OTS/SiOx patterned substrate.

3. Results and discussion

3.1. Dewetting on the stripe-patterned substrate

Because the OTS is more wettable for PS films than SiOx, the PS films on OTS stripes are thicker and appear darker under the optical microscopy than those on SiOx stripes. The thickness difference between the OTS stripes and the SiOx/Si stripes can be calculated from the AFM cross-section analysis (Fig. 2). Before spin-coating PS, the height difference between the OTS stripes and the SiOx/Si stripes is approximately 0.84 nm (Fig. 2(a)), and after spin coating of PS, the difference become ca. 1.73 nm (Fig. 2(b)). Therefore, the film thickness difference of PS on the OTS stripes and the SiOx/Si stripes is about 0.89 nm (1.73 − 0.84 nm). Fig. 2(c) schematically shows the height contrast between the OTS and SiOx stripes after deposition of PS.

Soon after the film was annealed at 170 °C for 0.5 min, dewetting was initiated. Unlike Sharma's 3-D simulation results [5–7], in which the dewetting started with local depression on the center of the less wettable stripes, in our study, the film rupture initiated at each of the boundary between the more wettable stripes (OTS) and less wettable (SiOx) stripes by the formation of holes (Fig. 3(b)). In the meantime, the film surface away from the boundaries remained undisturbed and flat. The microscale wettability contrast (chemically heterogeneous) and the height contrast (physically heterogeneous) between the OTS and SiOx stripes may explain these phenomena. When heated above the glass transition temperature (T_g), the films on the boundaries became the most sensitive parts to the nucleation dewetting. As a result, the hole formed along the boundaries as shown in Fig. 3(b). (Although differentiating true spinodal dewetting from heterogeneous nucleation dewetting requires a careful consideration of kinetic data of the dewetting structure, for the relatively thicker film ($t \approx 45$ nm) in our study, we believe that the film is spinodally stable or the spinodal parameter is weak, and the films rupture through nucleation. See Xie et al. [22] and Kargupta et al. [7]). Once a hole is formed, it grows on the substrate due to both the conjoining pressure near the contact line and the surface tension force engendered by the circumferential curvature of the hole. Because there are numerous nucleation sites (and therefore numerous holes) along the boundary of both kinds of stripes, these growing holes coalesce along the stripes and form straight rims as seen in Fig. 3(c). These rims contracted towards the center of the stripes because of the surface tension force engendered by the rim curvatures. The rim moving velocity on the high wettable OTS stripe is slower than that on the less wettable SiOx stripe. The rims on the SiOx stripes have coalesced and formed PS lines at the stripe center, while the rims on the OTS stripes have just met and not coalesced yet (Fig. 3(e)). After further annealing, all the rims coalesced and finally formed PS lines and rested on the center of each stripe. The pattern evolution process can be seen more clearly in the cross-section analysis image (In Fig. 4 curve c, d and f correspondence to the images c, d and f in Fig. 3, respectively). From Fig. 4, we can see that the initial ditches (curve c) first shrank to form the moving rims (curve d), and then the rims coalesced and formed PS line (curve f) on the

