Direct-Write Thermocapillary Dewetting of Polymer Thin Films by a Laser-Induced Thermal Gradient

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The demand for lithographic methods that provide rapid, high resolution patterning with a maximum degree of control continues apace. Laser direct-write (DW) is an attractive alternative to the more ubiquitous, slower vacuum chamber particle beam DW techniques, as it can achieve up to cm s⁻¹ patterning rates. These laser techniques, however, come at the cost of reduced resolution and require high numerical aperture (NA) immersion objectives (and even the overlapping of multiple beams) to achieve their most impressive sub-wavelength results. In addition, the materials employed for both laser and charged particle DW are often themselves expensive, designer materials. While nanomachining by femtosecond ablation can also achieve sub-micrometer patterning in a general set of materials, it often results in rough features due to the high-energy nature of the ablation process. By taking advantage of the interaction between optical and thermal effects, we have developed a positive-tone DW technique that can achieve sub-wavelength patterning by non-linear overlap effects in a conventional polymer system with relatively inexpensive free-space optics, where the resulting features are robust enough for transfer to the underlying substrate. Further, this method skips the usual development step and promises the possibility of a solvent-free lithographic technique.

We recently introduced focused laser spike (FLaSk) annealing (Figure 1a) as a DW analog to laser spike annealing (LSA). LSA, where annealing is performed by rapidly scanning a high intensity continuous or pulsed laser across an absorbing substrate, has been utilized as an alternative to a standard thermal treatment in semiconductor technology and also for the annealing of soft materials, such as the post-exposure bake of chemically amplified photoresists and for inducing the microphase separation of a polystyrene-poly(methyl methacrylate) block copolymer. In this technique, the temperature and annealing time can be controlled by selection of laser intensity and exposure time to perform the anneal while avoiding unwanted effects, such as material degradation or component lateral diffusion. FLaSk utilizes continuous visible or near-IR light and a high NA objective to accomplish LSA on a micrometer or sub-micrometer scale and has been similarly demonstrated for full 3D post-exposure bake of absorbing-dye-doped chemically amplified resists and the 2D ordering and alignment of a polystyrene-polydimethylsiloxane block copolymer film swollen with ≈40 vol% toluene solvent from surrounding vapor. In this latter study, the ordering mechanism was based on large thermal gradients (1–1000 K) that occurred from substrate absorption to drive a type of cold zone annealing. Here, we perform DW FLaSk dewetting of a polystyrene (PS) homopolymer thin film by using the same gradients to drive thermocapillary-induced dewetting.

Dewetting has been utilized as a method to generate nanopatterns in thin films of metals and polymers through film-stability-based self-assembly, most generally under near-global heat provided by a hotplate or large-area pulsed LSA. In these techniques, the driving force is the large change in film surface energy due to increased temperature leading to formation and growth of isolated droplet features. A related technique based on the flow of liquids down a thermal gradient (the thermocapillary effect) has been developed to form large area nanopattern arrays and, most recently, for the nanoscale removal of a protective thin film by resistive heating of carbon nanotubes. The generalized expression for thermocapillary force is:

\[ \mathbf{\tau} \cdot \mathbf{\nabla} \gamma = \frac{d \gamma}{dT} \nabla T \]

Where \( \mathbf{\tau} \) is the shear stress, \( \mathbf{\nabla} \) the surface normal, and \( \gamma \) the surface tension. The surface tension almost always decreases with temperature, leading to a net force down the thermal gradient. In the case of the nanopillars, the thermal gradient was generated along the film normal by using a heated substrate under a thin film, an air gap, and a floated cooled substrate to create sharp (~50 K μm⁻¹) thermal gradients, which drives formation of the pillars. The nanotube patterning employed similar magnitude gradients to displace a protective thin film above only the higher-resistivity, conducting tubes, with the gradients emanating from the nanotubes being essentially 1D. For the FLaSk technique, the in-plane gradients generated radially from the spot can be equal to or much greater than those.

