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Contact Line Pinning by Microfabricated Patterns: Effects of Microscale Topography

Yevgeniy V. Kalinin^{1,*}, Viatcheslav Berejnov², and Robert E. Thorne³

¹School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY USA

²Department of Mechanical Engineering, University of Victoria, Victoria, B.C. Canada

³Physics Department, Cornell University, Ithaca, NY USA

Abstract

We study how the microscale topography of a solid surface affects the apparent advancing and receding angles at the contact line of a liquid drop pinned to this surface. Photolithographic methods are used to produce continuous circular polymer rings of varying cross-sectional size and shape on hydrophilic silicon wafer surfaces. Drops of water and glycerol are dispensed into the areas bounded by these rings, and critical apparent advancing and receding angles are measured and correlated with the parameters that characterize the ring cross-section. For much of the examined parameter space, the apparent critical angles are independent of ring height and width and are determined primarily by the slope of the ring's sidewalls, consistent with a model due to Gibbs. For ring heights below a few micrometers, the critical angles decrease below the values predicted by the sidewall slopes alone. These results provide data for calculation of hysteresis on naturally rough surfaces, and demonstrate a simple method for controlling and enhancing contact line pinning on solid surfaces.

Keywords

Contact line; pinning; asperities; contact angle; contact angle hysteresis; drop; roughness; Gibbs inequalities

Introduction

The contact angle of a liquid drop dispensed onto a solid surface is not unique but can vary over a finite range. As pointed out more than a half century ago, the roughness of the surface influences this range of contact angles ^{1, 2}. A simple argument following from the work of Gibbs ^{3, 4} can be used to estimate the effect of roughness.

A contact line will not advance (recede) on a flat surface until the contact angle reaches the critical advancing (receding) contact angle θ_a (θ_r). The difference between these angles $\theta_r - \theta_a$ gives the contact angle hysteresis, which characterizes the strength of the pinning that inhibits drop motion relative to the surface. Suppose that the contact line reaches a region of the surface (an asperity) that is inclined at angle ϕ with respect to the average surface plane, as illustrated in Fig 1. In this region the local advancing contact line will not displace until the local contact angle measured with respect to the inclined surface exceeds the critical advancing angle θ_a . The apparent maximum advancing angle (Figure 1 (a)) measured with respect to the

* yvk2@cornell.edu .

original plane will then be $\theta_a^* = \theta_a + \phi$. Similarly, the minimum apparent receding contact angle (Figure 1(b)) will be reduced by ϕ : $\theta_r^* = \theta_r - \phi$, ($\theta_r^* \geq 0$). The contact angle must thus satisfy

$$\theta_r^* = \theta_r - \phi \leq \theta \leq \theta_a + \phi = \theta_a^*, \quad (1)$$

known as the Gibbs inequalities⁵. Oliver *et al.*⁴ verified the increase in maximum apparent advancing angle at the edges of millimeter-high pedestals for a wide range of liquids.

Shuttleworth and Bailey⁶ and Bikerman⁷ invoked this mechanism to explain contact angle hysteresis on real surfaces, which have roughness on length scales extending from atomic dimensions to perhaps a few tens of micrometers. If the scale of the roughness is small, then an observer will measure the apparent contact angle relative to the average surface plane, rather than the local (or "true") contact angle. However, if the scale of the roughness is too small, the limits of the Gibbs inequalities observed with macroscopic asperities may not be reached. An understanding of how pinning depends upon the dimensions of asperities is thus important for understanding hysteresis on both natural and engineered surfaces.

Experiments using a variety of liquids and solid surfaces have explored how surface topography affects contact line pinning and liquid spreading. Mori *et al.*⁸ examined spreading of oleyl alcohol and diethylene / ethylene glycols on surfaces with microsteps, formed either by cleaving mica or by depositing a gold layer on an otherwise flat surface. Extrapolating from their data, they suggested that steps smaller than 30–50 nm would be ineffective in pinning the advancing line. A similar result for AgI was obtained by Ottewill *et al.*⁹. Ondarcuhu *et al.*¹⁰ studied liquid polystyrenes on annealed alumina surfaces. Steps with heights as small as 2–10 nm pinned the receding line, and the critical step size required for effective pinning increased with the radius of gyration of the polymer. Abbott *et al.*¹¹ studied pinning by self-assembled monolayer films on gold that were scratched using a scalpel. Scratches $\sim 0.1 \mu\text{m}$ wide pinned less strongly than $\sim 10 \mu\text{m}$ wide scratches. Dejonghe *et al.* studied spreading of liquid tin at 1173 K on Si/SiO₂ and found that steps $1.5 \mu\text{m}$ high and with walls sloped at 90° created using photolithographic techniques did not pin effectively¹².