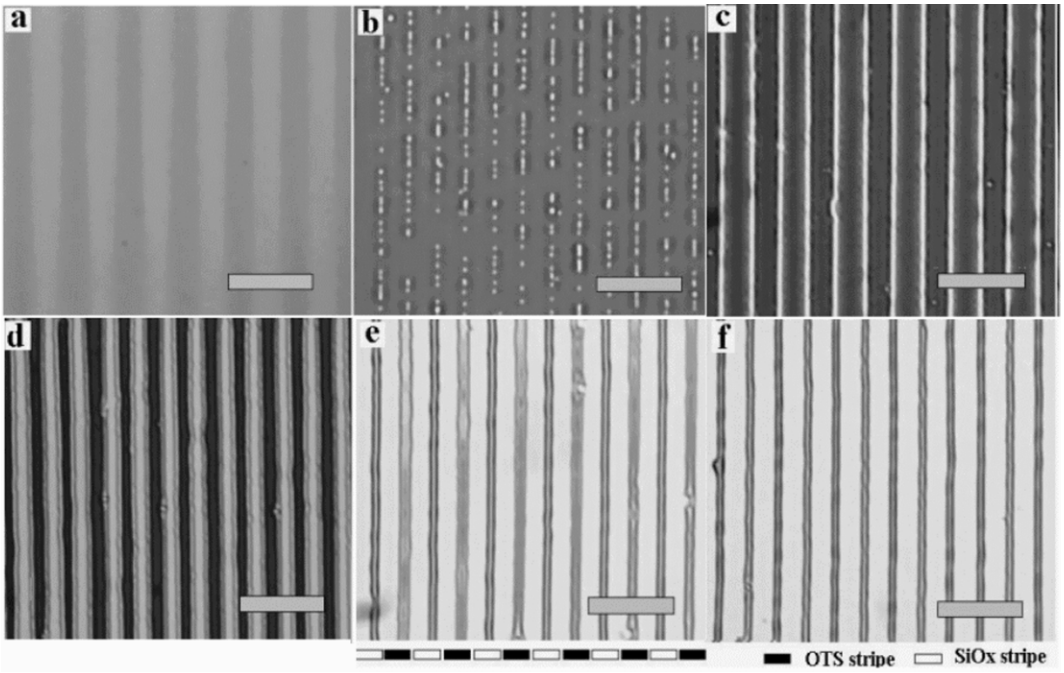


Fig. 3. Morphology evolution of the 45 nm thin PS film on OTS stripe-patterned substrate. The substrate has alternating OTS stripes and SiOx stripes. The film was annealed at 170 °C for 0 min (a), 0.5 min (b), 1 min (c), 5 min (d), 8 min (e) and 40 min (f), respectively. The scale bar is 30 μm.

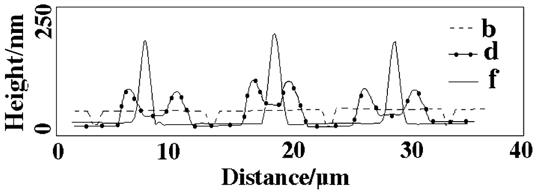
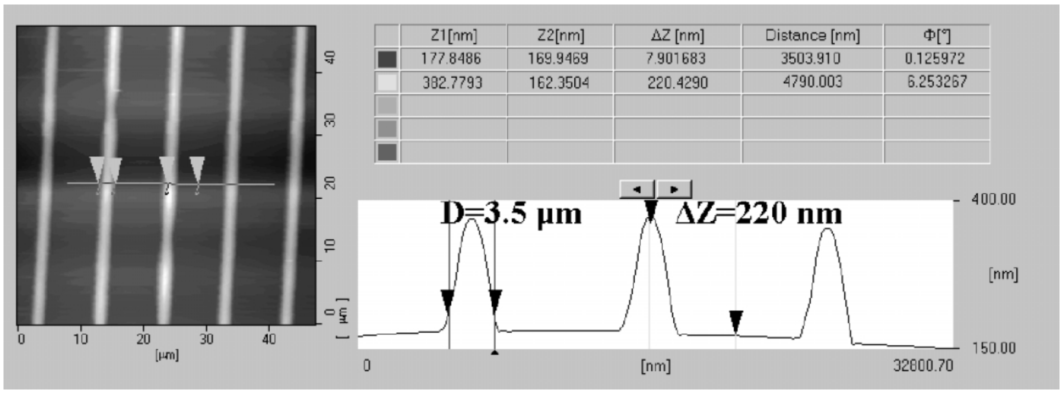


Fig. 4. AFM cross-section analysis (average line profile) of the PS film morphology evolution process on three consecutive stripes. Curve (c), (d) and (f) correspond to the image (c), (d) and (f) in Fig. 3.

stripes. There are no complex structure formed during the retraction of the rims and this is another evidence which confirms that the thick film in our study is spinodal stable. Otherwise, some secondary structures would form ahead of the moving rims and the contact line would not be straight [7]. The final dewetting morphology was shown in Fig. 3(f). Those so-called quasi-steady structures (PS lines) remained stable for a long time and did not disintegrate into droplet array even after annealing at 170 °C for 120 min. But we believe that they will break into drops for longer annealing time due to the Rayleigh instability. The dewetting film pattern was a replication of the substrate pattern and a good templeting achieved. We found that the film pattern replicated the surface pattern only if all the dewetting was initiated by the wettability and height difference between the stripes before the nucleation of the thin film on other parts of the stripes started. In Fig. 3(f), we can also observe other interest phenomena: the final dewetting pattern is much smaller than the original PDMS stamp pattern. As shown in Fig. 1(a), the original stamp has a pattern of 10 μm (in width) with protruded and recessed stripes. Fig. 5 is the cross-section analysis of the image of Fig. 3(f). We found that after dewetting, the polymer film transferred onto the center of the stripes as a result of mass conservation and the polymer lines are about 3.5 μm in diameter and 220 nm in height. This result shows that the pattern direct dewetting is not only an appropriate method to pattern thin polymer film with high degree of order, but also a good way to reduce the size of the micropattern.

