

# Lithographically induced self-assembly of microstructures with a liquid-filled gap between the mask and polymer surface

Paru Deshpande<sup>a)</sup> and Stephen Y. Chou

*Department of Electrical Engineering, NanoStructure Laboratory, Princeton University, Princeton, New Jersey 08544*

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We have observed that a featureless polymer thin film on a flat plate that is separated from another flat plate by a liquid filled gap can self-assemble into a periodic micropillar array. Moreover, we have observed that if there is a pattern on one of the plates, the boundary of the pillar array will align with the boundary of the pattern resulting in single domain arrays. The phenomenon is believed to be due to the unstable growth of surface waves in the polymer system caused by an attractive Coulombic interaction between the top plate and polymer. A transition temperature has been found below which ordered patterns are not observed in the bilayer system. This self-assembled phenomenon suggests a novel way of controlling flow in microfluidic devices. © 2001 American Vacuum Society. [DOI: 10.1116/1.1414015]

## I. INTRODUCTION

Microfluidic devices have opened up a new array of applications for micro- and nanofabrication techniques. Such devices are finding novel applications in biology for proteomic, genomic, and chemical analyses.<sup>1-3</sup> Typically devices are patterned using conventional photolithography. Subsequent pattern transfer into the substrate produces the necessary features required to control fluidic flow. The devices are then capped with a cover plate resulting in enclosed channels. The cap can be formed using wafer bonding techniques<sup>4-6</sup> or using an elastomer to provide a tight seal.<sup>7,8</sup> In either case, an effective seal is critical to the proper function of the device. Furthermore, the device cannot be modified once the cap has been applied.

In this article we discuss the formation of polymer structures by lithographically induced self-assembly (LISA).<sup>9,10</sup> We show that a mask separated from a thin polymer film by a fluid can cause the film to form periodic structures under appropriate conditions. The polymer structures bridge the gap between the substrate and the mask. The result is a network of connected voids in a sealed structure. This technique, we believe, offers a novel approach to forming microfluidic channels that are self-sealing and that can be modified after the device has been filled with fluid.

## II. EXPERIMENT

LISA is a process by which a mask placed a distance above a thin polymer melt induces the polymer to self-assemble into periodic structures or large mesas.<sup>9,10</sup> A Coulombic interaction between the mask and polymer induces the growth of surface instabilities in the polymer melt. A low surface energy mask favors the formation of discrete pillars since the polymer is prevented from spreading after touching the mask surface. A higher surface energy mask leads to mesa formation since individual pillars can more easily

merge together; this process is termed lithographically induced self-construction (LISC).<sup>10</sup> In our previous experiments, the region between the mask and polymer film was either air or vacuum.<sup>9,10</sup> In this article we report on the influence of a viscous, liquid layer between the mask and polymer on the formation of LISA pillars.

Figure 1 shows the setup of the experiment. The polymer used was polymethyl(methacrylate) (PMMA) having a molecular weight of 2000 Da and polydispersity less than 1.1.<sup>11</sup> The glass transition temperature  $T_g$  was measured by differential scanning calorimetry to be 90 °C. A solution of 4% (by weight) PMMA dissolved in chlorobenzene was spun onto a silicon substrate giving a film thickness of 125 nm as measured via ellipsometry. The PMMA sample was then dipped into a perfluoropolyether (PFPE) oil<sup>12</sup> resulting in a bilayer polymer system [Fig. 1(a)]. This oil was chosen because it is stable at the highest temperatures used in this experiment and is also sufficiently transparent to permit imaging.

The mask features were etched into thermally grown silicon dioxide on a silicon substrate. The spacers were 350 nm high and the protruding mask patterns were 100 nm high. The mask was coated with a fluorinated surfactant to ensure easy separation of mask and polymer after the process was complete. The mask was then placed onto the sample and the whole assembly was placed into a preheated press. A pressure of 300 psi was applied to hold the mask against the polymer substrate [Fig. 1(b)]. This pressure was sufficient to force the spacers to the bottom of the PMMA film when the system was heated above the glass transition temperature  $T_g$  of PMMA. The spacers ensure that the mask patterns do not contact the initially flat PMMA surface. The gap between the mask patterns and PMMA surface was 200 nm and was filled with PFPE oil.