Aside from the step height dependence¹³, the apparent angles may depend upon the radius of curvature at the edge separating low and high slope surface regions⁴ and upon the roughness of the edge^{14, 8}. Miller *et al.* studied wetting of PTFE films by water¹⁵ and found that vacuum-deposited thin films with steps of height on the order of 80 nm significantly affected spreading. For steps with RMS roughness values of 84 nm, the advancing angle was consistent with the Gibbs inequality while the receding angle was not. The variable (and often ill-characterized) lateral scale and correlations of the surface roughness in these previous experiments have made detailed quantitative studies — that might lead to a general model relating surface roughness and contact angles^{16, 17, 18, 19} — difficult.

Here we explore contact line pinning by microscale asperities through systematic study of liquid drops confined by micropatterned rings. We use photolithography to fabricate continuous millimeter diameter rings with widths from $4 \mu\text{m}$ to $\sim 50 \mu\text{m}$, heights from $\sim 0.2 \mu\text{m}$ to $\sim 5 \mu\text{m}$, and having well-defined and well-characterized cross-sectional shapes. Figure 1 gives a schematic illustration of rings with trapezoidal and rounded cross-sections, and Figure 2 shows actual ring profiles as measured using a scanning electron microscope (SEM), a focused ion beam (FIB) and an atomic force microscope (AFM). After filling the rings with liquid we determine the critical apparent contact angles θ_a^* and θ_r^* that correspond to drop depinning, and correlate these angles with the parameters that characterize the ring cross-section. Pinning increases with the slopes of the walls, but decreases when the ring thickness is reduced below $\sim 2 \mu\text{m}$. Microscale rings provide a simple way to enhance pinning of drops

to surfaces. They can improve reproducibility of physical and chemical processes that occur inside drops, and simplify automated image analysis of the evolving drop contents²⁰.

Materials and methods

Pattern fabrication

Rings were fabricated on flat p-doped Si wafers (<100> orientation, 100 mm diameter, 525 μm thick). The wafers were washed in boiling Nanostrip® mix for 3 minutes to remove organic residue and render their surfaces hydrophilic. The final wafers provided a chemically uniform and exceptionally flat substrate. The surface is hydrophilic, with water contact angles immediately following treatment close to 0°. A strongly hydrophilic substrate surface ensures that liquid dispensed within a ring will spread to the ring. It also makes contact line depinning from the ring easy to detect, as the liquid rapidly spreads once the line leaves the ring.

Ring patterns prepared using CAD software (L-Edit, Tanner Research, Inc.) were printed on masks using an optical pattern generator capable of $\sim 1\ \mu\text{m}$ lateral resolution. Si wafers prepared as described above were spin-coated at 1000 rpm to 6000 rpm with Shipley S1800 series photoresists, based upon Novolac diazoquinone. Photoresists of increasing viscosity (S1805, S1813, S1818, S1827) were used to create films of increasing thickness from 0.2 μm to 5.3 μm . Spin-coated wafers were baked on a hotplate, placed in an EV620 contact aligner, and exposed with a broadband UV dose (365–405 nm) through masks held in soft contact. The exposed films were then developed in metal-ion-free developer (AZ-300MIF) and post-baked on a hotplate. The exact times and values for the process depended upon the photoresist. Table 1 gives some sample process parameters and the resulting advancing and receding contact angles for water. The thickness of each film was measured using a Rudolph FTM optical interferometer. Figure 3 (a) shows an optical image of a patterned wafer while Fig. 3 (b) shows an optical image of a ring.

