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Focused Laser-Induced Marangoni Dewetting for Patterning Polymer Thin Films

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(Additional Supporting Information may be found in the online version of this article.)

**ABSTRACT**

Highly-localized focused laser spike (FLaSk) heating of polymer thin films is a resist- and developer-free alternative to 2D laser direct write for creating patterns on the single micron or, by exploiting overlap effects, submicron scale. The massive temporal and spatial thermal gradients and resulting thermal Marangoni stresses generated by FLaSk are an effective means for the directed dewetting and patterning of such films. Here, the general applicability of this technique to glassy amorphous polymer thin film systems is investigated through systematic investigation of film thickness, glass transition temperature, and polymer mobility. The results reveal that the important parameters are the film thickness (coupled to the optical heating effects through anti-reflection coating effects) and the high-temperature polymer melt mobility, allowing for generation of single features with linewidths of down to ~1 μm. Further, the introduction of spatial mobility variations by using polymer brushes, bilayers, and microphase separated block copolymers leads to additional profile manipulation effects (i.e. spontaneous 2D pattern generation and flattened top profiles).

**KEYWORDS:** Thermocapillary forces, Dewetting, Laser direct write, Block copolymers, Polymer thin films
INTRODUCTION

Dewetting has been utilized as a method to generate nanopatterns in thin films$^1$, including metals$^{2-5}$ and polymers$^{5-9}$ through film-instability-based self-assembly, most typically by heating a thin film over a large area provided by a global heat source (e.g. a hotplate or oven) or by a defocused pulsed laser. Additionally, in polymer systems, the evolution of dewetting profiles of uniform and multilayer thin films has been used as a metrology method for determination of the polymer mobility. In these studies, the behavior is primarily dominated by the driving forces of prepatterned$^{10-13}$ or fluctuation-induced gradients$^{14}$ in film height, $h$. Though considered less frequently, similar effects can be induced by gradients in the fluid properties (i.e. surface tension, $\gamma$, and viscosity, $\eta$) of the film, as expressed by the general 2D lubrication equation:

$$\frac{dh}{dt} = -\nabla \cdot \left( \frac{h^2 \nabla \gamma}{2\mu} + \frac{h^2}{3\mu} \left( \nabla^2 h \right) \right)$$

(1)

The physical implication of (1) is that gradients in surface tension can be expected to generate mass transport until balanced by the thickness gradient terms. This effect, referred to as the thermocapillary or Marangoni effect causes mobile polymer to be driven from areas of lower surface tension to higher surface tension. This was utilized for arbitrary pattern generation in polymer thin films by Ellison and coworkers$^{15}$ through the direct patterning of surface tension by lithographic UV breakdown of PS, which, when subsequently melted, would form positive-tone replicas of the mask pattern used to generate the pattern. Troian and coworkers$^{16,17}$ similarly employed the coupling of surface tension and temperature, as characterized by the (generally) negative Marangoni coefficient, $\delta \gamma / \delta T$, for the patterning of PS. In this case, vertical thermal gradients (~50 K µm$^{-1}$) were employed for the formation of large area semi-regular nanopillar arrays generated by growth of spontaneous fluctuations at some dominant feature wavelength.

In both of the above examples, the entire polymer film was processed in the melt state and was therefore at a relatively uniform viscosity. To the authors’ knowledge, the significance of viscosity gradients has yet to be specifically investigated, but the coupled forces of surface tension gradients and viscosity gradients are necessarily in play during thermocapillary effect experiments that are driven by horizontal thermal gradients. In this case, only regions of the film above the glass transition, $T_g$, are sufficiently mobile to undergo dewetting, such as was recently demonstrated by Rogers and coworkers$^{18}$ for the displacement of a protective small-molecule thin film coating above nanotube circuits using resistive heating. While the driving forces due to surface tension and height gradients, are expected to dominate and were shown to well-predict the evolved profile in the small-molecule case, the viscosity of polymer films can vary by orders of magnitude near $T_g$ and likely will have a large effect on the evolution and final thickness profile of the polymer film.

Heating via wide-area laser beam excitation allows for not only control of the temperature of a sample, but also provides a fine degree of control of the temporal heat input. Though employed by the semiconductor community for many years, laser spike annealing (LSA) has only recently been translated into soft matter systems by Ober, Thompson, and colleagues.$^{19-21}$ We have extended this concept to a high
resolution laser direct write process, called focused laser spike (or FLaSk, illustrated in Figure 1) annealing. In this way, the LSA also incorporates sub-micron spatial control and allows for extreme gradients exceeding 1000 K µm⁻¹, two orders of magnitude greater than previously employed. These massive temporal and spatial thermal gradients and resulting thermal Marangoni stresses in polymer thin films generated by FLaSk annealing are much greater than the driving forces associated with conventional dewetting and can therefore be used as an effective means for the rapid directed manipulation of soft matter. We have employed FLaSk as a way to induce dewetting of homopolymer films and, at sub-dewetting doses, the ordering and alignment of the block copolymer (BCP) domains in single-microdomain thick films. This method has since been used by others to study, for example, the Marangoni-stress-induced rupture of liquid films and patterning of molten amorphous silicon. Most recently, an intermediate method between LSA and FLaSk has been used by Majewski and Yager to accomplish similar alignment using a focused line source for laser zone annealing of a BCP film via swept line heating scans.

