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# Solvent assisted capillary force lithography

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**Abstract**

Capillary force lithography (CFL) utilizes the capillary-filling phenomenon of a polymeric melt into a cavity to pattern the polymer film coated on a substrate. Most CFL approaches are realized at high temperatures. The solvent-assisted CFL method proposed here realizes patterning at ambient temperature. A swollen PDMS (poly(dimethysilane)) stamp by solvent is placed in contact with a polymer thin film. As the solvent reserved in the PDMS stamp diffuses into the polymer film, the polymer can be dissolved or swollen. Then the capillary force drives the pattern formation. By carefully choosing the experimental conditions, it is possible to produce highly regular and reproducible nano- to micrometer scale polymer patterns using the same microscopic patterned mold. Complex polymer patterns can also be fabricated through the multiple printing.


*Keywords:* Capillary force lithography; Photolithography; Polystyrene

## 1. Introduction

The ability to fabricate patterns with nanometer resolution is of great importance for manufacturing advanced electronic, optical and mechanical devices [1–3]. Current research focuses on printing processes other than conventional photolithography to increase the range of patterning applications and to overcome the high cost problem and diffraction limit. A number of lithographic techniques are being developed. Among which, 'soft lithography' [4,5], the name of a set of non-photolithographic methods that relies on a reusable template, generally fabricated of poly(dimethysilane) (PDMS), to fabricate high-quality micro- and nanostructures directly from the template to the substrate have been explored extensively. Soft lithography includes microcontact printing (μCP) [6], micromolding in capillaries (MIMIC) [7], solvent assisted microcontact molding (SAMIM) [8], microtransfer molding (μTM) [9], replica molding (REM) [10,11], and near optical field photolithography [12]. Significant work in this area has been done.

Along with soft lithography, capillary force lithography (CFL) has proven to be quite fruitful [13–17]. It is a simple and effective tool for patterning. It employs capillarity, a useful concept for the patterning of polymer materials and combines the essential features of imprint lithography [18]—molding a polymer melt with the prime element of soft lithography—the use of elastomeric stamp. When the polymer film is thick enough, polymer melt can fill up the void space between the polymer and the mold completely, thereby generating a negative replica of the mold. Anisotropic dewetting occurs when the polymer film is relatively thin with respect to the intrusion depth of the stamp. Separate lines with reduced dimensions located at the feature edges of the original stamp can also be fabricated [15,19,20].

In all the lithographic techniques described above, the excellent elastomeric property of PDMS is a key factor. It allows PDMS mold to be used widely in replicating patterns with high fidelity [21,22]. But it also brings the drawbacks such as deformation and swelling. To overcome the effect of deformation, composite stamps with a stiff layer supported by a flexible layer have been proposed and extend the capability of soft lithography to the generation of 50–100 nm features [23]. Reversely, the deformation of PDMS stamp has also been utilized for size reduction and new patterns generation. Xia et al. were able to create patterns with size-reduced and size-promoted features by intentionally applying external forces to laterally deform the stamps during contact printing [24]. Guo et al. also gained size reduction and new patterns different from those features on the stamps by applying pressure perpendicular to PDMS stamp to achieve its vertical deformation [25].

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In this paper, we present a solvent assisted capillary force lithography (SACFL) by using the swollen PDMS mold. Our method differs from capillary force lithography in that it uses solvent instead of temperature to soften the material. When a swollen PDMS mold is put contact with the polymer thin film surface, the solvent kept in PDMS mold will diffuse into the polymer film. The polymer dissolved then form structures along the vertical walls of the stamp due to capillary rise. Here, we studied the patterning behavior of a polystyrene (PS) film under a microscopically patterned PDMS stamp. PS is a very familiar polymer and has been studied extensively [26–28]. Through the modulation of experimental conditions, we can tune the size of the polymer patterns obtained. Cross-patterning polymer patterns can also be fabricated. This approach is suitable for large-area patterning, and has strong points such as simplicity, high speed and low cost.