The photoresist film thickness determines the height of the fabricated rings. Deviations from the average thickness over the central portion of the wafer (away from the edge bead) are a few percent. AFM images show that the films are smooth with a height roughness of less than 10 nm over lateral distances of about $\sim 1\ \mu\text{m}$ (data not shown). Since the rings have heights of $\sim 200\ \text{nm}$ and larger, this roughness is unlikely to be important in pinning liquid contact lines. Rings of the same geometry (height, width and wall slopes) fabricated using different photoresists (e.g. more viscous S1818 and less viscous S1813) yielded critical contact angles that were the same within our experimental error of ± 4 degrees, as shown in Table 2.

Creating steep walls

Exposure in soft contact mode was used to produce rings with steep sidewalls having average slopes that do not depend upon the film thickness²¹. To verify this, a Zeiss Supra 55VP SEM operating at 0.8–0.9 keV acquired images of fabricated rings, first with the substrate perpendicular to the line of sight and then with the substrate tilted at 30° (Figure 2 (a)–(c)). For a substrate perpendicular to the line of sight, the sidewall slope $\tan(\phi)$ can be determined by dividing the ring height by the measured difference in the apparent widths of the top and bottom of the rings. For a substrate tilted at angle τ , the slope is calculated using

$$\tan(\phi) = \frac{\sin(\tau)}{\frac{l}{h} - \cos(\tau)} \quad (2)$$

where h is the ring height (film thickness) and l is the measured width of the projection of the sidewall at this tilt angle (Figure 1 (d)). The resulting angles ϕ are listed in Table 2.

SEM, FIB and AFM images (e.g., Figure 2 (d) and (f)) show that the walls are not, in fact, perfectly flat, but exhibit multiple submicrometer steps that run along the circumference of the ring. These steps, known as edge fringes, result from diffraction of the incident and reflected UV light ²¹. In addition, the corners of the ring (corresponding to B and C in Figure 1(c)) are not perfectly sharp, but have a radius of curvature of roughly 200 nm.

Creating "rounded" walls with smaller slopes

Sidewalls with smaller slopes were obtained by increasing the separation between mask and substrate to ~10–30 μm . With this "proximity mode" exposure, the light spreads out after passing through the mask, smearing the sharp border between exposed and unexposed areas on the substrate ²¹. Profiles of these rounded rings were difficult to characterize with SEM. Instead, tapping mode AFM images were acquired using a Digital Instruments Nanoscope IIIa controller and a multimode head equipped with MicroMasch CSC12/3 AFM tips, which have a full tip cone angle of less than 20° and a tip height of 15–20 μm . Tips with small cone angles provide accurate imaging as long as this angle is smaller than $90^\circ - \phi$, where ϕ is the sidewall angle. Figure 2(g) shows AFM cross-sections of proximity mode rings. For a 30 μm mask-substrate separation, most sidewall angles are close to 28° .

Additional variation in ring shape could be obtained by increasing the developing time. The surface layers of photoresist dissolve more slowly than those closer to the substrate, an effect known as surface inhibition ²². This effect can be used to create "mushroom"-shaped structures. By increasing the developing time for ~2.6 μm high rings of S1827 from 47 s to 77 s, some overhang was obtained, but unfortunately the ring perimeter developed substantial roughness. This prevented effects due to the increasing wall steepness to be separated from those due to perimeter roughness.

Contact angle measurements

Maximum advancing contact angles were measured using the century-old tilting plate method ²³. This method is well suited to studying drops with very large contact angles on flat surfaces. It is less sensitive to isolated ring defects than the method of overfilling liquid on a horizontal substrate ⁴, because it reduces the contact line length that reaches the critical angle just before depinning. The maximum advancing angles obtained by these methods should be comparable ²⁴

Starting with the substrate horizontal, a small liquid volume was dispensed onto the area surrounded by a ring, and then the substrate was rotated 90° to a vertical orientation. The drop was photographed and the advancing angle measured from the photograph. If the contact line did not depin from the ring at 90° , the substrate was rotated back to 0° and the drop removed with a pipette. Another drop about 2 μl larger in volume was dispensed onto the same area and the process repeated until the maximum drop volume for which the contact line remained pinned at 90° was determined. Figure 4 shows images of horizontal and vertical drops. The maximum apparent advancing angle θ_a^* before depinning at 90° was determined at this volume from the contact angle at the lowest point on the advancing edge (Figure 4(b)), where contact line motion began. Minimum receding angles were determined by removing the liquid with a pipette on a horizontal substrate. If all the liquid could be removed to leave only a thin film bounded by the ring (as in Figure 4(c)), then the apparent receding angle was assumed to be 0° . Contact angles measured using a goniometer typically have accuracies of no better than $\pm 2^\circ$ ²⁵. Contact angle data presented here are averages over at least three measurements, having a typical standard deviation of roughly 4° . Consistency of results was verified by superposing drop images from successive measurements.

