ARTICLE

Micromolding in Capillaries Using Swollen Elastomeric Stamp

Jin-xia Shi, Zheng Wang, Ping-sheng He*, Hai-yang Yang

University of Science and Technology of China, Department of Polymer Science and Engineering, Hefei 230026, China

(Dated: Received on October 25, 2005; Accepted on February 15, 2006)

Micromolding in capillaries of a micro-square array was carried out for polystyrene solution in acetone by means of swollen polydimethylsiloxane (PDMS) elastomeric stamp. The resulting micro-cubic poles were isolated and separable when the added amount of the polystyrene solution was small. Some special distorting micro-patterns in the micro-square array were observed because of shrinkage resulting from the varying evaporation rate of solvent at different places.

Key words: Micromolding in capillaries, Swelling, Polydimethylsiloxane, Elastomeric stamp

I. INTRODUCTION

Soft lithography (SL) is a new rapidly developing micro-fabrication technology recently used to form micro-patterns and micro-structures [1-4]. SL technology includes a set of micro-fabrication techniques which include micro-contact printing (μCP), micromolding in capillaries (MIMIC), solvent-assisted micromolding (SAMIM) and replica molding (REM). The key element in SL is an elastomeric stamp with excellent elasticity and compact texture, which is favored to transfer the micro-patterns on silicon template formed by UV lithography into the surface of a substrate. The fidelity and precision of micro-patterns on the substrate are dependent on the quality of the elastomeric stamp. Polydimethylsiloxane (PDMS) [5] is one of the most appropriate materials at the present time.

The elastomeric stamp often contacts certain organic solvents in the process of SL. The swelling of PDMS in the organic solvent is one of the problems in SL, so it is necessary to avoid swelling of the PDMS stamp. As with everything in nature, this phenomenon could be good or bad, and it may be possible to use the swelling characteristics of PDMS elastomeric stamps advantageously in the procedures of SL. In fact, the characteristic of easy deformation of the swelling polymer has been utilized by Yang *et al.* in SL [6,7]. They elongated the swollen elastomeric PDMS stamp and built up the so-called second machining and integration of orderly structure. In this work, we introduced some significant phenomena in MIMIC with a swollen PDMS elastomeric stamp.

Polystyrene (PS) solution in acetone sometimes stops going ahead in micro-channels and does not arrive at the other end of micro-channel in MIMIC. Of course, the main factor is the combined result of viscosity of the polymer solution, surface free energy of the substrate and the PDMS stamp, but the solvent absorbtion by the PDMS stamp could be another important factor as well. Thus, what will happen if a swollen PDMS stamp is used in MIMIC? In this work, we chose acetone as a solvent because it can swell PDMS to some degree but not too obviously.

*Author to whom correspondence should be addressed. E-mail: hpsm@ustc.edu.cn

II. EXPERIMENTS

A. Materials

PDMS, Sylgard 184, was purchased from Dow Corning, including prepolymer (A) and curing agent (B). PS was prepared in our lab. Acetone, H_2SO_4 (98%) and H_2O_2 (30%) are all AR grade and purchased from Shanghai No.1 Reagent Factory.

Silicon template with micro-cubic poles of size 8 μm×8 μm square was produced by the Micro-Electron Institute of Tsinghua University with conventional photolithography.

The substrate was normal microscopic slide glass. It was immersed in chromic acid mixture for 24 h, then immersed in saturated NaOH solution in alcohol for another 8 h, and finally washed with distilled water and dried by nitrogen before using.

A GALEM/CTV optical microscope (Nanjing Chiang-Nan electro-light Group Company) with CCD component was used to observe the patterned substrate surface and take pictures.

B. Preparation and swelling of PDMS stamp

According to the procedure for Sylgard 184, the prepolymer (A) was homogeneously mixed with curing agent (B) with the ratio of 10:1 by weight. Then the mixture was cast on templates patterned with micro-cubic poles on it and cured at 70 °C for 4 h. Finally the PDMS stamp with accurate replication of micro-cubic holes was gently removed from the template.

ISSN 1003-7713/DOI:10.1360/cjcp2006.19(6).527.3

The edge parts without any micro-cubic holes of the PDMS stamp were cut off and cleaned carefully. The swollen PDMS stamp was obtained by immersing the stamp in acetone for 48 h at the room temperature.