The system was heated for times ranging from 3 to 20 min at temperatures of 120–160 °C to induce the formation of LISA structures [Fig. 1(c)]. The oil does not thermally decompose at these temperatures and has a vapor pressure

<sup>a)</sup>Electronic mail: pad@ee.princeton.edu

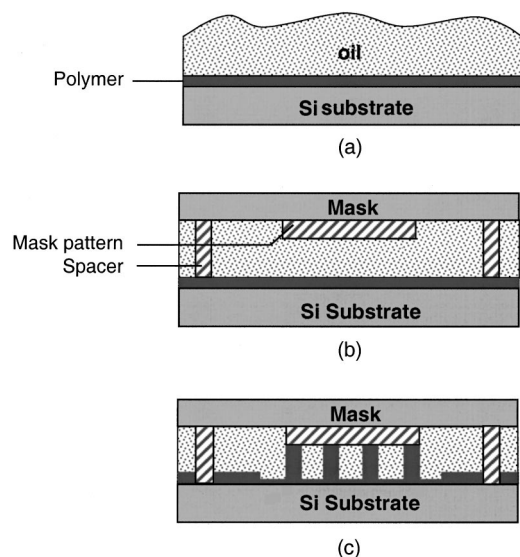


FIG. 1. Experimental setup of LISA process in bilayer system: (a) a 125 nm film of 2 K PMMA is spun onto a silicon substrate and coated with PFPE oil; (b) a patterned silicon mask is held in close proximity to the film. Spacers ensure that a uniform gap of 250 nm is maintained between the mask and polymer film. (c) As the system is heated above the glass transition temperature of the PMMA, the film is observed to self-assemble into ordered pillar arrays that are aligned to the mask patterns. When the process is complete, the system is cooled thus fixing the self-assembled polymer structures. The mask is then removed allowing examination of the patterns formed in the bilayer system.

less than  $10^{-2}$  Torr.<sup>13</sup> A set of control experiments was also performed for which oil was not used. The system was then cooled and the mask was removed so that the resulting features in the bilayer polymer film could be examined. The mask was inspected to ensure that no polymer remained on the mask. This was always the case suggesting that the removal of the mask did not damage the LISA features that had formed.

### III. RESULTS

Figure 2 shows the results for an experiment run at 135 °C for 9 min. For this temperature, trials run for shorter times resulted in self-assembled features that did not completely fill the region below the mask. Figure 2(a) shows the observed LISA pattern without oil which is well ordered with a fairly uniform pillar diameter of 4.5  $\mu\text{m}$  as measured by atomic force microscopy. Figure 2(b) shows the result for the same experiment with oil present between the PMMA and mask. In this case, the pillars have nonuniform size and shape. In general, the pillars are not circular but instead appear to have spread on the surface of the mask in an irregular fashion. Some of the largest features may be the result of pillars merging together. Although the degree of order in this case is less than that observed with an oil gap, some semblance of periodicity can be seen. Along the perimeter of the triangle pattern, some pillars are arranged in a roughly periodic fashion; however, the random size and shape of the pillars prevents the long range order seen with an air gap.

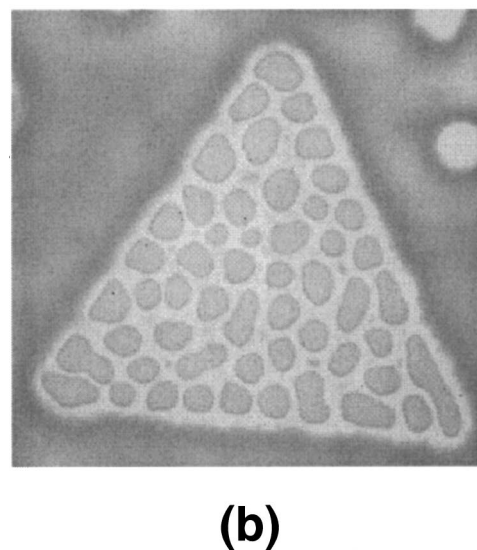
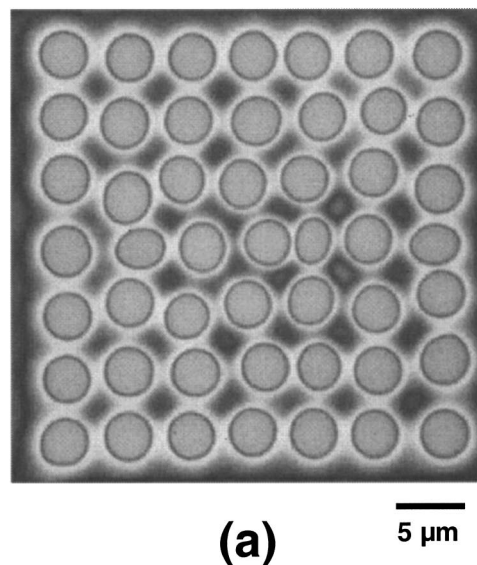
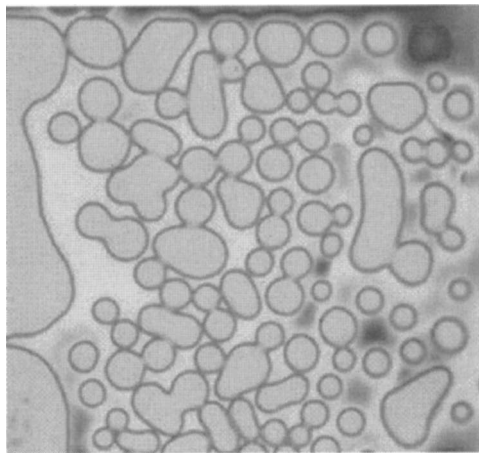