To confirm that the contact angles measured as described above were not affected by, for example, mechanical vibrations, contact line depinning from the ring was examined by imaging at 6000 frames per second or higher using a Phantom V7.1 digital high-speed camera. High-speed imaging (Figure 5) shows that the maximum instantaneous contact angle achieved immediately prior to depinning agrees with the contact angle obtained by tilting and visual measurement, which averages over any fluctuations. Figure 5(a) shows one such image of a drop, and Figure 5(b) shows how the drop boundary, obtained from a sequence of images, evolves as the drop slips off of a ring. For drops pinned to larger rings, when liquid is removed to measure receding angles the thin film can break. High speed imaging shows that the contact line remains pinned to the ring, and the break occurs via dewetting from the Si wafer surface within the ring and within roughly 100 μm of the ring.

Measurements were performed using HPLC-grade water and glycerol, liquids having similar surface tensions, somewhat different densities, and viscosities, differing by a factor of ~ 1000 .

Results

Contact angles on bare wafers

The maximum advancing contact angle for water on hydrophilic Si wafer surfaces was close to 0° , but varied somewhat with fabrication process details. Contact angles grew with time following fabrication, presumably due to surface contamination, increasing to 10° and sometimes more over a period of roughly 1–2 months. This contrasts with contact angles for water pinned to rings, which showed no variation with time over a two month period and no variation with the contact angle of the substrate.

Contact angles on photoresists

Table 2 gives the advancing and receding contact angles for water on uniform films of several photoresists within the same family. Photoresists, like most organic polymers, are somewhat water permeable. Water absorption may change the contact angles, as has been observed with the polyimide Kapton²⁶. Our experimental tests showed that when a drop was left on the surface for several minutes, film pinning properties did not change and the film beneath the drop did not swell, although AFM measurements of tip force versus distance were somewhat modified. Thus, during the three minutes required for a typical contact angle measurement, the effects of water absorption on the properties of the film can be neglected. The maximum advancing and receding angles of glycerol on photoresists were roughly 63° and 18° , respectively.

Pinning by the boundary between a hydrophilic wafer disk and a surrounding continuous photoresist film

To examine drop pinning by an edge at which the surface steps up in the advancing direction, hydrophilic bare wafer holes were fabricated in an otherwise continuous photoresist film. In this case the contact line may be pinned either at point A or at point B in Figure 1(c) (as the liquid advances from the left of A; C and D are very far from A and B). Pinning at point A may occur due to the surface energy difference while pinning at point B may occur due to the changing slope of the film (and perhaps also due to any surface energy difference between the sidewall and top of the film). The pinning strength may depend upon the curvature at point B^{27, 8, 10} and upon the film thickness^{28, 29}. However, we find that for photoresist thicknesses between 0.4 μm and 5.4 μm , the maximum apparent advancing angle corresponding to contact line depinning matches the advancing angle measured on uniform unpatterned photoresist films, and does not depend upon film thickness. The step up in the advancing direction provided by a hydrophilic hole in a continuous film thus does not enhance pinning of the advancing line. This is consistent with the purely geometric considerations of Gibb's inequality Eq. (1), which

predicts that the maximum apparent advancing angle at the hole's edge (corresponding to point B in Figure 1(c)) will be the same as the advancing angle on a flat surface.

