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Thermocapillary Multidewetting of Thin Films

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ABSTRACT

Thermocapillary dewetting of liquids and molten films has recently emerged as a viable alternative to conventional microprocessing methods. As this thermal gradient-induced mechanism is universal, it can be applied to any material. This work explores the sequential dewetting of materials with varying melting points, including polymers and metals, to create aligned morphologies. The variation in melting point allows for the dewetting of single layers at a time or mobility-limited simultaneous dewetting. As a result, a variety of multimaterial structures can be produced with built-in alignment, such as arrays of concentric circles, lines with periodic segmentation, or islands on holes. This approach employs photothermal methods to induce the necessary thermal gradient, manipulating several variables in order to influence the consequent structures. Adjusting laser power and light intensity allows for the control of temperature for selective dewetting of films; altering beam size and exposure time affects the extent of dewetting in terms of diameter size; overlap effects and simultaneous dewetting can result in complex architectures. This controlled writing of patterns also presents a technique to create both masks at low temperatures for conductive multilayers as well as templates for electrospray deposition.

INTRODUCTION

Marangoni forces describe the general family of surface stresses that result from changes in surface tension along a gradient. Thermocapillary forces are one of these and can be expressed as the surface shear caused by a thermal gradient because of the thermal change in surface tension:

$$\vec{\boldsymbol{\tau}} = \frac{d\gamma}{dT}\vec{\boldsymbol{\nabla}}\boldsymbol{T} \quad (1)$$

Thermocapillary forces have become increasingly common in the patterning of polymers and other soft matter[1] because of their universal nature—any material that can be melted, can be shaped. Further, the smaller the thermal source is in spatial extent, the larger the corresponding driving force. This means that highly localized heat sources can rapidly pattern a wide range of materials, and, since the thermal excitation can also lead to the melting of material, the patterned material can both start and end in an immobile state. Because $d\gamma/dT$ is negative in most materials, subjecting films to concentrated hot spots produces a shear force radially down the thermal gradient. In this way, focused laser spike (FLaSk) excitation with continuous wave lasers has been used to apply thermocapillary shear to polymer thin films and can result in either dewetting[2-5] or shear-induced reordering[6, 7] by inducing thermal gradients of up to 1000 K/μm. Past work has explored FLaSk dewetting as a direct write technique and has explored the effects of different molecular weights[3], thicknesses[2, 3], and writing speeds[5], with the conclusion that film mobility, as expressed by the temperature dependent viscosity, has the largest effect on resulting patterns of any patterns. For example, when the laser writing occurred too quickly for the material to dewet, periodic patterns would appear along written lines[5]. Similar effects were observed when bilayers were employed with low mobility materials on top and high mobility materials underneath, such as high molecular weight (MW) polymer on low MW[3] or silver on polymer[4]. In this work, we instead explore the potential to sequentially pattern materials with different softening points, allowing for the individual dewetting, or non-dewetting, of materials in multilayers. Polymers, such as poly(styrene) (PS) and SU-8, have low softening temperatures, making them ideal candidates for low temperature patterning. Metal thin films, in contrast, have high softening points, but low melt viscosities, and therefore require higher temperature to pattern but can be patterned very rapidly. This technique provides an avenue to fabricate high resolution arrays that can evolve during a multistep patterning process or flexible patterned metallic thin films for electronics, with individual features reaching 1.35-μm in diameter.

EXPERIMENTAL SECTION

Experimental system

FLaSk dewetting was performed using circularly polarized 532 nm light from a Laser Quantum Opus 6W diode pumped solid state laser system. Power was controlled by an Isomet IMAD-T110L-1.5 acousto-optical modulator (AOM) and measured with a power meter (Thorlabs S121C) 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. A 0.25 numerical aperture objective lens was used throughout all experiments. 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 a red light source. Motion of the sample for direct write was controlled by a Mad City Labs MCL-MOTNZ stage with 1”X1” of lateral mechanical travel integrated with 200 nm of piezo-controlled axial travel. Both the stage and an AOM were controlled by a MATLAB program.

Materials studied

Table 1: Materials used and their corresponding molecular weight and softening temperatures, with glass (g) or melting (m) transition indicated

Material	MW (g/mol)	T_s (˚C)
Epon SU-8	240	82 (g)
Poly(styrene)	35,000	100 (g)
Gold	197	1064 (m)

Several materials were studied for their different softening points to demonstrate the applicability of FLaSk dewetting on various materials. Poly(styrene) (Sigma Aldrich, PS) is used for its moderate glass transition temperature for a polymer. Epon Resin SU-8 (Hexion), an oligomeric epoxide commonly used as a negative tone photoresist, is used without photoactive additives as the softest material, allowing for rapid, low-temperature patterning. Sputtered gold acts primarily as a heating substrate to conduct heat from the focused beam to the target polymer layers. Its high softening point requires much higher powers to dewet, but can be separately dewetted, hence demonstrating the need for an indirect patterning method through a polymer template.

Sample types

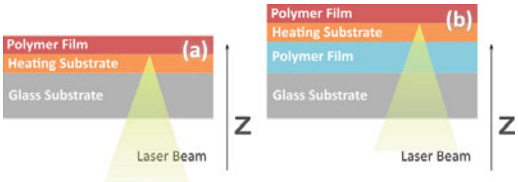

Figure 1: Multilayer configurations: (a) Bilayer with a polymer on gold heating substrate, (b) Triple layer with a thick polymer film underneath heating substrate

The materials were prepared as thin films on a glass substrate according to the configurations shown in Figure 1. For the bilayer system that uses SU-8 (Figure 1a), a 172-nm gold film was first sputtered onto a 1-mm thick glass substrate. SU-8 solution was then spun onto this substrate to produce a 96.6-nm film. In the three-layer configuration used for SU-8 / Au / PS (Figure 1b), a thick PS film (>20-µm) is spun onto a similar glass substrate. Following this first layer, 30.93-nm gold and 96.6-nm SU-8 were deposited in a similar manner to the double layer in Figure 1a.