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Figure 1. a) Schematic of FLaSk patterning of a thin PS film on silicon. b) Effects (computed by transfer matrix method) on the surface reflectivity of the polymer film considered as an ARC. c) Expected peak temperatures (solid) and thermal gradients (dashed) from FEM simulations for the bare wafer (black) and a 60 nm PS ARC (shown in grey). The thermal histories of the film start on the grey curve (at a lower effective power) and gradually move to the black at the exposure power as the film dewets. d) AFM analysis of isolated dewetted lines written at different powers and 100 μm s⁻¹ write speed. The scan of a single line is shown in the inset (with materials schematic added). The extracted features are as indicated in the inset: i) trench FWHM (black, filled symbols), ii) ridge FWHM (grey, filled), iii) trench depth (black, empty), and iv) ridge height (grey, empty).

generated in either previous technique. Beyond this, FLaSk provides these gradients on-demand to a sub-micrometer region of the film, thus enabling a DW technique.

To understand the mechanism of 2D FLaSk dewetting, it is important to first consider the temperature of the silicon substrate during writing. Determining this is complicated by the fact that the polymer layer acts as an anti-reflective coating (ARC) for the silicon. The transfer matrix method (described in the Supporting Information) was used to determine the expected ARC effect for the simplest case of purely normal incidence, which should apply at the laser focal point (Figure 1b). In a dewetting process, both thinning and thickening occur, since the formed trench generates a surrounding ridge by material displacement. Considering only one cycle of the periodic film thickness ARC effect, it is possible to identify three regimes of dewetting behavior (indicated in Figure 1b): I) where thinning the film increases reflectivity and thickening decreases it, II) where any sizable change in thickness will result in an increase in reflectivity, and III) where thinning the film decreases reflectivity and thickening the film increases it. Each of these regimes can be expected to have different pattern formation behaviors. For example, in (III) the temperature initially increases as the material thins, raising the risk of crossing the damage threshold, but then cools, making it unlikely that full dewetting will occur. (II) can be considered the “safest” simultaneously dewets and then cools. This is a highly complex process since the film will heat faster when it is thicker and thus likely thins before the peak temperature is reached; however, the largest magnitude thermal gradients, which are spatially in front of the temperature peak, may be experienced during this process. As a result, the full kinetics will have to remain for future work, but could be approached by an elaboration of the 1D method developed by others. Regardless, it can be seen that for the power range employed (200–320 mW) gradients of approximately 100–1000 K μm⁻¹, around an order greater than those from vertical dewetting, can be expected.

The results of this dewetting can be observed by AFM, as shown in Figure 1d for isolated FLaSk lines patterned at different powers at a write speed of 100 μm s⁻¹. Each line shows two distinct features, a trench formed by dewetting and the accompanying ridge due to the displacement of material from the trench. As can be seen, with increasing power the trench width (measured as the FWHM of the bottom of the trench to the top of the ridge) increases roughly linearly from ±0.4 to ±1.2 μm, while the depth (defined from the film surface) increases rapidly until it asymptotes at the full thickness (here ±50 nm at ±230 mW). Ridge height grows linearly, even past the asymptotic limit of the trench depth, due to the fact that the ridge width (defined as the FWHM from the surface of the film) remains relatively stable compared to the trench width,
An interesting distinction between dewetting and ablation is the displacement of material as opposed to its complete removal as would be the case with ablation. Due to this, the patterning behavior of lines as the line-to-line distance decreases is of considerable interest. An analogous phenomenon has been recently used to increase the feature resolution and pitch of nanotip indentation fabricated gratings by exploiting the overlap of the material displaced by formation of a trench.\(^{16}\)

While there are highly dynamic processes involved in material's displacement by FLaSk, further FEM simulation (Figure 2b,c) can elucidate some of these behaviors. To accomplish this, full 3D electromagnetic and thermal static simulations of second-line patterning were performed using the observed cross-section ratios from Figure 1d as a starting point (details in the Supporting Information). The critical factor is the effect of film thickness on the optical absorption of the substrate. As shown in Figure 1b, for regime (I) lines, thicker portions of the PS film lead to higher optical absorption, while thinner films lead to lower optical absorption. The net result is that a line patterned with a majority of the focal intensity within a trench will have only increasing from \(\approx 0.3\) to \(\approx 0.45\) \(\mu\)m. This difference in feature size may be explained due to the fact that, while the trench includes increasingly more material that is above the flow temperature of the PS, the ridge is always in a low mobility region of the film, leading to a buildup. One significant feature of both the lines and ridges is that they are below both the width of the optical spot (FWHM for ideal NA = 0.4 focus is 0.66 \(\mu\)m) and the thermal spot size. By the metric of either feature, the apparently linear feature increase of the single FLaSk lines still manages to possess regions of sub-optical limit resolution.