Pinning by rings with trapezoidal cross-sections

Unlike holes, rings have both an inner edge (providing a step up in the advancing direction) and an outer edge (providing a step down in the advancing direction) with which to pin the contact line. For a ring with a trapezoidal cross-section having sufficiently sharp edges as shown in Figure 1(c), as the ring is filled with liquid (on the left side of the ring in Figure 1(c)), the contact line will eventually move across the ring's flat top from B to C and become pinned at its outer edge C. From Eq. (1), the maximum apparent advancing angle at this edge will be larger than that at the inner edge B by the sidewall angle ϕ . The outer edge then controls depinning of the advancing contact line. The critical apparent advancing angle should then be independent of the ring width given by the distance between the inner and the outer edges at the top of the ring¹. When the substrate is inclined, the advancing line will be pinned at the outer ring edge and the receding line will be pinned at the inner edge, producing a small drop distortion that depends on the ring width.

We find that the maximum apparent advancing angles are indeed much larger than those obtained on films with holes (when there is only a single edge) or on uniform unpatterned films. As shown in Table 2, maximum advancing angles θ_a of water drops on unpatterned photoresist films are ~ 80 – 90° ; on films patterned with rings, the maximum apparent contact angles θ_a^* can be more than 150° . For glycerol drops, the maximum advancing angle increased from 63° on an unpatterned S1827 photoresist film to 130° on films patterned with rings. The comparable increases seen with water and glycerol suggest that the origin of the increase is primarily geometric, as assumed by the Gibbs' inequalities. For both water and glycerol, the receding angle on films patterned with rings decreased to 0° in all cases.

Figure 6(a) shows how the critical advancing angle θ_a^* for water varies with ring radius R , for fixed ring height h , width and sidewall slope. The critical angle θ_a^* is independent of R over the examined range from 1.4 to 4.5 mm, corresponding to drop volumes from 5 μl to $\sim 100 \mu\text{l}$. Since the drop volume and radius strongly affect the drop's mechanical response to external vibrations, this suggests that the measured maximum contact angle is not reduced by external mechanical noise and is a robust measure of drop pinning.

Figure 6(b) shows that the maximum apparent contact angle is independent of the ring width in the range 4–50 μm . This is consistent with the simple considerations that lead to Eq. 1, and implies that the outer ring edge is responsible for the enhanced pinning provided by rings.

Dependence on ring height

Figure 7 shows how the apparent advancing angle for water depends upon ring height. For heights beyond $\sim 2 \mu\text{m}$, the apparent advancing angle is roughly independent of height, but for smaller heights the apparent advancing angle decreases with decreasing height. This same height dependence was observed for rings of widths between 4 and 50 μm . A similar height dependence was observed for glycerol. This suggests that ring breaks or other defects are not responsible for the height dependence. No obvious ring defects were visible in an optical microscope, although defects at the outer ring edge may be important. Pinning of drops to holes in continuous films does not depend upon film height, confirming that the outer ring edge is responsible for pinning of the advancing line.

¹At least for rings whose width is small compared to the drop diameter. For inclined drops, distortions caused by pinning of the advancing (receding) contact line at the outer (inner) ring edge may affect the contact angles.

In contrast with the advancing angle, the apparent receding contact angle is independent of ring height down to $0.4\ \mu\text{m}$. In all cases, the drops could be reduced to thin films, corresponding to a receding angle of 0° . Since $\theta_r - \phi$, the difference between the receding angle on the unpatterned substrate and the sidewall angle, is less than 0° , a significant reduction in pinning strength is required before any effect on the receding contact line and contact angle becomes evident. For ring heights below $0.4\ \mu\text{m}$ it became difficult to form films, and depinning from the rings may have been masked by dewetting of the substrate.

Dependence on sidewall slope

According to the Gibbs inequalities Eq. 1, the critical apparent advancing angle should be the sum of the advancing angle on a continuous film and the angle of the ring sidewall. Consequently, increasing the sidewall steepness should increase the critical apparent advancing angle. To check this, we fabricated trapezoidal rings in contact mode with steep sidewall angles of $\sim 55^\circ$, and somewhat rounded rings in proximity mode with sidewall angles of $\sim 28^\circ$ measured at roughly half the ring height and $\sim 45^\circ$ measured immediately above the substrate. Experimentally, large slopes confined to a small height ($<1\ \mu\text{m}$) in the immediate vicinity of the substrate are less effective in pinning the contact line, as one would expect from ring height dependence in Figure 7. As a compromise, the sidewall angle at half the ring height was used to characterize the sidewall slope of proximity mode rings. Rings with steeper sidewalls do indeed pin the advancing line more strongly, with apparent advancing angles decreasing from 165° for contact-mode rings to $\sim 133^\circ$ for proximity mode rings.