## 2. Experimental

Polished test-grade silicon wafers were purchased from the General Research Institute for Nonferrous Metals, China. The silicon substrates with a 2 nm thick layer of native $SiO_X$ were degreased by ultrasonic cleaning in acetone, and then cleaned in a solution with 70 vol% concentrated sulfuric acid and 30 vol% hydrogen peroxide at 80 °C for 1 h. Subsequently, the substrates were rinsed repeatedly with deionized water and dried under nitrogen gas. Polystyrene (PS, $M_w = 114, 200$) was purchased from Aldrich. PDMS (Sylgard 184) and its kit (curing agent) were purchased from Dow Corning. Casting the prepolymer Sylgard 184 and its kit in a ratio of 10:1 on the photoresist thin films patterned by photolithography and curing at 65 °C for 4 h, then the PDMS stamp with relief structures as negative replicas of the structures in the photoresist master was formed. The PDMS stamp can be separated from the patterned photo-resist freely just by peeling off the PDMS stamp form the master because PDMS adheres poorly to the photo-resist due to its low surface energy. The detailed process has been given in the literatures [4,5]. Two kind configurations of PDMS stamps were used: one is concave squares with width of 5 μm and another is line patterns with a width of 5 μm spaced by 5 μm. Then the PS solutions were spin coated onto the freshly cleaned silicon wafers to produce thin films with a thickness of ~290 nm. Film thickness was determined by a multiple wavelength ellipsometry (Uvisel ER Ellipsometer, JOBIN YVON S.A., France). The PDMS stamp was dipped in solvent (The stamp can be reused more than ten times). The solvent is chosen depending on the polymer used. Here tetrahydrofuran (THF) is chosen because of its soluble ability to PS and the swelling to PDMS. After kept in THF for a few second, PDMS mold was taken out. THF that was still remained on the surface of the stamp was blown off by nitrogen gas. Then the stamp was placed on the PS-coated substrate and a slight pressure (200 g/cm$^2$) was applied to the system to form an intimate junction. Subsequently, the system was kept undisturbed for a certain time. The mold was removed from the surface and the obtained polymer structure was characterized with atomic force microscopy (AFM) (SPI3800N Probe Station, Seiko Instruments Inc., Japan) in tapping mode (Silicon tips on silicon cantilevers with spring constant 2 N/m were used).

## 3. Results and discussion

Fig. 1 summarizes the procedure for patterning the thin polymer films by solvent assisted capillary force lithography. This method shares an operational principle similar to that of capillary force lithography in utilizing capillarity. When a liquid wets a capillary tube and if the wetting results in lowering the free energy, the wetting leads to the capillary rise of the liquid [13]. Cross-linked PDMS can be swollen in a number of solvents. Swollen PDMS stamp still has good mechanical strength to be used. Due to swelling, the PDMS mold can act as a solvent container. Under a slight pressure, a prepatterned and swollen PDMS stamp is brought into contact with the thin polymer film surface. The reserved solvent molecules will diffuse into the thin polymer film across the contact because of the gradient of the solvent concentration between these two surfaces. The thin polymer film in contact with the raised parts of the PDMS stamp can be dissolved or swollen. The polymer dissolved is squeezed out from the areas of contact and filled into the grooves where structures are formed along the vertical walls of the stamp due to the capillary rise. When the PDMS stamp is