In our prior work, we presented the dewetting of thin polymer films (e.g. polystyrene (PS)) as a grayscale form of resist-free positive-tone lithography. In LSA of polymer thin films, one key aspect of the process is that the films, being so thin, are essentially kept at thermal equilibrium with the underlying semiconductor across their whole thickness. In the case of FLaSk dewetting, however, the polymer film affects the heating of the semiconductor (and thus the polymer) due to its nanoscopic thickness which creates an anti-reflection coating (ARC) effect. During dewetting, since the local polymer film thickness determines the amount of incident laser excitation that is locally absorbed, this ARC effect becomes time-dependent, effectively coupling the surface temperature to the extent of dewetting.
In this prior work only a single thickness and a single polymer type and molecular weight were studied, however, it was clear that the intrinsic properties of the film (optical, thermal, and fluid) in this coupled process determined not only the shape of the film height profiles, but also led to interesting overlap effects from nearby (multiple) line scans. The patterns formed from dense line arrays resulted in subwavelength gratings independent of the laser spotsize. This behavior, along with a desire to possess the greatest possible degree of control in the patterning and transition to other polymer systems, makes it desirable to explore the effects of different polymer attributes on the resulting dewetted profiles. Here we explore the effects of (i) thickness, (ii) molecular weight, (iii) various polymers, (iv) the use of a brush layer or a bilayer film, and (v) solvent swollen films.

**EXPERIMENTAL**

**Thin Film Preparation**

The experimental parameters explored are summarized in Table 1. Lightly doped p-type silicon substrates ([100] orientation, 10 Ω·cm) were coated with various polymer films: three PS films of different MW (35 kg mol⁻¹, Aldrich, 280 kg mol⁻¹, Aldrich, 900 kg mol⁻¹, Fluka), one polyvinylacetate film (PVAc 50 kg mol⁻¹, Alfa Aesar), one polyvinylpyrrolidone film (PVP 630 kg mol⁻¹, Alfa Aesar), and one block copolymer film (polystyrene-b-polydimethylsiloxane, PS-b-PDMS, 42 kg mol⁻¹, 26.2% PDMS, Polymer Source). All films were cast from 1.8 wt% solutions of propylene glycol monomethyl ether acetate (PGMEA) or butanol to prepare films of 50-110 nm thickness by spin coating. The film thickness was determined by ellipsometry with a J. A. Woollam Co. M-2000D spectroscopic ellipsometer. For the samples where a brush layer was employed, the wafers were first coated with hydroxyl terminated polystyrene (3 kg mol⁻¹, Polymer Source) and heated to 170°C for 16 hrs in a vacuum oven. The wafers were then rinsed with toluene to remove the unreacted brush component before application of the polymer thin film which would undergo FLaSk.

**FLaSk Annealing**

FLaSk zone annealing was performed using circularly polarized 532 nm light from a
Coherent Verdi V10 diode pumped solid state laser system. Power was controlled by the system controller and measured with a power meter (Newport 818-UV) using an in-path partially reflecting mirror placed before the lens. The power meter was also positioned after the objective to determine the amount of light that reached the sample relative to the standard positioning of the meter. The objective lens used was a Zeiss LD Achromplan 20X objective with a numerical aperture of 0.4. The last optic before the objective was a green dielectric mirror, allowing for simultaneous imaging in transmission via a camera mounted above the stage with red and near-IR light from a white light source. Motion of the sample for direct write was controlled by a Physik Instrumente PIMars™ piezostage with 300 μm of travel on all three axes mounted on a PI M-686 stage for larger motion. Both the stage and an electronic shutter were controlled by a LabView program. All lines were patterned at a speed of 100 μm s⁻¹. Since the focus of the laser had to be set manually, patterns were done as a grating with the focal point shifted vertically by 300 nm (about 1/10 the axial height of the focal spot) between lines (Figure S1). Analysis of the resulting patterns indicated optimized focus as the most “intense” (i.e. most-dewetted) lines in the grating. This is also where the atomic force microscope (AFM) thickness profile measurement was taken. A solvent vapor environment was established for patterning of a PS-b-PDMS film in the same way as previously described. Samples were surrounded with a trough of toluene, with the vapor pressure controlled to ~85% of saturation by a cut glass cover to provide ~140% increase in swollen film thickness for up to 30 min of patterning. For all experiments, measurement was conducted up to a power the profile height plateaued or, as will be indicated, where laser induced damage of the substrate occurred as seen by visible plasma in the patterning video feed and also by permanent scarring of the underlying silicon. This damage occurred at laser powers corresponding to >1400 °C surface temperature, the melting point of silicon.