The ultimate goal for most lithographic processes is pattern transfer into the underlying substrate. Therefore, pattern transfer into silicon and FIB cross-sectioning was approached to demonstrate the capabilities for the technique (Figure 2a).

It can be seen that at this power and focus the individual lines consist of \(\approx 0.85\) \(\mu\)m width trenches bounded by \(\approx 0.5\) \(\mu\)m rectangular buildups, with trench depth of \(\approx 0.78\) \(\mu\)m. The accessible depth of patterning can be increased with the selectivity of the utilized polymer, but indicates that sub-micrometer pattern transfer is even possible with a conventional polymer (like PS). An interesting distinction between dewetting and ablation is the displacement of material as opposed to its complete removal as would be the case with ablation. Due to this, the patterning behavior of lines as the line-to-line distance decreases is of considerable interest. An analogous phenomenon has been recently used to increase the feature resolution and pitch of nanotip indentation fabricated gratings by exploiting the overlap of the material displaced by formation of a trench.\(^{16}\) While there are highly dynamic processes involved in material's displacement by FLaSk, further FEM simulation (Figure 2b,c) can elucidate some of these behaviors. To accomplish this, full 3D electromagnetic and thermal static simulations of second-line patterning were performed using the observed cross-section ratios from Figure 1d as a starting point (details in the Supporting Information). The critical factor is the effect of film thickness on the optical absorption of the substrate. As shown in Figure 1b, for regime (I) lines, thicker portions of the PS film lead to higher optical absorption, while thinner films lead to lower optical absorption. The net result is that a line patterned with a majority of the focal intensity within a trench will have only increasing from \(\approx 0.3\) to \(\approx 0.45\) \(\mu\)m. This difference in feature size may be explained due to the fact that, while the trench includes increasingly more material that is above the flow temperature of the PS, the ridge is always in a low mobility region of the film, leading to a buildup. One significant feature of both the lines and ridges is that they are below both the width of the optical spot (FWHM for ideal NA = 0.4 focus is 0.66 \(\mu\)m) and the thermal spot size. By the metric of either feature, the apparently linear feature increase of the single FLaSk lines still manages to possess regions of sub-optical limit resolution.

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a lower peak temperature. Alternatively, when some portion of the incident intensity is within the ridge, a hotspot can develop with a size independent from the actual beam spot, but rather depending on the overlap. Based on this, several distinct regimes of behavior can occur. This can be seen clearly in the second line patterned, which is shown for several values of the offset between the first and second line in Figure 2d–g. As the beam spot approaches the ridge, at first (offsets between 0-0.1 μm) the temperature is insufficient to generate any line formation. Then, (at offsets of 0.2–0.4 μm) a reduced spot due to overlap and ARC effect causes the formation of very high resolution lines. Once the overlap becomes great enough (0.5–0.7 μm), the spot fills the ridge leading to larger lines and complete dewetting of the ridge (allowing for some of the uniform periodicities observed at these spacings). Finally (>0.5 μm), the line reaches the other side of the ridge and causes the formation of an entirely new line. The formation of these second lines does not necessarily leave the same spacing between the patterned region and the ridge as the line that formed it, leading to the potential for each of the successive lines to display a differing behavior. This is shown for increasing numbers of lines patterned at different spacings in Figure S2 in the Supporting Information.

Having now developed some intuition for the patterning mechanisms, it is useful to approach a systematic set of patterns. Figure 3a–d shows several characteristic 1D grating patterns. As the periodicity changes, several regimes of patterning occur. This is shown for two sets of gratings starting from different-sized single line patterns (>0.83 μm in the black trace corresponding to the shown SEMs in Figure 3a–d and ~0.72 μm for the grey trace). First, (not shown) the ridge spacing will be equal to the separation minus the line width when the lines are far enough away not to interact. Then (>2 μm), a bifurcated line width regime (shown for 1.4 μm in Figure 3a) will begin with alternating large and small ridges as discussed above and spacings equal to exactly the write spacing, since every line written is a line patterned. Once the widths of these features approach the isolated feature size, their width difference can be seen to narrow, as each patterned line finds itself in a very similar environment as the one prior due to the filling of the ridge observed in Figure 2. With decreasing separation, the bifurcation increases (and some spacing bifurcation is also observed) due to the overlap effect shown in Figure 2d–g until high resolution (down to ~70 nm) features are observed for the smaller line (Figure 3b for 0.7 μm, possessing ~0.1 μm features). Finally, the smaller feature disappears entirely (>0.5 μm writing spacing), thus leading to an increase in the feature-to-feature distance. After this transition, multiple lines will pattern a single feature in a relatively uniform fashion (Figure 3c for 0.4 μm), but this behavior will only be stable down to a certain point, shown with ~70 nm features for 0.2 μm writing spacing in Figure 3d.