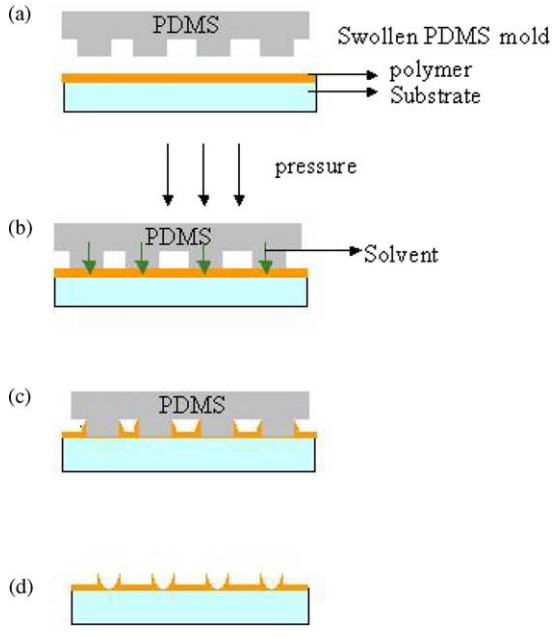


Fig. 1. Schematic illustration of solvent assisted capillary force lithography: (a) PDMS mold with the desired topography is swollen by the solvent, (b) the swollen PDMS mold is pressed on a thin polymer film spin-coated on a substrate, (c) the solvent molecule diffuses into the thin polymer film and the polymer climbs up the confining walls of the recess due to the capillary force, (d) the mold is removed to reveal the polymer pattern.

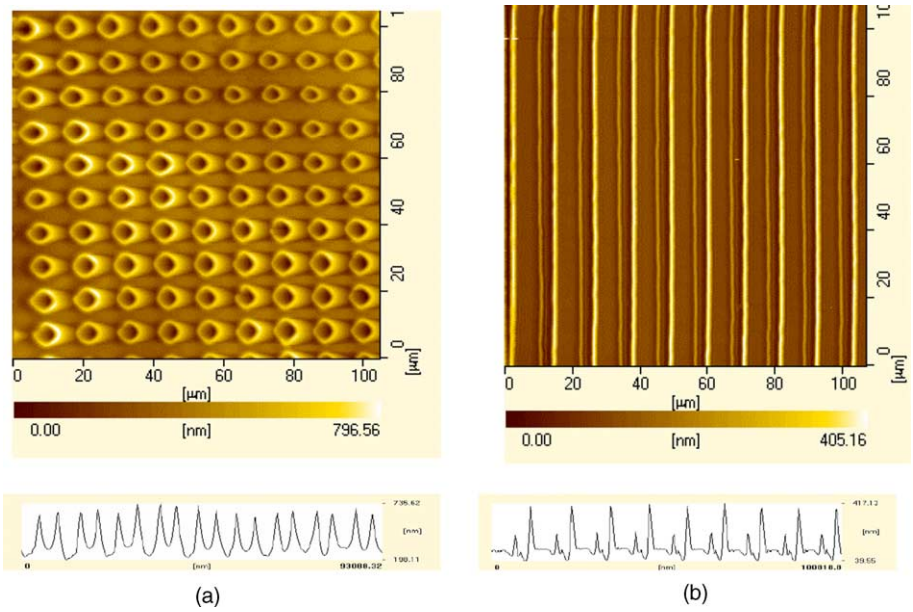


Fig. 2. AFM images of the polymer patterns formed on thin PS films by the experimental setup shown in Fig. 1 with a PDMS stamp having (a) square and (b) stripe patterns. The cross-sectional profiles of the AFM images are shown in the bottom.

lifted up, patterning of thin polymer film is realized. As indicated, the key element of this procedure is the swelling of PDMS stamp by a solvent and the conformal contact between the elastomer stamp and the thin polymer film. We can tune the swelling degree of PDMS stamp by control the time of dipping in the solvent. PDMS has a very low reactivity toward the polymers and its low surface tension is sufficient to allow its separation from the polymeric structure. Fig. 2 displays the examples of structures fabricated on thin PS film with solvent assisted capillary force lithography. The PDMS stamps used consisted of stripes and squares. If the mold leans a little toward one side, an asymmetric structure results such that the striped patterns with two different heights.