Imaging

AFM imaging was performed with a Veeco Dimension 3100. Analysis of results was performed with an automated MATLAB script which averaged each 1D profile of 3-5 2D line scans for each power and extracted the heights (depths) and FWHM of the ridge (trench) structures along with the accumulated variance. The variance of these averaged 1D scans was used as the error bars for the experimental results and includes effects of (1) slight changes in focus between adjacent lines, (2) instability in the power during 2D line scans, and (3) any non-uniformity in the films from debris etc. The overall feature height, \( h_f \), was taken as the sum of the trench depth and ridge height (i.e. \( h_f = h_t + h_r \)), while the feature width, \( w_f \), was taken as the sum of the trench FWHM and 2x the mean ridge FWHM width (i.e. \( w_f = w_t + 2w_r \)), see Figure 1b.

Simulations

Simulations of the FLaSk process were conducted using the commercial package COMSOL Multiphysics for thermal finite element method simulations. The light source was modeled with the analytical form of a Gaussian-shaped optical excitation, with spatially mapped reflectivity based on the film height profile as an ARC. Thermally-dependent optical absorptivity and thermal conductivity of the doped silicon were used. For the thermal simulation, the effects of the boundary were mitigated by extending the limits of the
FIGURE 2 (a) Evolution of film height profile for a typical sample (80 nm PVP 630 kg mol\(^{-1}\)) at different laser powers. (b) Normalized thickness profiles, \(H(Y)\), versus normalized width, \(Y\).

simulation cell to the point where setting the boundary to a constant temperature would no longer affect the simulated profile. This amounted to a 100 μm radius hemisphere of simulated substrate.

To simulate time evolution, a MATLAB wrapper was employed to incorporate the generated profile into a finite difference simulation of (1), using temperature-dependent surface energy\(^{31}\) and temperature and thickness-dependent viscosity\(^{32}\) functions for PS from the literature. After a height profile change of 3 nm or a translation of 100 nm was reached, the time-independent thermal profile was recalculated for the new ARC profile by the finite element simulation. This method implicitly assumes the following: (i) thermal transport occurs faster than and (ii) independent of materials transport, and further, (iii) that the substrate is always at a thermal steady state. We note that condition (i) is definitely not the case in the early stages of the heating, or else optical damage of the substrate, as will be discussed later, would occur in almost all cases, condition (ii) is the least reasonable assumption overall as the heated polymer must necessarily dissipate its thermal energy to the surrounding material, and condition (iii) disregards the thermal tail that occurs in the temporal profile due to finite thermal dissipation time (though this tail rapidly drops below the \(T_g\)). Nevertheless, this simplified method can be expected to at least aid in developing intuition for the dynamical evolution of \(h(t)\). Movies of a simulated dewetting process are included as Movie S1 (T-profile) and Movie S2 (h-profile), Supplementary Information.

RESULTS

For the various film parameters investigated in this work, we considered three measures of the profile: (i) the final profile shape and the power evolution of the (ii) height and (iii) width of the feature. In the case of (i), it was determined that the profiles (beyond the lowest power lines) when normalized by the total height and width of the feature (i.e. \(H(Y)=h(Y)/h_f, Y=y/w_f\)), rapidly converged to a single universal profile shape for a given set of parameters (Figure 2),
FIGURE 3 Evolution of profiles for PS films with MW 280 kg mol$^{-1}$ for various film thicknesses: (a) the maximum profile height ($h_f$) versus power, (b) the combined profile FWHM ($w_f$) vs. power, and (c) normalized profile shapes at the highest measured power. A weak secondary ridge feature that occurs in thicker samples is highlighted by arrows in (c). Laser induced damage occurred in the case of the 77 nm film at powers >280 mW.

as has been shown for stepped features.$^{11}$ Such normalized profiles are very useful for comparison purposes.

**Influence of Film Thickness**

The effect of an intermediate refractive index material (for most polymers, 1.4≤$n$≤1.8) on a higher refractive index material (for silicon, $n$~4.1) results in an oscillatory anti-reflective coating (ARC) effect, with the maximum substrate/film reflectivity of ~35% occurring at zero thickness of polymer. As previously identified, there are several distinct regimes of ARC thickness: (I) less than the ideal ARC thickness (where the substrate reflection increases with decreasing thickness and decreases with increasing thickness), (II) near the minimum-reflectivity (~8%) ARC thickness (where the substrate reflection increases with any sizable thickness change), (III) greater than the ideal ARC thickness, but significantly less than the second peak reflection point (where the substrate reflection decreases with decreasing thickness and increases with increasing thickness), and (IV) near the second peak thickness (where the substrate reflection decreases with any sizable thickness change). At any thickness near or greater than regime IV,
Influence of Polymer Molecular Weight

The importance of molecular weight for various properties of polymers (most critically here, its influence on the glass transition and melt viscosity) is well known. To assess the effects of this parameter, four PS samples (18 kg mol\(^{-1}\), 35 kg mol\(^{-1}\), 280 kg mol\(^{-1}\), and 900 kg mol\(^{-1}\)) were patterned. These are all above the entanglement molecular weight (\(M_e \approx 13 \text{ kg mol}^{-1}\)).\(^{33}\) The corresponding \(T_g\)s are \(\approx 90^\circ\text{C}, \approx 95^\circ\text{C}, \approx 100^\circ\text{C},\) and \(\approx 105^\circ\text{C}\) respectively.\(^{34}\) Figure 4 shows the evolution and final normalized profiles for regime I films (less than ideal ARC thickness). [Note: regime (II) and (III) for the 35 kg mol\(^{-1}\) and 900 kg mol\(^{-1}\) samples are shown in Figure S2].