3.2. Dewetting on the square-patterned substrate

The transient morphology evolution of 47 nm thin PS film are shown in Fig. 6. As mentioned earlier, on physicochemically patterned substrate, dewetting was initiated by the microscale difference of height and wettability. As a result, on a square patterned substrate with alternating SiOx (recessed squares) and OTS (grids), the film rupture on the square occurred by the formation of holes around the square periphery after heated at 170 °C for 1 min (Fig. 6(b)). Later, these holes coalesced and formed the moving rims. The shape of the moving rim from square changed to circular. Finally, a droplet formed in the center of the square. Note in this regard that the edge of the square in contact with the polymer acts as a defect-like site from which the mass is driven away. Meantime, the dewetting on the OTS area also proceeded as the dewetting on the Si squares had occurred for some time. A faster rim growing velocity on the Si squares than on the OTS areas was obviously observed from the growing process shown in Fig. 6. This might be a result of the lower wettability of the square area (Si). Like on the Si square, on the OTS area, the film rupture on the edge of the OTS grids occurred by the formation of holes around the grids' edges. Later, these holes coalesced and formed the moving rims. With increasing annealing time, the square moving rims contracted inwards the OTS area and the square became larger and larger. At this time, most of the PS moved to the corners of the four squares due to mass accumulation (Fig. 6(e) insert showed a moving rim before most of the mass coalesced at the corner of the squares.). Finally, the moving rims met and formed oval-shaped PS lines between the two adjacent square and larger spherical droplets formed at the corners of the four squares due to mass accumulation. The final dewetting pattern (Fig. 6(f)) resembles the 2-D image of a face-centered cubic structure. No further transient morphology was observed even after annealing at 170 °C in a vacuum oven for 36 h. The structure in Fig. 6(f) appears to be equilibrium one. Another interest finding in Fig. 6(f) is that the drops located at the middle line between two



	Z1[nm]	Z2[nm]	ΔZ [nm]	Distance [nm]	Φ[°]
■	177.8486	169.9469	7.901683	3503.910	0.125972
□	382.7793	162.3504	220.4290	4790.003	6.253267
■					
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Fig. 5. The cross-section analysis (average line profile) of the image in Fig. 3(f). After dewetting, the polymer lines were about 3.5 μm in diameter and 220 nm in height.

