DOI: 10.1002/smll.200600121

Surface-Tension-Driven Patterning: Combining Tailored Physical Self-Organization with Microfabrication Methods**

*Kahp Y. Suh**

Keywords:
- capillary flow
- dewetting
- patterning
- surface tension

Thin liquid or polymer films offer fertile ground for many micro/nanofabrication and controlled physical self-organization processes.[1,2] For example, conventional optical lithography utilizes modification of the chemical structure of a thin photoresist by radiation. Also, imprinting-related lithographies generate resist relief patterns in a thermoplastic or ultraviolet (UV)-curable resin by using a high mechanical pressure or a physical contact followed by UV irradiation ("top-down" approaches).[3,4] In parallel, many physical forces such as capillarity,[5] dispersion forces,[6] or mechanical stress[7] drive the surface of a thin film into a regularly ordered structure ("bottom-up" approaches). It is widely accepted that a combination of these two approaches could solve many unraveled challenges to produce complex devices with a minimum feature size below 50 nm.[8,9] Recently, the semiconductor industry has made incredible advances in achieving features close to ≈50 nm in size. For traditional optical systems, however, a further reduction in the feature size may not be economically viable. Moreover, it is very difficult to develop a fast, reliable, and cheap patterning method using a top-down or bottom-up approach alone for this regime because of low cost effectiveness and high technological barriers. Thus, precise control over physical forces that govern self-organization at small-scale dimensions is of great importance to meet future demands, covering the regime from 10 to 50 nm.

In contrast to the chemical self-assembly that exploits chemical interactions between a self-assembled monolayer and a substrate, physical self-organization takes advantage of the physical forces that are mentioned above.[10] Of these, dewetting (or surface tension) is one of the useful concepts that can be used in the self-construction of thin liquid films. However, the versatile use of surface tension as a lithographic tool has been restricted due to the lack of controllability.[11] In a recent paper, Scherer and co-workers demonstrated an interesting experimental study for creating regularly spaced line patterns in an evaporating thin film through guided evaporation and dewetting.[12] The line width was typically on the order of a few micrometers but even reduced to below 100 nm by incorporating self-assembled colloidal quantum dots into the solution. Three conditions were suggested to form narrow lines instead of conventionally observed rings or drops: 1) Evaporating solutions between two partially wettable surfaces, 2) the presence of pinning points, and 3) the presence of foaming surfactants to lower surface tension. Briefly, they used an aqueous solution containing a foaming surfactant such as bovine serum albumin (BSA), sodium dodecyl sulfate (SDS), or others between two cover glasses or two silicon wafers. Subsequently, the solution was left to evaporate for a few hours, rendering long strip patterns growing perpendicular to the three-phase contact line with an apparent periodicity. It was reported that the line width depended upon the gap distance between two covering plates, not by other geometrical or material parameters. In addition, bubbles in the solution led to a structure shaped like "lollipops". These findings are truly intriguing since evaporating liquid films typically generate semi-ordered drops or rings after evaporation due to Rayleigh instability.[13]

As can be seen from water drops in a splash, a long, freestanding liquid jet or thread favors perturbations and is broken into drops as it lowers the surface area. For a quasi-static motion, it would be desirable to merge all the fluid into one sphere, corresponding to the smallest surface area. However, this is usually not the case; the fluid is broken into many similar-sized drops often with satellite drops. Rayleigh found that surface tension has to be counterbal-

[*] Dr. K. Y. Suh
School of Mechanical and Aerospace Engineering
Seoul National University, Seoul 151-742 (Korea)
Fax: (+82) 2883-0179
E-mail: sky4u@snu.ac.kr

[**] The author is grateful for financial support from the Micro Thermal System Research Center of Seoul National University for reproduction of the color figures.

anced with inertia, which opposes fluid motion over long distances. By equating these two forces on a fluid cylinder of radius r, Rayleigh suggested an optimal wavelength, $\lambda = 9r$ (fastest growing mode), which is in good agreement with experiments. Accordingly, the timescale t_0 on which perturbations grow and eventually break the jet is given by a balance of surface tension and inertia, yielding[13]

$$t_0 = \left(\frac{r^3\rho}{\gamma}\right)^{1/2} \quad (1)$$

where ρ is the density and γ is the surface-tension coefficient of the fluid. For pure water with $r = 1$ μm, one finds that $t_0 = 0.1$ μs, which means that the liquid jet would be broken into drops extremely quickly.