**Influence of Polymer Type**

The ability to use different polymers is desirable for several reasons including for use of non-toxic deposition solvents and to optimize etch resistance. A result of changing polymer chemistry is, of course, a change in polymer properties, most notably the \(T_g\). Of course, the surface tension, \(\gamma\), and the Marangoni coefficient, are also affected, but for
FIGURE 5 Evolution of height profiles for low $T_g$ (PVAc) and high $T_g$ (PVP) films alongside PS films of comparable MW for film thickness ~50 nm: (a) $h_f$ vs. power, $w_f$ vs. power, and (c) normalized profile shapes at the highest measured power. Laser induced damage occurred in the case of the PS 900 kg mol$^{-1}$ sample at powers >330 mW and in the PVP film at powers >300 mW.

hydrocarbon polymers, these properties tend to remain within ±20%. Additionally, the polymer-substrate interaction would be expected to change, however, as will be discussed, such driving forces are relatively small compared to the extreme thermal gradients generated in FLaSk experiments.

To explore the importance of polymer selection, two glassy polymers, polyvinylacetate (PVAc, $T_g$~30 ºC) and polyvinylpyrrolidone (PVP, $T_g$~170 ºC) were chosen to compare to PS ($T_g$~100 ºC) at two similarly paired MWs: PS 35 kg mol$^{-1}$ : PVAc 50 kg mol$^{-1}$ and PS 900 kg mol$^{-1}$ : PVP 630 kg mol$^{-1}$. Figure 5 shows the evolution and final normalized height profiles for ~50 nm films (i.e. regime I) of these polymers.

**Viscosity Modification via Brush and Bilayer**

An additional method to effect the mobility of the polymer thin films was explored by incorporation of a brush layer on the substrate. We used an ~8 nm (determined by ellipsometry) PS brush layer, which should increase the mobility (or equivalently decrease the effective viscosity) of some finite thickness of the adjacent overlaying PS film. It was confirmed by AFM phase measurement (Figure S3) that the brush remained attached to the silicon substrate after complete dewetting of the polymer film (as determined by when the
FIGURE 6 Evolution of height profiles for PS films with MW 280 kg mol\(^{-1}\) with and without a PS brush layer for film thicknesses ~50 nm: (a) \(h_f\) vs. power, (b) \(w_f\) vs. power, and (c) normalized profile shapes at the highest measured power. The vertical dashed line in c,d indicates highest power where segmented trench profiles occur, AFM scan shown in (d) with a full Z-scale of 45 nm, showing a segmented trench.

measured trench depth is equal to the originally measured film thickness. The evolution and final normalized profiles of PS 280 kg mol\(^{-1}\) with and without the brush are shown in Figure 6.

At low powers, film dewetting produced a segmented profile, with the linewidth varying periodically along the path of the line (i.e. the x-direction). To investigate if this effect could be amplified through a more extreme variation in layered viscosity, a two-layer system of ~40 nm of PS 35 kg mol\(^{-1}\) under a layer of ~40 nm of PVP 630 kg mol\(^{-1}\) was generated by spinning from orthogonal solvent systems (PGMEA and butanol respectively) to generate a regime II (near ideal ARC thickness) film. The segmented profiles persisted to complete dewetting with the observed segment period varying with laser power/feature height. Figure 7 shows the profile parameter evolution.
FIGURE 7 Height and width profiles of segmented line patterns arising from a bilayer film comprised of ~40 nm PS having a MW of 35 kg mol$^{-1}$ covered with a ~40 nm PVP having a MW of 630 kg mol$^{-1}$: (a) $h_f$ vs. power, (b) $w_f$ and segmentation period ($\lambda_p$) vs. power. (c) AFM images for a film written at 280 mW, with a full Z-scale of 95 nm. (d) AFM images for a film written at 325 mW, with a full Z-scale of 130 nm.