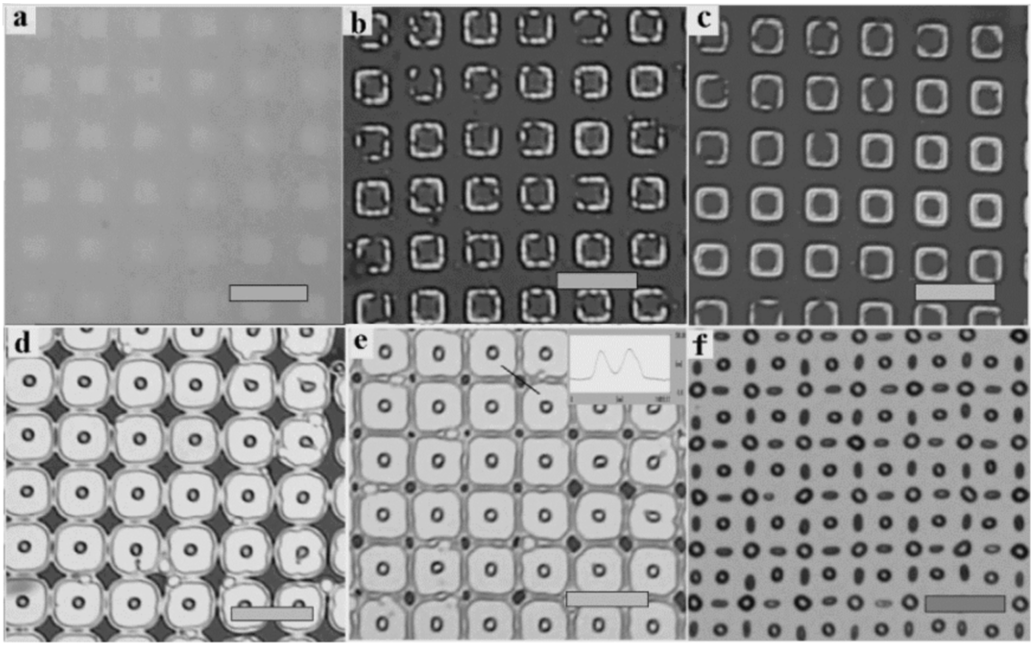

Fig. 6. Morphology evolution of 47 nm thin PS film on OTS squares patterned substrate. The substrate has alternating OTS and SiOx squares. The film was annealed at 170 °C for 0 min (a), 0.5 min (b), 1 min (c), 8 min (d), 12 min (e) and 20 min (f), respectively. The scale bar is 30 μm.

squares are oval shape rather than the circular shape drops at four corners of the squares. We believe that the polymer would need an excessive energy to change the overall shape to circular shape. The overall shape drops may be kinetically stable in our study, though the spherical drop may be thermodynamically stable in general surface wetting phenomena.

3.3. Patterns transfer

The final dewetting pattern can be transferred onto the PDMS elastomer. Casting prepolymer, Sylgard 184 on the dewetting pattern and curing at 65 °C for 4 h, after peeled off, the PDMS molds with relief structures as negative replicas of the dewetting structures were formed (Fig. 7). Comparing Fig. 7(a) with Fig. 1(a), it can be found that for the striped-pattern, the width of the trench shrank from 10 to 3.5 μm. While for the original squared-pattern (Fig. 1(b)), after dewetting and pattern transfer, more complex structures like Fig. 7(b) are formed. It illustrated that the dewetting provided a new way to reduce the pattern size and change the pattern morphology. These PDMS elastomer can be used as stamp in soft lithography for future pattern process.

4. Conclusion

In conclusion, we show a fast and reproducible process that can pattern thin polymer film at micrometer scale by

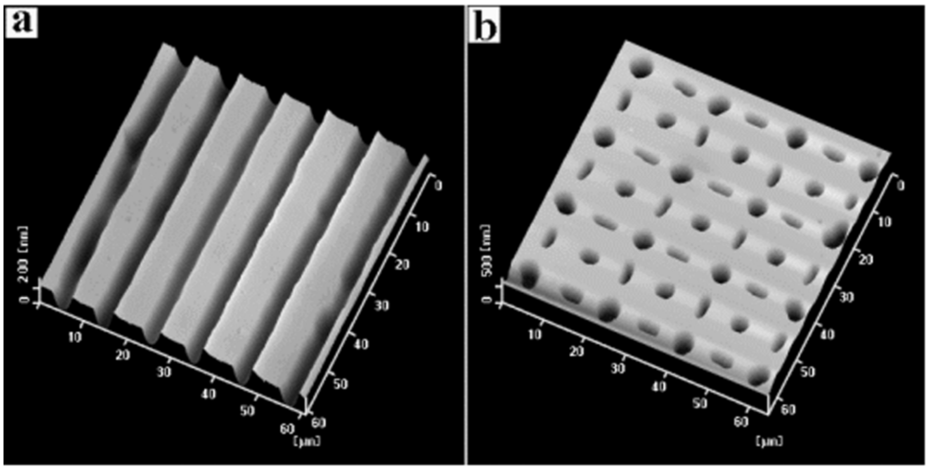

Fig. 7. Dewetting pattern was transferred onto the PDMS elastomer. Image (a) and (b) are negative replicas of Figs. 3(f) and 5(f), respectively.

regularly patterned SAMs as template to direct the dewetting of thin polymer film. In principle, the process shown here could be extended to other material deposited on a partially wetting surface. Complex pattern can be achieved by using simple PDMS stamps. These patterned polymer films can be transferred onto the elastomer mold or used in future microfluid device. It can also be used as resists for ion etching to transfer pattern to the underlying substrate.

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