However, as shown in Figure 8, the measured critical apparent advancing contact angles are in general somewhat larger than are predicted using the Gibbs inequalities Eq. (1) and the measured sidewall angles and critical advancing angles on uniform films, so that contact line pinning is stronger than predicted.

Discussion

The present results show that the maximum advancing contact angles of liquid drops on solid surfaces can be greatly increased using microfabricated patterns. The key is to provide an outer edge (a step down in the advancing direction) with a steep sidewall to which the advancing line can pin. As qualitatively predicted by the Gibbs inequalities Eq. 1, the outer edge of a microfabricated ring increases the maximum apparent advancing angle measured with respect to the substrate plane relative to that observed on a flat substrate uniformly coated with the ring's material; a step up in the advancing direction (as provided by a bare disk on an otherwise flat coated substrate) has no effect on the maximum advancing angle. The size of the advancing angle increase is proportional to the sidewall angle. This increase is a geometric rather than chemical effect, with comparable increases in maximum apparent advancing angle obtained for water, detergent solutions and glycerol.

However, we find two significant departures from the predictions of Equation 1. First, as shown in Figure 8, pinning by rings with heights greater than $\sim 2\ \mu\text{m}$ is unexpectedly strong, with the maximum advancing angle for water exceeding the prediction of Eq. 1 by roughly 20° . The reason for this is unknown. One possible explanation is pinning by edge fringes, visible in the SEM and AFM images of Figure 2(a, d and f). These result from interference of incident UV light and the light reflected from the substrate during exposure of the photoresist. They have a characteristic size of $\lambda/2$ or $\sim 200\ \text{nm}$, sufficiently large to provide some pinning. Another possibility is that the advancing angle on the sidewall may differ from that on a continuous film, perhaps due to differences in the chemistry of exposed and developed photoresist from unexposed photoresist. Overdeveloping the rings can result in edge roughness⁸ and in an overhanging lip²², and these could increase pinning, although SEM images provided no evidence for these features.

A second discrepancy with the simple considerations of Gibbs that lead to Eq. 1 is shown in Figure 7. The maximum advancing angle, while being independent of ring height for heights larger than $\sim 2 \mu\text{m}$, decreases with decreasing ring height at smaller heights. Decreases in the strength of contact line pinning when the height of surface features (e.g., associated with steps or roughness) becomes small have been observed in a variety of experimental systems^{8–12}, with the characteristic size scale varying from $\sim 1 \mu\text{m}$ to $\sim 10 \text{ nm}$. Proposed origins for this decrease include the finite thickness of the liquid-vapor interface^{31, 32, 12, 33}, van der Waals forces between the liquid-vapor surface of the drop and vapor-solid surface of the substrate³³, mechanical vibration of the drops^{27, 13} and, in the case of liquid polymers, the viscoelastic properties of the liquid¹⁰.

For water at room temperature, the thickness of the liquid-vapor interface is on the order of 1 nm ³⁴, too small to account for our observed decrease in pinning strength at the micrometer scale. Simple calculations show that van der Waals attractions between the liquid-air surface and the substrate-air surface are also far too small to reduce the strength of contact line pinning at the micrometer scale.

Mechanical noise and resulting drop vibrations can drive contact lines past asperities of any size, provided that their amplitude is large enough, and could in principle account for the height dependence of pinning^{27, 13}. Ambient noise levels have been found to cause reductions in the maximum advancing angle of a few degrees³⁵. While vibrations may reduce the time-averaged contact angle (as measured by eye) at which depinning occurs, they should not prevent the instantaneous contact angle from reaching the extreme value observed in the absence of vibrations. As shown in Figures 5(a) and (b) we used high speed imaging at frame rates of 6000 fps to examine the dynamics of the contact line at depinning. Image time series show that the maximum instantaneous contact angle reached before the line locally depins is equal to the angle determined in time-averaged measurements (whose results are shown in Figure 6–Figure 8.) Thermally generated vibrations may allow the contact line to depin from defects smaller than $\sim 0.1 \mu\text{m}$ ³³, but their amplitude is likely too small to appreciably affect pinning to micrometer high rings.