**Solvent-Swollen Block Copolymer Thin Films**

Our previous study of the FLaSk annealing of PS-$b$-PDMS revealed the importance of solvent-swelling in driving the thermal gradient-induced ordering of BCP thin films. Toluene is expected to have an influence on the Marangoni stresses through several effects, including (i) sharpening of the thermal gradient by evaporative cooling and (ii) alterations to the thermocapillary and (iii) additional “solvocapillary” effects due to the presence of solvent vapor. Though not the focus of the previous study on PS/PDMS domain ordering via FLaSk, one observation was that in the dewetting regime of FLaSk in the presence of toluene vapor, features were flat-topped, that is, trench-only. This is a potentially desirable effect for lithographic patterning as it can set a maximum height of the film and reduce feature-to-feature interactions. It is rather difficult to study this effect in homopolymer or weakly-segregating BCP films.
FIGURE 8 (a-c) Evolution of profiles for PS and PS-b-PDMS films with comparable MW for film thicknesses ~50 nm: (a) $h_f$ vs. power, $w_f$ vs. power, and (c) normalized profile shapes at the highest measured power. (d-e) Schematic of expected solvent-vapor induced profile reconstruction. (d) In a homopolymer or weakly-segregated BCP system (blue), solvent (orange) allows for complete erasure of the dewetted profile, while in a strongly-segregated BCP (e, second copolymer microdomains shown in green), only small displacements are allowed due to presence of microdomains.

for the simple reason that the increased mobility imparted by a swelling solvent vapor can lead to an “erasing” of features by thickness gradient-driven mass transport once the transient thermal field is removed (Figure 8d), i.e. a refilling and healing of the trench. In the case of strongly-segregated systems, it is possible that the gel-like state of the swollen but still microphase-separated system will, on experimental timescales, immobilize the profile against large transport displacements leading to smoothing rather than erasing (Figure 8e). For this reason, the same PS-b-PDMS films with an underlying PS brush exposed to toluene vapor were investigated for solvent-influenced height profile parameters, with results shown in Figure 8a-c.

DISCUSSION
The studies on the homopolymer films reveal some interesting common behaviors. The most easily observed is the influence of film thickness (Figure 3). One of the key features of patterning by FLaSk dewetting is the coupling between the optical, thermal, and fluid properties of the heated film/substrate system. Changing the thickness of the film greatly affects the ARC
effect which thereby modifies the heating of the silicon substrate as outlined above. As a result, the film thickness had the greatest observed effect on the profile evolution of the homopolymers with some intuitive results. Regime II films demonstrate the narrowest profile widths and require the least input energy to evolve, being near the ideal ARC thickness. In contrast, the regime II and III films, which cool on thickening as they are near or above the ideal ARC thickness, have less variation in the profile widths due to the less-effective heating resulting from the thicker films in these regimes. Less intuitive is the fact that the feature heights, $h_f$, of all films approached a value of 120~140 nm regardless of their starting thickness; this being accomplished by the appearance of an additional weak secondary ridge feature to incorporate displaced polymer at increasing powers (Figure 3c). Further, this apparent maximum height of the film (120~140 nm) is observed in all of the films patterned in this study.

The significance of this maximum height is not immediately apparent. This value could represent an asymptotic approach to the second point of maximum reflectivity (occurring at ~160 nm); however, this does not explain how the film beyond this highest point stays mobile enough to grow the ridge feature. One possible explanation is that as the thickness of the low-thermal conductivity film increases, the thermal dissipation to the substrate from the upper surface region is reduced. The displaced polymer can therefore remain at an elevated temperature longer allowing for the evolution of the profile including formation of the secondary ridge features seen in the regime II and III samples.

To further investigate the mechanism giving rise to the height profile shapes, the thermal profiles were simulated (Figure 9a). As an appropriate point of comparison, the height profile whose trench depth was equal to the initially measured thickness (i.e. when complete dewetting was first achieved) was used. Interestingly, this occurred at roughly the same incident power (275-280 mW) for all three initial film thicknesses. More surprising is that all three samples for a proportional simulated incident power of 98-103 mW (calibrated to optical damage of the bare wafer occurring at 355 mW in experiment vs. 132 mW in simulation) give almost identical thermal profiles for all regime films, with a peak temperature within 3%. This error is well below the experimental error in beam intensity (5%) and far below the associated error in temperature (a non-linear function of power). Further, this similarity in simulated temperature for these final profiles extends over the full experimental range (Figure 9b).

The result that different-regime films produced the same temperature profile for a similar incident power is significant—considering the large bounding range of reflectivity (and thus peak temperature) values between a bare wafer (35%) and an ideal polymer ARC (8%, Figure 9b), one might expect vastly different thermal profiles arising from the different experimental dewetted height profiles. This result suggests that the film dewets to a point where a specific thermal profile is achieved, likely a kinetically-trapped solution of the governing lubrication equation (1) (see Supplementary Movies for co-evolution of the approximate temperature and height profiles).
FIGURE 9 Simulated results of thermal profiles using experimental height profiles. (a) Film height profiles (dashed lines) and simulated in-plane temperature (solid lines) profiles for PS films with MW 280 kg mol\(^{-1}\) in three different film thickness regimes (I, II, III) at experimental conditions associated with complete dewetting. (b) Simulated peak temperatures vs. incident power for bounding conditions of a bare silicon wafer and optimal PS ARC plotted along with plots for the profiles shown in (a). The three experimental height profiles, when used as inputs to the simulation, deliver remarkably close simulated results.