The diffusion of the solvent is a tempered process. Capillarity occur when the polymer at the interface is dissolved, then the process of diffusion, dissolution and capillarity keeps a balance. Through the modulation of experimental conditions we can modulate the dimensions of gained polymer patterns. There are many factors which may affect the quality of the patterning features, such as the thickness of the polymer thin film, the pressure employed, and so on. Here we mainly discuss the effect of contact time and study the patterning behavior of a PS film under a microscopically patterned PDMS stamp with recessed and protruding lines. We tune the lateral dimensions of the polymer lines through the modulation of the contact time and further control the sum of solvent molecular diffused. Fig. 3 shows the surface topographies obtained from PS films with the same thickness and contacting with the same PDMS mold for different times. As we can see from Fig. 3(a), a pair of thinner stripes in the trench of mold has been obtained when the contact time is short. The height of these stripes increase with the contact time till the solvent kept in the PDMS mold volatilized completely. When these stripes grow higher and reach the roof of PDMS mold, the two polymeric lines eventually merge into one and fill the grooves of the stamps. In this case, the negative replicas of the stamps can be obtained. When dissolved polymers cannot fill the grooves completely, patterns like Fig. 3(d) can be obtained. In some case, the polymer pattern along the channels is not uniform because the mold leans a little toward one side. When the polymer film is thin, the solvent kept in the PDMS mold can dissolve this thin polymer film completely. We can also tune the lateral dimensions of these two lines through the change of the initial polymer film thickness.

This method can also be used to generate more complex patterns from simpler ones. Fig. 4 shows the application of multiple printing in forming new patterns. The patterns were generated by a double-printing procedure: a swollen PDMS stamp having parallel lines on its surface was contact with the polymer surface for $\sim$0.5 min first. Then the stamp was removed, cleaned with ethanol, re-swollen with THF solvent, and re-contacted with the polymer surface for another $\sim$0.5 min, with the orientation of the lines rotated by $\sim$90°. Because the PDMS possesses good elasticity, it can make conformal contact with the patterned polymer surfaces over relatively large areas. As indicated, the second polymeric microstructures only form at the contact area. The patterns under the groove of PDMS mold are not affected. By rotating for different angles between these two moldings, we can produce patterns with a variety of shapes. Through the change of contact time for each molding, the stripes generated can have different height.

The precondition in this method is the dissolution of polymer by the solvent preserving in the PDMS mold. In solvent assisted microcontact molding (SAMIM), [8] solvent