Defects in rings such as gaps or scratches, regions of reduced thickness, or surface contamination could be more important for rings of small height. However, maximum advancing angles did not depend upon ring width, and were reproducible for different rings having the same height. If the outer ring edge is not sharp, then the contact line may meander on the edge and the apparent angles may depend upon the degree of meandering³⁰.

Another possibility is that there is a characteristic size for the metastable local jumps of the contact line as it advances across the ring and down its sidewall, and that the maximum advancing angle decreases when the ring height becomes smaller than this characteristic size.

Conclusions

The present work provides additional insight into the nature and origin of contact angle hysteresis. Microfabricated 3D ring structures provide good control over relevant dimensions of micrometer scale features that pin a liquid contact line, and allow systematic study of how these dimensions affect advancing (and receding) contact angles. Rings even a few micrometers high provide large enhancements in maximum advancing angles over uniform films and films patterned with holes for all liquids studied, and the enhancement is primarily a geometric rather than chemical effect. As ring heights are decreased below $\sim 2 \mu\text{m}$ this enhancement decreases. The origin of this decrease and its characteristic size is unknown. A more detailed examination of the actual depinning process, including the evolution of the shape

of the contact line and its position on the sidewall with increasing substrate inclination, may be useful in resolving this mystery.

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Figure 1.

Pinning of a drop's contact line by a microfabricated ring. (a) At the advancing edge of the drop, the contact line is pinned by the ring's outer sidewall, producing an apparent advancing angle θ_a^* much larger than the local angle θ_a . (b) At the receding edge, the large contact angle θ_r formed with the inner sidewall prevents drop dewetting when θ_r^* is small. (c) Geometry for measurement of the ring sidewall angle ϕ .

Figure 2.

(a)–(c) SEM images of rings fabricated in soft contact mode, acquired with the substrate at a 30° inclination. Dashed lines A, B and C correspond to the lines A, B and C seen in cross-section in Figure 1(c). The distance between lines A and B as seen in Figure 2 corresponds to the variable l in Figure 1(c). (b) and (c) have the same ring heights but different widths while (a) and (b) have the same widths but different heights. (d) A view of the sidewall roughness (evident in (a) at original resolution) at higher magnification. This roughness may be due to edge fringes. (e) Cross-section of a ring fabricated in soft contact mode. The ring was cut and then imaged using a focused ion beam (FIB). The substrate inclination angle is 45° . (f) Amplitude AFM image of the sidewall of a ring fabricated in soft contact mode, showing

fringes similar to those in (d). (g) AFM profile of a ring fabricated in proximity mode, with a larger separation between the photomask and substrate than in (a)–(f).

Figure 3.

(a) A Si wafer with an array of ring patterns (b) One of the circular patterned areas shown in (a). R indicates a 24-sided polygonal S1827 photoresist ring $50 \mu\text{m}$ wide and with a radius of 1.4 mm . W_i indicates the hydrophilic wafer surface onto which the drops are dispensed. W_o is the hydrophilic wafer surface that surrounds the ring, which allows easy detection of depinning events from the ring. P is the surrounding photoresist. The water drops shown in (a) reside in the areas marked as W_i in (b). Drop pinning experiments using these polygonal rings and using circular rings gave identical results.

Figure 4. Sample images of water drops pinned to rings. (a) A 160 μl water drop pinned to a 6.0 mm in diameter ring on a horizontal substrate. (b) A 72 μl water drop pinned to a ring 6.0 mm in diameter on a vertically oriented substrate. (c) A thin water film produced by withdrawing liquid from the drop. The corresponding contact angle is assumed to be zero.

Figure 5.

High frame rate images of drop depinning. (a) Side view of a vertically-oriented drop acquired less than $166\ \mu\text{s}$ before the advancing line depins. The advancing angle is $\sim 127^\circ$, consistent with observations by eye. (b) Superimposed contours of the drop after depinning, obtained from a series of frames $166\ \mu\text{s}$ apart. The leftmost contour corresponds to the drop shown in (a). The solid black contour shows the drop immediately after depinning. Depinning starts at the ring, and the drop boundary just above the ring moves at $\sim 0.1\ \text{m/s}$.