The second general observation is the relative stability of the height profile shape to changes in polymer parameters. Samples prepared using differing molecular weights (Figure 4) or polymer chemistries (Figure 5), both of which change the viscosity and the dependence of the viscosity on temperature (including the large effect of the glass transition), show nearly identical height and width profiles. The only minor differences that can be seen are a slight narrowing of the trench and widening of the ridge at higher molecular weights. This points out an additional observation—the measured behaviors did not appear to correlate significantly with the selection of polymer, but (other than the aforementioned profile effect) did correlate strongly with the MW. More specifically, the three lower MW polymers employed (PS 18 kg mol\(^{-1}\), PS 35 kg mol\(^{-1}\), and PVAc 50 kg mol\(^{-1}\)), showed very similar evolutions in their linewidth and height with variation in the laser power as did the three higher molecular weight polymers (PS 280 kg mol\(^{-1}\), PS 900 kg mol\(^{-1}\), and PVP 630 kg mol\(^{-1}\)), which required higher power and resulted in thinner lines (though, as discussed above, still possessing the same maximum feature height).

This similarity between different polymers occurred despite the fact that there is evidence that the temperatures reached during processing can be greatly different even at the same power. For example in Figure 5, it can be seen that the evolution plot of feature height and width vs. power for the PVP 630 kg mol\(^{-1}\) polymer ends well before the evolution plot of the feature height and width vs. power for the PS 900 kg mol\(^{-1}\) polymer (295 vs. 325 mW), which in turn ends before the PS 280 kg mol\(^{-1}\) plot (325 vs. 340 mW). As the maximum power plotted in these cases signifies the transition from heating to optical damage of the substrate, it is clear that the dynamic thermal environments of these polymers are quite different. This is despite the fact that the samples follow a nearly identical structure-power trend, which, based on the simulated results shown in Figure 9, are merely paths to
achieve the same thermal profile in the underlying substrate that satisfies (1). These results therefore indicate that the only important predictor of the final profile of a particular homopolymer for a given initial film height, power, and substrate is the asymptotic high-temperature melt viscosity (i.e. the prefactor, $K$, of the Vogel equation $\eta = Ke^{D/(T - T_g)}$, which is known to depend strongly on molecular weight and on the entanglement molecular weight. The reason that optical damage (to both the film and underlying silicon substrate) was observed at lower powers for the higher molecular weight and higher glass transition polymers was not that it was necessary to reach the damage threshold of the silicon to displace the polymer, but rather the damage threshold was reached before there was sufficient time to displace the polymer at the asymptotic melt viscosity. As the entanglement molecular weight is generally on the order of 10 kg mol$^{-1}$, this may also explain the shift between the two molecular weight groupings. An odd implication of this phenomenon is that the height profile is, much as the case with the gratings studied in the prior study, independent of the magnitude of the initial thermal spike upon exposure, but rather the temperature of the system will rise to a point sufficient to impart the mobility necessary to reach the final thermal profile perpendicular to the write direction.

Another important consideration is that the lines are evolving in 2D. While it has not yet been possible to predictively generate the experimental profiles, likely due to the complex nature of the characteristic timescale of viscosity evolution, preliminary time-dependent simulations of equation (1) reveal that, in the case of complete dewetting, polymer motion is primarily in the direction ($x$) of the advancing beam due to thermal asymmetry of the ARC-modified spike (Figure S4). This means that polymer is not expected to backfill completely-dewetted lines or greatly affect the surrounding ridge structure after the laser has passed, such as can occur on the introduction of a liquid droplet to an existing trench. This is useful for translating between polymer systems, as it is well known that $T_g$ can vary greatly for even a single polymer as a function of film thickness (e.g. for PS from $~60$ to $~105$ °C for films from $~10$ to $~100$ nm). Further, it is likely that the controlling influence of the asymptotic high-temperature melt viscosity will extend to systems with differing transition behavior, such as crystalline polymers (i.e. much sharper transitions in viscosity) or materials, such as liquid crystalline or weakly-segregating BCPs, that possess order-order or order-disorder transitions, and thus multiple regimes of abrupt changes in melt viscosity. If so, the ability to transition the knowledge learned from one polymer to another should greatly simplify patterning guidelines for a specific targeted application.

The effect of a same-species brush (here PS) was also assessed (Figure 6). Such brush layers have been shown in the past to accelerate dewetting. In such conditions, we find that the height profile shape remains much the same, but the power necessary to achieve a given profile is reduced.

Despite this agreement between expectation and result, the effect of the brush on the dewetting is to a degree counterintuitive—the profile evolution’s insensitivity to polymer type suggests that the driving force due to the extreme gradient exceeds the influence of the
substrate. This is not surprising considering that FLaSk dewetting occurs at a much higher rate than conventional dewetting (transport occurring on the order of μm s⁻¹ vs. nm s⁻¹). For this reason, the influence of the brush may be to additionally affect a film property key to the FLaSk process, though it may be interesting in the future to study more drastic substrate-material interactions (e.g. non-wettable surfaces). As melt viscosity is apparently the most critical parameter, it is likely that the brush layer changes the effective viscosity of the polymer melt, as has been previously suggested.  