Table 2: Laser power densities to dewet materials at their respective thicknesses

Material	Power Density (mW/μm^2)	Film Thickness (µm)
SU-8 (on Gold)	0.2027	0.0966
Gold	173.439	0.172
SU-8 (on Gold-PS)	10.406	0.0966

The top-most polymer film was dewetted in each sample through a bottom-up exposure, with the laser beam heating the system through the glass and heating substrate. Due to the different softening points of each material (Table 1), they required different power densities to dewet (Table 2). This power also differed within each sample type depending on film thickness, with thicker films dewetting at higher powers. Each experiment was conducted with dot exposures at varying exposure times and power densities. The experimental setup's *z*-stage can also be controlled to alter beam size and, consequently, power density while keeping numerical aperture constant.

Iodine etching

The dewetted polymer pattern can also act as a template through which underlying film can be patterned by etching. A 20 wt-% iodine solution in water was used to etch gold by drop casting and then immediately rinsing in deionized water. The sample was then dried at room temperature.

RESULTS & DISCUSSION

SU-8 on Gold

SU-8 on gold bilayer samples were patterned in a dual stage process, beginning with the dewetting of the SU-8 layer and followed by dewetting the gold. SU-8 was heated using an out of focus beam obtained by moving the *z*-stage down by 175 μm, which effectively reduced the thermal gradient induced at any given power and made for an overall larger spot. This was to avoid damage and crosslinking to SU-8 that can occur during the gold dewetting step if the SU-8 is not removed sufficiently far away from the heated gold. To compensate for this, a higher power of 100 mW was used at a 5s exposure time. This allowed for the creation of larger patterns in SU-8, followed by the subsequent dewetting of the underlying gold without damage to create 2~4 μm dewetting patterns in the gold film. Hierarchical arrays of two different spot-to-spot distances were studied.

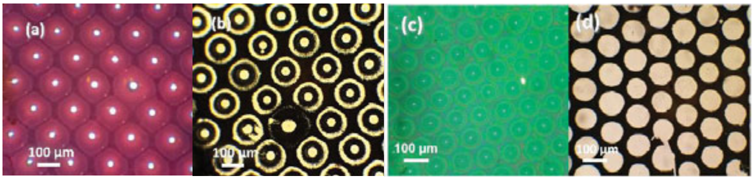

Figure 2: Pre- and post- iodine etched SU-8 / Au: (a) – (b) 150-μm spacing, (c) – (d) 100-μm spacing

Post-etched images in Figure 2-b, d reveal the dewetted pattern formed in SU-8 by etching of the underlying gold. At a 150-μm spot-to-spot distance (Figure 2-a, b), a secondary dewetted region was produced concentric with the central spot. After etching, the result is a 17.35μm width and 126.21μm central diameter ring surrounding a 42.30μm spot. These features arose due to the presence of Airy disks in the defocused beam, exposing the thin, low softening point SU-8 to a sufficient thermal gradient for dewetting. The ring and spot dewetting therefore focus material towards an inner ring, which can be seen as brighter intensity in the optical patterns and remain after etching. At a smaller pitch of 100-μm (Figure 2-c, d), however, these secondary features were not observed, resulting in only an array of 94.81μm spots. The combination of dewetting and etching of the gold results in a pattern of optical apertures that can evolve in two steps. Additionally, by lowering the power, the Airy disk was less able to push material back towards the centre. The net result is that film overlap between individual holes can counteract secondary dewetting such that only larger singular holes are created

SU-8 on Gold on Poly(styrene)

Triple layer dewetting was conducted using focused exposures on SU-8 at 15mW for 1s each. After gold etching, a high-resolution array of features ~1.35μm in diameter is produced in the underlying gold. The characteristic trench-ridge pattern of FLaSk dewetting is evident in the outer ring around dewetted spots at a width of ~ 2.75μm. The fact that the etched gold has a much smaller radius than the dewetted ring indicates that the trench in SU-8 is very gradual as compared to other reported polymers, most likely because of its oligomeric nature. There is clear non-uniformity in the outer dewetted ring (Figure 3), though the etching pattern is very consistent. This non-uniformity is potentially caused by a variation in film thickness of PS, resulting from the blade coating process, which introduces non-uniformity in both the gold sputtering and the SU-8 spin coating.

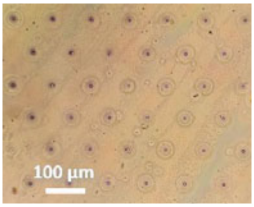

Figure 3: Dewetted SU-8 on Au/PS

Despite the relative closeness of poly(styrene) and SU-8 in glass transition temperatures (Table 1), SU-8 was selectively patterned without causing any damage to the layers underneath. This independent dewetting is possible due to the large differences in MW of the polymers (Table 1), which lead to vastly different mobilities even at temperatures exceeding the glass transition. The importance of this approach is that, as evidenced through the etching, the metal layer can be patterned in a resist-free fashion without damaging an underlying soft substrate, such as is relevant in flexible electronics.

CONCLUSION

This study illustrated the applicability of FLaSk dewetting to a variety of materials that differ in softening point. Dot features were dewetted on polymer-metal multilayers, manipulating laser power, exposure time, and spot size depending on material. Because of its dependence on film mobility, FLaSk can be used to independently or consecutively pattern films in a non-destructive manner. This versatile patterning technique can be explored in a variety of applications, such as the fabrication of flexible electronics or optics, by providing a polymer template to safely pattern metals on soft materials.

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