Returning to the experiment by Scherer et al., the importance of using a sandwiched geometry was mentioned in the paper; a drop of BSA solution on a surface left conventional ring-shaped patterns, which are ubiquitous and encountered in daily life, science, and engineering. A few comments as to why a sandwiched, evaporating film led to regularly spaced lines rather than broken drops are necessary at this point. First, the relation indicates that the timescale is increased with decreasing surface tension, which can justify the use of a surfactant in their experiment. More importantly, the liquid film was sandwiched between two partially wetting surfaces, for example, hydrophilic glasses or silicon wafers. Such a confined geometry gives rise to evaporation only in one direction (as compared to the three-dimensional evaporation in [Eq. (1)]) so that the perturbations would be greatly hindered. A rough approximation might lead to an exponent close to one, not three, thus significantly increasing the timescale by more than six orders of magnitude with an appropriate density.

The most crucial factor, although implicitly shown in the paper, is probably the interactions between surfactant molecules with the hydrophilic glass or silicon substrate. It is well known that these surfaces create a negative charge at neutral pH, resulting in nonspecific adsorption of protein molecules from the surrounding fluid (so called "biofouling").[14] In this sense, the surfaces were interacting with the protein molecules such that the region in contact with the solution would be covered with them at the final stage. Apart from protein molecules, other inert or fluorescein-labeled particles used in their experiment could interact with the substrate and suppress liquid breakup since dewetting is highly affected by the presence of particles in the film.[15] The fact that no pinning points were necessary for BSA lines whereas pinning points had to be artificially created to obtain lines for other surfactants strongly supports this explanation. This author believes that the above simple relation, along with a qualitative description presented in the paper, gives a deeper insight on the stability and structure formation of thin liquid films sandwiched between two parallel plates. Further information on the periodicity and shape of thin confined viscous or elastic films can be found elsewhere.[16,17]

It is noted that the presence of pinning points was essential to observe regular lines. Usually, surface-tension-driven self-organization or dewetting is very difficult to control because it is highly sensitive to surface defects, heterogeneity, and roughness. One example of controlling surface-tension-driven flow can be found in a technique called micromolding in capillaries (MIMIC),[18] where a precursor solution is allowed to flow inside a microfabricated channel network by spontaneous capillary flow and subsequently cured by heat or UV. When a colloidal solution flows inside the channel, a well-defined colloidal self-assembly can be obtained since the surface-tension flow is restricted two dimensionally. Another way to achieve surface-tension-driven self-assembly is to apply capillary forces on a predefined polymeric pattern.[19] These approaches attempted to combine a simple microfabrication method with a surface-tension-driven self-assembly process.

To allow for precise control over the location of pinning points and guidance to subsequent evaporation, Scherer et al. used standard photolithography. This is meaningful since it represents a practical way for a reliable self-organization process in a controlled fashion. They found that artificial pinning points, regardless of shape and size, steered evaporation in the desirable direction. Typical examples are shown in Figure 1. As shown in the figure, they tested for

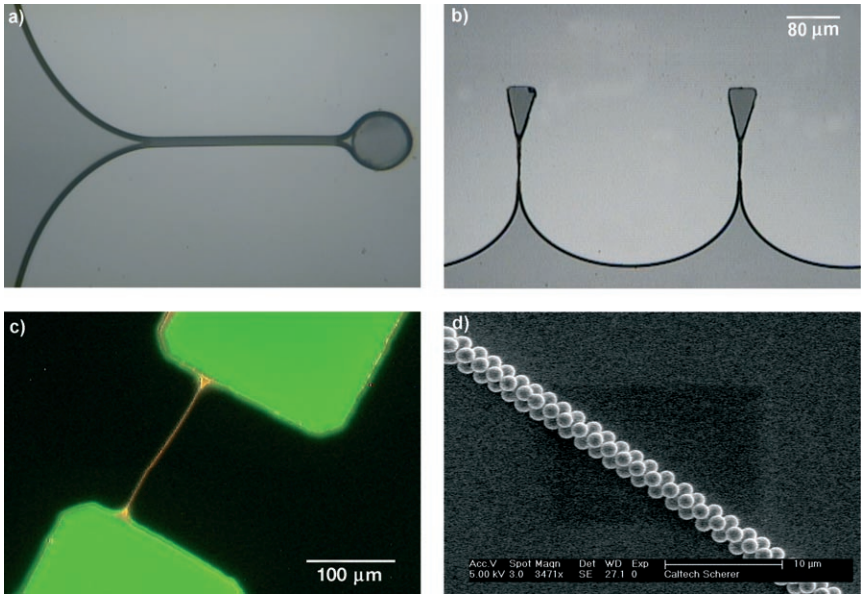

Figure 1. Results showing the effects of various pinning points and surfactants, and included self-assembled particles. a) A circular pinning point in a BSA solution. b) Triangular pinning points in a Triton X-100 solution. c) A quantum-dot line forming between two square pinning points. d) SEM image of self-assembled 2-μm-bead arrays. Reprinted with permission.[12]