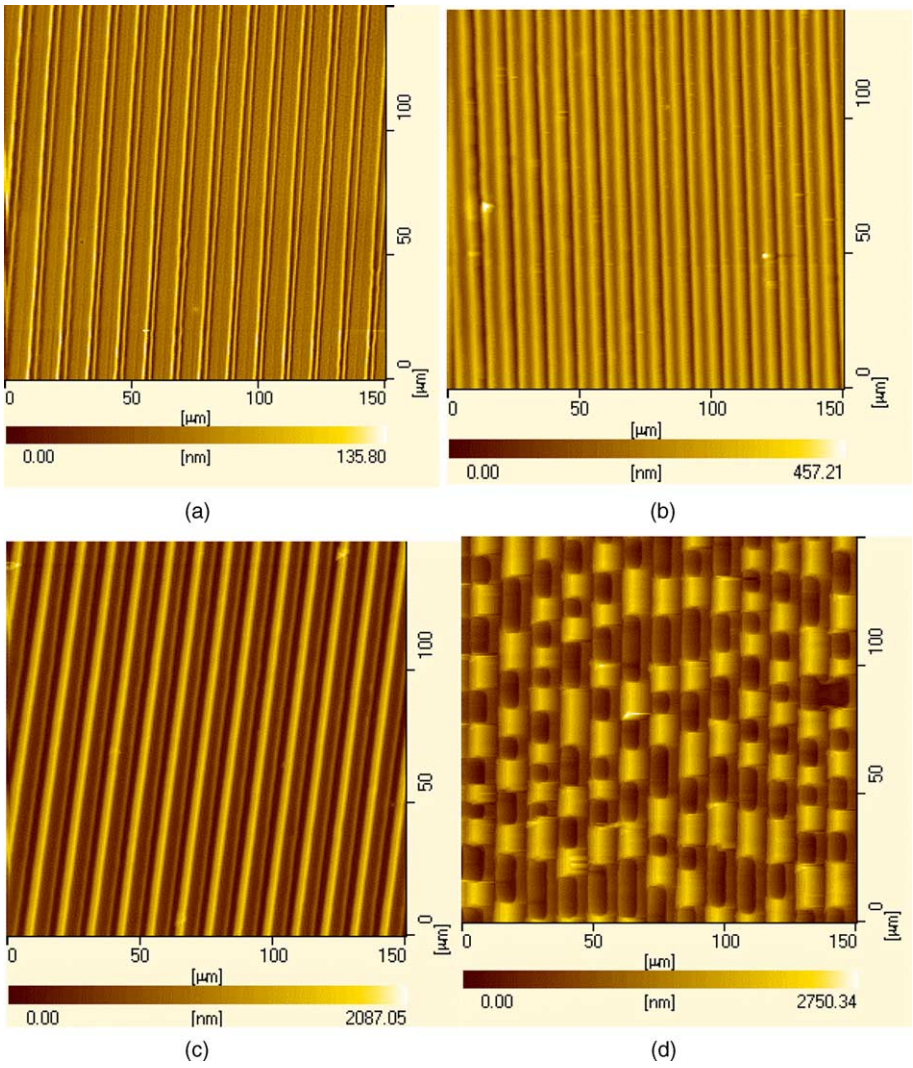


Fig. 3. AFM images of the polymer patterns obtained on thin PS films with a swollen PDMS contacting the polymer surface for different times: (a) 0.5 min, (b) 1 min, (c) 1.5 min, (d) 5 min.

also plays the key role. In SAMIM, a solvent wets the PDMS mold and liquid solvent fills the recessed regions on the surface of the PDMS mold in order to lower the free energy. When this PDMS mold is brought into contact with the surface of the polymer thin film, the solvent dissolves or swells a thin layer and polymer patterns opposite to that of elastomer stamp can be obtained. Here we utilize the solvent molecular kept in PDMS stamp to fabricate polymer patterns. Thereby, polymer patterns with tunable dimensions and multilayer polymer structures that cannot be made from SAMIM can be generated.

Our method differs from capillary force lithography in that it uses solvent instead of temperature to soften the material. Therefore, we can realize patterning at room temperature, and the high temperature needed in previous patterning method is avoided. It makes Cross-patterning of polymer film be possible. It can also be employed to fabricate organic devices without causing degradation. The ability to fabricate nanoscale and complex polymer patterns on the substrate makes this method much more attractive. The polymer patterns obtained can be further used in combination with reactive-ion etching to transfer these patterns into silicon [19,20] and other substrates. The combination with REM for the fabrication of high-resolution, second-generation stamps for soft lithography has also been demonstrated [29].

## 4. Conclusions

In summary, we proposed a solvent assisted capillary force lithography by utilizing the swelling property of PDMS and the principles of capillary force lithography. Through the modulation of experimental conditions, we can tune the dimensions of polymer patterns with the same microscopically patterned PDMS mold. Besides the fast and large area pattern ability, complex patterns can also be fabricated with this method conveniently. The method avoids the high temperature needed in conventional capillary force lithography and realizes patterning at room temperature. The polymer patterns obtained

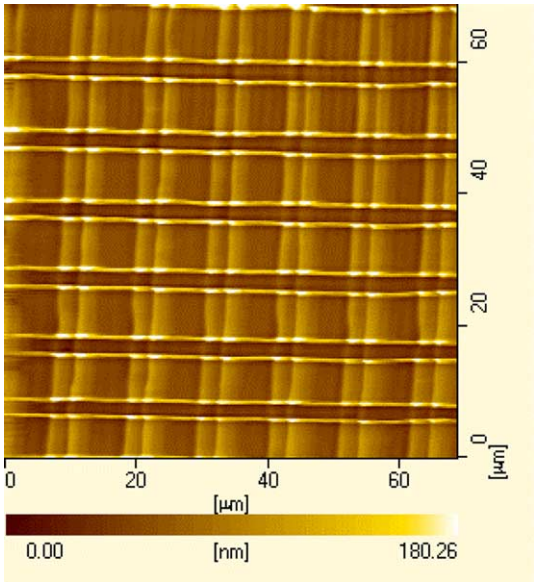


Fig. 4. AFM image of the polymer patterns obtained on thin PS films by pressing a swollen PDMS stamp on the sample of Fig. 2(b) with 90° to the existing stripes.

can be further used as mask to fabricate patterned substrate and elastomeric mold.

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