As the brush is anchored to the surface, it is expected that the effects of the brush only extend a certain distance into the interior of the film, depending on the MW and grafting density of the brush chains. For this reason, it may be anticipated that at temperatures close to the glass transition, the top and bottom of the film may behave differently before the film is rendered thermally uniform. Consistent with this, it was observed that a pattern of periodically oscillating feature height in the writing direction (i.e. h(x)) was observed at lower powers in the PS film with PS brush (Figure 7c), these “segments” are highly distinct to the line patterns present in other patterning conditions. To further explore this phenomenon, a system which would have highly different mobilities at all temperature ranges was fabricated by placing a high molecular weight polymer on-top of a second low molecular weight, different composition polymer as described above.

Such bilayer systems have previously been studied for both miscible materials such as alloyable metals and two MWs of the same homopolymer and also immiscible polymer systems such as the PVP/PS system used here. The many of the latter studies used combinations of PS and other polymers, including polymethyleneacrylate, poly(2-vinyl pyridine), and poly(4-vinyl pyridine) (P4VP). In these studies, when the top film possessed a higher viscosity than the bottom, it was observed that the dewetting of the top film progressed by displacement of the underlying layer. In the P4VP study, film inversion also occurred given proper kinetics to allow for preferential surface wetting conditions to occur. As compared to these studies, the FLaSk experiment possesses a much greater driving force for dewetting, such that the relative surface energies of the two polymers is likely irrelevant.

The result of laser writing at the same constant speed (100 μm s⁻¹) for the two-component bilayer films was that the oscillating h(x) pattern was extended to all observed powers (Figure 7). Interestingly, the shape of the depressions between the segmented spanning of polymer remained relatively circular irrelevant of power, but their spacing along x became smaller with increasing power. From the standpoint of patterning, this represents a significant increase in capabilities, where now a highly ordered 2D pattern may be implemented by the drawing of a single line in a homogeneous film. Determining a mechanism, however, is made difficult by the lack of knowledge of the compositional structure of the immiscible polymer regions in the dewetted film and remains for future work. Based on the previous results for bilayer dewetting, however, it may be expected that the more-viscous PVP is displacing the PS in the dewetted front, leading to a region of effectively higher MW, which is therefore more difficult to displace (Figure S5). One advantage of the bilayer system is that
additional mechanisms may be incorporated by manipulation of the initially weak polymer-polymer interfacial interaction. From the standpoint of patterning, it is also useful to note that the sequence of the pattern from the initiation feature that occurs during ramping of stage speed (Figure S6) is deterministic. i.e. for a given period, \( \lambda_f \), the center of a segment along \( x \) can be found every \( n\lambda_f + \delta \), where \( n \) is some integer and \( \delta \) is the characteristic size of the initiation, which is an artifact of ramping, dependent on power and response of the motion stage. This suggests that patterning 2D arrayed features should be greatly simplified.

The final tuning parameter investigated was solvent swelling. As discussed above, solvent swelling is not useful for homopolymer films due to erasure of the patterned features, however, the gel-like nature of a strongly-segregated BCP melt (here metastable spherical PDMS micelles in a PS matrix) prevents the full erasure of the thermally driven profile. At the same time, this system also shows the ability to pattern ridge-free structures (Figure 8), though complete dewetting down to the substrate surface was not observed. The mechanism for this likely arises from the fact that this spin coated, unannealed BCP system starts in a metastable state. The net effect is that there is a considerable ability to reorganize and accept displaced polymer by longer-range rearrangement, given sufficient driving energy as was employed for the domain restructuring and ordering in the previous FLaSk zone annealing study. As a result, the displaced polymer can order to both approach the thermodynamically-favorable cylindrical PDMS morphology and also to eliminate costly curvature in the surface of the film, though the displaced ridge material does reshape the trench and likely also results in a very gradual increase in the surrounding film height. While this may appear to be system-specific, the formation of metastable spherical micelles is a general feature of many BCP systems deposited from a selective solvent, and therefore, this behavior can be expected for any system that is sufficiently strongly segregated (e.g. polystyrene-b-poly(4-vinyl pyridine) and polystyrene-b-polysoprene). Further investigation of both FLaSk dewetting and zone annealing will undoubtedly feature other BCP systems that possess various desirable properties for ridge-free patterning (such as low etch contrast within the unpatterned film).