Figure 6.

Maximum apparent advancing angles θ_a^* for water on trapezoidal rings fabricated in soft contact mode versus (a) ring radius R (with a fixed width of $8 \mu\text{m}$) and (b) ring width w (with a fixed radius of 3 mm), for ring heights of (▲) $2.8 \mu\text{m}$, (■) $1.2 \mu\text{m}$, and (▼) $0.5 \mu\text{m}$. The dashed lines are guides to the eye.

Figure 7. Critical apparent advancing angle for water on trapezoidal photoresist rings (fabricated in soft contact mode) as a function of ring height. The ring radius and width were kept constant at 3.0 mm and 4.0 μm , respectively.

Figure 8.

Maximum apparent advancing contact angles θ_a^* for water versus outer ring sidewall inclination angle ϕ (Figure 1). Numbers beside each data point indicate the ring height in micrometers. The unfilled circle ($\circ$) is the measured contact angle for a drop on a bare wafer disk surrounded by a continuous photoresist layer. Filled circles ($\bullet$) are for rounded rings of heights greater than 2 μm fabricated by exposing the photoresist in proximity mode. Triangles ($\blacktriangle$) are for rings with trapezoidal cross-sections fabricated in soft contact mode. The solid line shows the prediction of the Gibbs inequality (1) obtained from the measured advancing angle on a uniform photoresist film and the measured angle ϕ .

Table 1

Sample process parameters for different photoresists, used to obtain rings of increasing height but with comparable sidewall slopes. Flat films of all resists gave similar advancing θ_a and receding θ_r contact angles, with a small dependence on the post-bake time.

Photo-resist	Spin speed and duration	Prebake	Exposure dose	Development time	Postbake	Final thickness	θ_a	θ_r
S1805	4000 rpm for 30 s	115°C for 45 s	20 mJ/cm ²	40 s	115°C for 60 s	0.50 μ m	81°	21°
S1813	4000 rpm for 30 s	115°C for 60 s	33 mJ/cm ²	45 s	115°C for 60 s	1.1 μ m	83°	27°
S1818	3000 rpm for 30 s	115°C for 70 s	42 mJ/cm ²	70 s	115°C for 60 s	1.9 μ m	81°	33°
S1827	4000 rpm for 30 s	115°C for 90 s	56 mJ/cm ²	80 s	115°C for 60 s	2.8 μ m	78°	28°
S1827	1500 rpm for 45 s	115°C for 120 s	84 mJ/cm ²	150 s	115°C for 60 s	4.5 μ m	78°	28°

Table 2

Comparison of measured critical apparent advancing θ_a^* and receding θ_r^* contact angles of water drops on rings of height h , microfabricated in contact mode from photoresists (PR), with those predicted by the Gibbs inequality Eq. (1) using the measured advancing θ_a and receding θ_r angles on uniform photoresist films, and the film sidewall angle ϕ determined by SEM measurements

h (μm)	PR	θ_a ($^\circ$)	ϕ ($^\circ$)	$\theta_a + \phi$ ($^\circ$)	θ_a^* ($^\circ$)	θ_r ($^\circ$)	$\theta_r - \phi$ ($^\circ$)	θ_r^* ($^\circ$)
0.5	S1805	81 ± 4	55 ± 6	136 ± 7.2	118 ± 4	21 ± 4	-29	0
			52 ± 6	133 ± 7.2	122 ± 4		-28	0
			48 ± 6	129 ± 7.2	122 ± 4		-26	0
1.1	S1813	83 ± 4	47 ± 6	130 ± 7.2	127 ± 4	27 ± 4	-19	0
2.5	S1827	78 ± 4	57 ± 6	135 ± 7.2	154 ± 4	28 ± 4	-24	0
2.8	S1827	78 ± 4	53 ± 6	131 ± 7.2	165 ± 4	28 ± 4	-21	0
			60 ± 6	138 ± 7.2	165 ± 4		-25	0
			60 ± 6	138 ± 7.2	145 ± 4		-25	0