A few interesting observations: first, it can be noted that more than two line spacings are never (or rarely, considering all samples fabricated) observed, at least at a noticeable enough difference to exceed the displayed error bars. Rather, there seem to always be either alternating line sizes (and spacings) or a single dominate size and spacing. Why this is the case is not entirely clear, but it is definitely convenient for the purposes of a lithographic technique. One unfortunate result for the small spacings is a side effect of multiple lines patterning the same feature, which is sensitive to process fluctuations. This is especially
Thermocapillary dewetting of a simple polymer system (PS) was demonstrated as a positive tone direct write process that can be used effectively for pattern transfer of sub-micrometer lines without the necessity of a development step. While this is already a useful technique, the patterning capability becomes even greater as the lines are brought together – due to the fact that the driving force for dewetting and pattern formation (proportional to thermal gradients) is a result of a combination of the optical exposure and the thermal properties of (primarily) the absorptive substrate, consecutively patterned lines near to one another possess anti-reflection effects leading to sub-wavelength thermal profiles. In this manner of decoupling the optical resolution from the resultant thermal pattern, isolated features down to <100 nm or grating patterns with near constant periodicity near the optical limit (0.5–1 μm) and line widths still below the optical limit either in a large-small alternation pair or constant size may be generated. The resultant polymer film height variation features are still robust enough for pattern transfer to the underlying substrate and therefore represent a new method to create high resolution features in a three step (resist deposition, laser patterning, and etching) process, eliminating the necessity for wet chemical development. To improve the resolution and consistency of this method, the current NA (0.4) could be increased. In addition, different thin film materials possessing either more beneficial properties for patterning or pattern transfer could be approached. In the former regard, it is not clear a priori what properties will lead to superior response, but it is likely that increasing the softening temperature and decreasing the mobility (such as with higher Tg or molecular weight polymers) could achieve a smaller extent of isolated dewetted features. Finally, it may be possible to employ water or alcohol soluble polymers to completely remove the need for hazardous chemicals from the lithographic process.

Experimental Section

Thin-Film Preparation: Lightly doped p-type silicon substrates ([100] orientation, 10 Ω·cm) were coated with films of PS (18 kg mol⁻¹, Sigma Aldrich) from 1.8 wt% solutions in propylene glycol monomethyl ether acetate to prepare films of 50–60 nm thickness by spin coating. The film thickness was determined by ellipsometry with a J. A. Woollam Co. M-2000D spectroscopic ellipsometer.

FlaSk Annealing: FlaSk zone annealing was performed using circularly polarized 532 nm light from a Coherent Verdi V5 diode pumped solid-state laser system. Power was controlled by a 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 Acroplan 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 with red and near-IR light from a white light source via a camera mounted above the stage. Motion of the sample for direct write was controlled by a Physik Instruments PiMars piezostage with 300 μm of travel on all three axes mounted on a PI M-686 stage for larger motion. Patterning was controlled by a LabView program that controlled both the stage and an electronic shutter.

Imaging: AFM imaging was performed with a Veeco Dimension 3100. Patterns were transferred from polymer into the underlying Si substrate using STS ICP-RIE. The etching gas is a mixture of C4F8/SF6 with a 2 min etching time at a power of 1200 W and gas rates of 50 and 80 sccm respectively. SEM imaging was performed on a JEOL 6700 microscope at 5 keV with 8 mm working distance for top views and 15 mm working distance for the 25° angled view shown in Figure 2a after focused ion beam milling with a JEOL 9320 FIB.

Simulations: FEM simulations of the FlaSk process were conducted using the commercial package, COMSOL Multiphysics. COMSOL allows for simultaneous solution of multiple differential equations in the same model. For this study, we used the packages for thermal conduction and electromagnetic waves.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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