various types of pinning points and surfactants: circular, triangular, or square pinning points (Figure 1 a–c) showed no appreciable changes. Interestingly, a quantum-dot line formed between two pinning points using a solution containing quantum dots if the distance between two points was sufficiently small (Figure 1 c). Although it is not clear whether single or multiple arrays of quantum dots were formed, this could provide a new route to fabricating interconnect wires. Using the same approach with 2-μm silica beads, they were able to fabricate a self-assembled bead array with minimal defects (Figure 1 d), which can be viewed as combining a top-down approach with bottom-up self-assembly. Finally, they found that small-sized beads could sometimes act as bridge between lines of BSA (<100 nm). Usually, an ultrathin line is intrinsically very unstable against breakup but might have been stabilized due to strong interactions between BSA and the glass substrate, as discussed earlier. As can be seen from a recent report on nanowire fragmentation mediated by dewetting,[20] a controlled dewetting process at this length scale would further allow for regular arrays of quantum objects.

In conclusion, the article highlighted here is of great benefit to unconventional patterning fields since it has made a major advance in controlling surface-tension-driven self-organization in combination with a traditional microfabrication method. If further tailored and controlled, dewetting or capillary flow could be a powerful, innovative self-assembly process for next-generation nanodevices.

[1] Y. N. Xia, J. A. Rogers, K. E. Paul, G. M. Whitesides, *Chem. Rev.* **1999**, *99*, 1823 – 1848.
[2] B. Michel, A. Bernard, A. Bietsch, E. Delamarche, M. Geissler, D. Juncker, H. Kind, J. P. Renault, H. Rothuizen, H. Schmid, P. Schmidt-Winkel, R. Stutz, H. Wolf, *IBM J. Res. Dev.* **2001**, *45*, 697 – 719.
[3] L. J. Guo, *J. Phys. D* **2004**, *37*, R123 – R141.
[4] B. D. Gates, Q. B. Xu, M. Stewart, D. Ryan, C. G. Willson, G. M. Whitesides, *Chem. Rev.* **2005**, *105*, 1171 – 1196.
[5] Y. A. Vlasov, X. Z. Bo, J. C. Sturm, D. J. Norris, *Nature* **2001**, *414*, 289 – 293.
[6] K. Y. Suh, H. H. Lee, *Adv. Funct. Mater.* **2002**, *12*, 405 – 413.
[7] N. Bowden, S. Brittain, A. G. Evans, J. W. Hutchinson, G. M. Whitesides, *Nature* **1998**, *393*, 146 – 149.
[8] S. W. Chung, D. S. Ginger, M. W. Morales, Z. F. Zhang, V. Chandrasekhar, M. A. Ratner, C. A. Mirkin, *Small* **2005**, *1*, 64 – 69.
[9] C. J. Hawker, T. P. Russell, *MRS Bull.* **2005**, *30*, 952 – 966.
[10] G. M. Whitesides, B. Grzybowski, *Science* **2002**, *295*, 2418 – 2421.
[11] Z. Y. Tang, N. A. Kotov, *Adv. Mater.* **2005**, *17*, 951 – 962.
[12] S. Vyawahare, K. M. Craig, A. Scherer, *Nano. Lett.* **2006**, *6*, 271 – 276.
[13] J. Eggers, *Rev. Mod. Phys.* **1997**, *69*, 865 – 929.
[14] K. C. Popat, T. A. Desai, *Biosens. Bioelectron.* **2004**, *19*, 1037 – 1044.
[15] K. A. Barnes, A. Karim, J. F. Douglas, A. I. Nakatani, H. Gruell, E. J. Amis, *Macromolecules* **2000**, *33*, 4177 – 4185.
[16] P. G. Saffman, G. I. Taylor, *Proc. R. Soc. London Ser. A* **1958**, *245*, 312 – 329.
[17] A. Ghatak, M. K. Chaudhury, V. Shenoy, A. Sharma, *Phys. Rev. Lett.* **2000**, *85*, 4329 – 4332.
[18] E. Kim, Y. N. Xia, G. M. Whitesides, *Nature* **1995**, *376*, 581 – 584.
[19] K. Y. Suh, H. H. Lee, *Adv. Mater.* **2002**, *14*, 346 – 351.
[20] M. E. Toimil-Molares, A. G. Balogh, T. W. Cornelius, R. Neumann, C. Trautmann, *Appl. Phys. Lett.* **2004**, *85*, 5337 – 5339.

Received: March 9, 2006
Published online on May 5, 2006