FIG. 2. Comparison of 9 min LISA formation in air and oil at 135 °C. (a) The LISA array formed in air is well ordered with a uniform pillar diameter of 4.5  $\mu\text{m}$  as measured by atomic force microscopy. (b) The pattern formed in the bilayer system is weakly ordered and shows a pillar size distribution of 2–7  $\mu\text{m}$ .

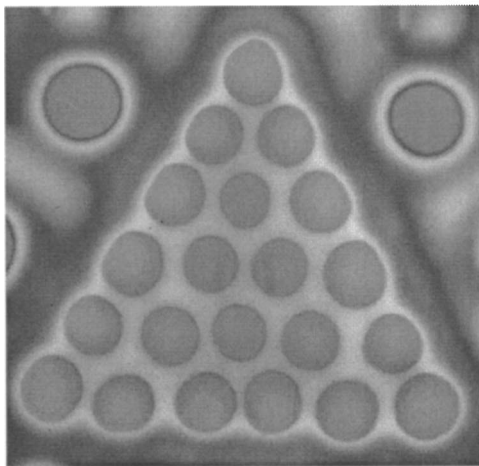
Figure 3 shows results for similar experiments run at 160 °C for 3 min. Figure 3(a) shows the observed formation without oil. Note the high degree of disorder and the broad distribution in feature size. Pillars sometimes merge together resulting in large mesas. In some cases, short-range order can be observed but single domain patterns like those in Fig. 2(a) could not be formed at this temperature. Figure 3(b) shows the result with an oil-filled gap. In this case, a high degree of order is observed. The PMMA pillars have a 4.8  $\mu\text{m}$  diameter and are quite uniform in size and shape. The pillar size is almost identical to that measured with an air gap at lower temperature.

Further experiments showed that the critical temperature at which ordered arrays of uniformly sized pillars could form in the presence of an oil layer was about 150 °C. At such



(a)

5 μm



(b)

FIG. 3. Comparison of 3 min LISA formation in air and oil at 160 °C. (a) The pillars formed in air show a broad size distribution and in some cases merge together to form large mesas. (b) The LISA array formed in the bilayer film is well ordered with a uniform pillar diameter of 4.8 μm.

temperatures, ordered LISA patterns could not be formed without oil for the given experimental conditions used in this study.

#### IV. DISCUSSION

There are several parameters that are modified when an oil-filled gap replaces an air gap. Most notably, the relative surface energies are changed. Figure 4 shows an expanded view of the triple interface where the polymer touches the mask. The contact angle at the interface is related to the surface tension associated with each interface and is given by the expression

$$\gamma_{\text{PMMA/air}} \cos \theta + \gamma_{\text{PMMA/mask}} = \gamma_{\text{Mask/air}}, \quad (1)$$

where  $\gamma$  is the surface tension associated with the interface and  $\theta$  is the contact angle.<sup>14</sup> When the air is replaced with oil, two changes occur. First, the interface between the

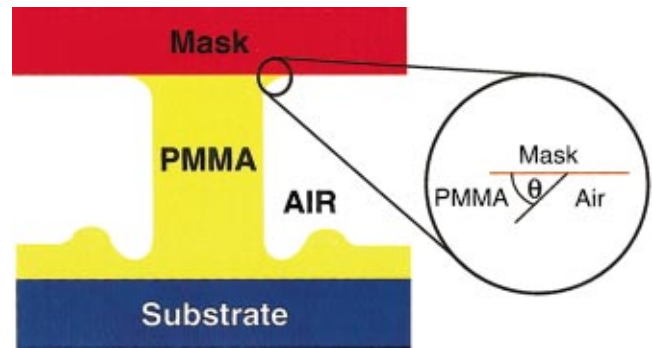


FIG. 4. Schematic of triple interface showing contact angle of PMMA on mask surface. By replacing the air with oil, the interface energies are modified thus changing the contact angle.