**CONCLUSIONS**

Through the investigation of the resultant material line profiles with changes in polymer and processing parameters, we have determined key mechanisms for the formation of the film thickness profile of polymer thin films induced by a highly spatially and temporally localized heat source (gradient magnitudes of 100-750 K \( \mu \text{m}^{-1} \) and 3,000-75,000 K \( \text{s}^{-1} \) respectively). The coupled optical, thermal, and fluid effects of a focused laser beam incident upon a substrate-supported thin polymer film result in a normalized profile evolution of 1-2 \( \mu \text{m} \) linewidth features relatively independent of the choice of polymer, its glass transition, molecular weight, and the character of the substrate. These parameters did, however, have other effects on the profile evolution: the substrate (bare silicon vs. PS brush on silicon) effects and the glassy polymer molecular weight affected the power necessary to initiate dewetting; the glassy polymer molecular weight affected the non-normalized feature linewidths, while the glass transition temperature only determined whether or not
substrate damage would occur before polymer dewetting. These effects are coupled in that if the polymer could not dewet fast enough on the timescale of optical heating, substrate damage occurred. The only parameter that caused a significant difference in the final profile shape was the polymer film thickness. More specifically, ARC effects led to shifts in the power dependence and the height profile shape itself showed a more complex evolution, adding a weak secondary lateral ridge to the structure. Of the parameters explored, the highest resolution features (nearing 1 μm combined width at full dewetting) occurred at the highest molecular weights with film thicknesses near the ideal ARC thickness (~80 nm).

Simulated heating profiles revealed that these final film shapes all experienced the same peak temperature and thermal distribution. Taken together, these results indicate that not only is FLASk dewetting highly controllable, but its final static results, at least for glassy homopolymer systems, are largely independent of polymer parameters while the dynamics may be to a large extent predicted by asymptotic high-temperature melt viscosity and surface mobility. As one means of controlling these dynamics, the use of a brush layer on the substrate was investigated. This was shown to accelerate the dewetting, reducing the necessary power and thus potentially serving as a means to extend this approach to higher glass transition systems (beyond the high molecular weight, well entangled PVP, \( T_g \sim 170 \) °C, already demonstrated). Further, it was also shown that gradient dynamics induced by layered polymers of differing mobilities (or a mobile brush layer) could lead to more complex 2D height (\( h(x,y) \)) patterns. Finally, it was shown that in a solvent swollen but still microphase separated BCP high-mobility system, the restriction on micron-scale motion (by the still-segregated BCP gel) allowed reconstruction of the profile to eliminate the top ridge. Given all of these mechanisms of control, along with the previously demonstrated use of scan overlap to generate subwavelength patterns, this work opens up the possibility for, in addition to lithographic mask patterning, direct patterning of functional polymer systems which may not be possible via other fabrication methods. In the future, multiplexing and more sophisticated predictive modeling of both the single and multiline 1D and 2D patterns could develop this technique as a viable alternative to other lithographic methods and also continue to provide insight to this fascinating regime of polymer dynamics.

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FIGURE S1 (a) Optical image of typical line series for analysis with $z$ focus increasing from bottom-to-top and power increasing from right-to-left. The region of best focus for AFM analysis is identified by locating where the lines are visible at low power (marked for this image by the white dashed line). (b) AFM image of region of best focus with $z$-scale of 150 nm.
FIGURE S2 Evolution of height profiles for PS films with various MW for film thicknesses (a-c) ~50 nm and (d-f) ~110 nm: (a,d) the maximum profile height ($h_f$) versus power, (b,e) the combined profile FWHM ($w_f$) vs. power, and (c,f) normalized profile shapes at the highest measured power.
FIGURE S3 Averaged AFM phase line scans of single dewetted lines. Large deviations correspond to changes in height while the level regions correspond to the exposed substrate (center) and the surrounding film (far left and right of the plot). In the case of the bare silicon sample (black trace), there is a difference in phase value between the substrate and surrounding film, while there is no difference in the experiment with the PS brush, indicating that the surface retains the brush component despite the high temperatures briefly encountered during the exposure.

FIGURE S4 Results of temporal simulation of complete dewetting of a 50 nm PS film, showing the (a) height ($h$), (b) temperature ($T$), (c) height change rate ($\frac{dh}{dt}$), and (d) thermal gradient magnitude ($|\nabla T|$) profiles. It can be seen that the thermal profile is off-center and the thermal gradient is strongest towards the advancing front due to the ARC effects. This results in the height change occurring mainly in advance of the laser spot. $h$-scale in (a) is 0-160 nm, $T$-scale in (b) is 50-500 °C, $\frac{dh}{dt}$-scale in (c) is -2.4-0.8 μm/s, and $|\nabla T|$-scale in (d) is 0-100 K/μm.
Figure S5 Proposed mechanism for evolution of oscillating lines based on prior research on bilayer films.\textsuperscript{1,2} (a) The initial state of the film is a high MW PVP layer placed above a low MW PS layer. When the laser initiates dewetting, the more viscous PVP top layer displaces the PS bottom layer creating a region of the film of higher PVP concentration and therefore higher molecular weight (b).
FIGURE S6 AFM image of a PVP/PS bilayer sample written with alternating-scan direction lines. A large initial feature is always observed at the start of the line corresponding to the additional dwell that occurs as the stage ramps to full speed. Color scale is 120 nm.

MOVIE S1 Simulated time evolution of film height profile during writing at 95 mW of absorbed power. At this power the film is not completely dewetted, but a steady state height profile is rapidly achieved with a majority of displaced polymer being pushed ahead of the moving beam.

MOVIE S2 Simulated time evolution of the temperature profile in the film shown in MOVIE S2.

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