PMMA and oil is of much lower energy than that between PMMA and air. The second change occurs at the mask/air interface, which becomes a mask/oil interface. Although this second interface energy is changed, the interface is still of very low energy since the fluorinated surface coating on the mask is quite compatible with fluorinated polymers such as PFPE. From Eq. (1) we can see that when an oil gap replaces an air gap, the equality can only be maintained with a reduced contact angle because  $\gamma_{\text{PMMA/oil}} < \gamma_{\text{PMMA/air}}$ . The result is that with an oil gap, polymer can more easily spread on the mask surface rather than being fixed in the shape of a pillar. This is likely the reason that the pillars in Fig. 2(b) have an irregular shape and size distribution.

At higher temperatures, discrete, ordered pillars are observed with an oil gap, while the pillars with an air gap have irregular shapes. This phenomenon implies a change in the relative interface energies. For the air gap polymer system at 160 °C, the surface tension of PMMA to air will drop by 1.9 mN/m (about 7%) compared with that at 135 °C.<sup>15</sup> Equation (1) shows that the contact angle should decrease, consistent with the polymer spreading observed. On the other hand, the observation of the excellent ordered pillar array at 160 °C with an oil gap suggests that as the temperature increases, either the surface tension between the PMMA and the oil increases, or the difference between the surface tensions of the mask/oil interface and the PMMA/mask interface decreases, or both. Clearly, the different temperatures and the different gap materials offer new avenues for controlling the LISA process.

#### V. APPLICATIONS IN MICROFLUIDICS

The results of this experiment suggest novel applications of this process in microfluidic applications. LISA (or LISC) with an air gap provides a unique means of forming self-sealing microfluidic channels and reservoirs. Furthermore, LISA with an oil gap suggests that nanostructures can be formed *after* the device has been sealed and filled with fluid. In many cases, uniform heating of the device to form LISA structures may be undesirable but localized heating can be used to control the location of patterns. For example, a focused laser beam can be used to modify microfluidic struc-

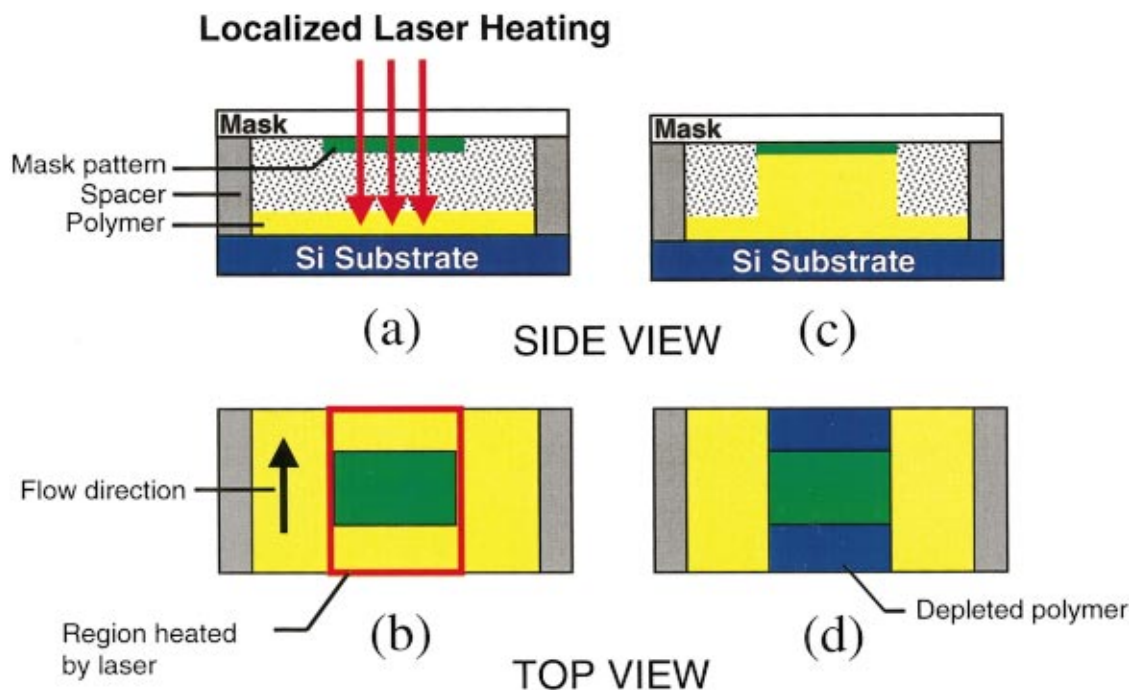


FIG. 5. Proposed technique for modifying microfluidic devices. (a) Side view showing localized heating using a focused laser beam through a transparent mask. The laser energy is absorbed by the polymer and raises the temperature of a localized area above the glass transition temperature of the polymer. The region being heated is shown in the top view of (b). A region larger than the desired pattern must be heated in order to form the LISA structure. (c) Side view of the completed structure and (d) top view showing the surrounding region depleted of polymer. In this case, the heated area was chosen such that the cross sectional area for the flow direction is reduced.

tures in a serial write manner.<sup>16</sup> This is diagrammed schematically in Fig. 5. Such flexibility in customizing microfluidic devices may allow for many new applications but further study is required to determine the viability of laser induced LISA formation.

## VI. CONCLUSIONS

In conclusion, we have demonstrated the formation of ordered LISA pillar arrays in PMMA when an oil layer is present between the PMMA surface and mask. The oil modifies the interface energies leading to disordered patterns with nonuniform size. This effect is only overcome at higher temperatures at which point ordered LISA pillar arrays can be formed. Future work will concentrate on characterizing the impact of the oil layer in more detail but the principle effect impacting pattern formation with an oil-filled gap is the modified interface energies. Finally, we would like to pursue the application of this concept in the development of microfluidic devices. We believe that the LISA phenomenon is a novel way of modifying fluid flow at the micron scale. LISA patterns could be used to restructure channels after the microfluidic system has been sealed. In particular, a focused laser could be used in a serial write fashion to modify devices even after they have been filled with fluid.

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<sup>1</sup>S. C. Jakeway, A. J. de Mello, and E. L. Russell, *Fresenius J. Anal. Chem.* **366**, 525 (2000).

<sup>2</sup>G. H. W. Sanders and A. Manz, *TrAC, Trends Anal. Chem.* **19**, 364 (2000).

<sup>3</sup>D. Figeys and D. Pinto, *Electrophoresis* **22**, 208 (2001).

<sup>4</sup>M. A. Gretillat, F. Paoletti, P. Thiebaud, S. Roth, M. KoudelkaHep, and N. F. deRoos, *Sens. Actuators A* **60**, 219 (1997).

<sup>5</sup>M. Stjernstrom and J. Roeraade, *J. Micromech. Microeng.* **8**, 33 (1998).

<sup>6</sup>C. G. J. Schambmueller, M. Koch, A. G. R. Evans, and A. Brunnschweiler, *J. Micromech. Microeng.* **9**, 176 (1999).

<sup>7</sup>D. C. Duffy, J. C. McDonald, O. J. A. Schueller, and G. M. Whitesides, *Anal. Chem.* **70**, 4974 (1998).

<sup>8</sup>J. D. Xu, L. Locascio, M. Gaitan, and C. S. Lee, *Anal. Chem.* **72**, 1930 (2000).

<sup>9</sup>S. Y. Chou and L. Zhuang, *J. Vac. Sci. Technol. B* **17**, 3197 (1999).

<sup>10</sup>S. Y. Chou, L. Zhuang, and L. Guo, *Appl. Phys. Lett.* **75**, 1004 (1999).

<sup>11</sup>2K PMMA available from Sigma-Aldrich.

<sup>12</sup>Krytox 1514 available from Dupont.

<sup>13</sup>Krytox oil data sheet available from Dupont.

<sup>14</sup>See for example, P. G. de Gennes, *Rev. Mod. Phys.* **57**, 827 (1985).

<sup>15</sup>*Polymer Handbook*, edited by J. Brandrup, E. H. Immergut, and E. A. Grulke (Wiley, New York, 1999), pp. VI/527.

<sup>16</sup>S. Y. Chou (unpublished).