C. MIMIC

The surface with micro-cubic holes of the swollen PDMS stamp was put in tight contact with the pre-cleaned substrate glass by putting appropriate pressure on the stamp. Some amount of PS acetone solution with 5% concentration was dropped around the PDMS stamp, then it was kept at the room temperature for 24 h in order to dry completely. After gently removing the PDMS stamp, the patterned substrate was obtained.

III. RESULTS AND DISCUSSION

A. Micromolding in capillaries by the swollen elastomeric stamp

The results were quite different and depended mainly on the amount of PS solution added in MIMIC with a swelling PDMS stamp. In MIMIC, there were some empty and unconnected micro-cavities between the stamp and substrate. When the amount of dropped PS solution was small compared to the total volumes of all micro-cavities, a very regular isolated micro-cubic poles array was obtained (Fig.1(a)) in the area covered by PDMS stamp. When we scraped lightly with needlepoint on the patterned surface of the substrate, the nicked micro-cubic poles shifted from their quondam place, indicating that these micro-cubic poles were isolated from each other (Fig.1(b)). On the other hand, if the amount of dropped PS solution was excessive compared to the total volumes of all cavities, a micro-cubic poles array connected with a very thin PS film was obtained (Fig.2(a)). Figure 2(b) shows the resulting connected micro-cubic poles when they were scraped lightly by a needlepoint, as in the case of Fig.1.

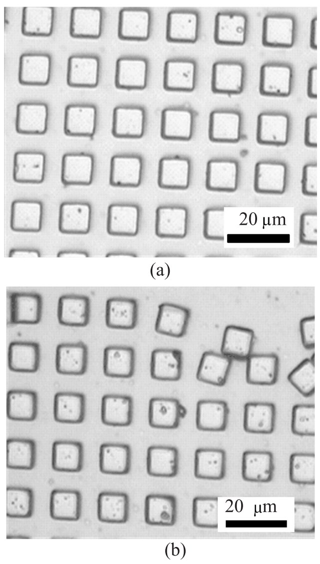

FIG. 1 (a) Micro-cubic poles array produced by MIMIC using swollen stamp. (b) The micro-pattern was scraped by a needlepoint at the right corner.

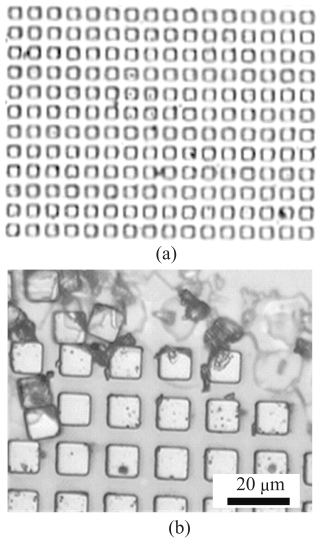

FIG. 2 (a) Micro-cubic poles array produced by MIMIC when the amount of solution dropped was large enough. (b) The micro-cubic poles array was scraped by a needlepoint at the right corner.

Generally, the forming of connective channels between stamp and substrate is very important in MIMIC. However, the micro-cubic holes array of PDMS stamp was concave in our experiment and the micro-cavities between stamp and substrate glass were isolated from each other. The mechanism of the PS solution flow into the micro-cavities is shown in Fig.3. In using a swollen PDMS stamp in MIMIC, it was supposed that there was a layer thin liquid film between the swollen PDMS stamp and the substrate glass, and the inter-space of thin liquid film acted as a micro-channel in MIMIC, by which the PS solution could flow into the micro-cavities between the swollen PDMS stamp and the substrate glass. During the drying process in MIMIC, the solvent evaporated over time, and it was supplemented by the solvent absorbed in the swollen PDMS stamp. When the amount of PS solution was small, all solvent coming from the swollen stamp entered into the micro-cavities between the stamp and substrate glass and formed an isolated micro-cubic poles array without any connection by the PS thin layer. However, with a large enough amount of PS solution, the redundant PS solution formed a very thin PS film connecting each micro-cubic pole.

Here we name this method "micromolding in capillaries using swollen elastomeric stamp" (MIMICSES). The difference between MIMICSES and normal MIMIC is that the characteristics of micro-patterns in MIMIC-

ISSN 1003-7713/DOI:10.1360/cjcp2006.19(6).527.3

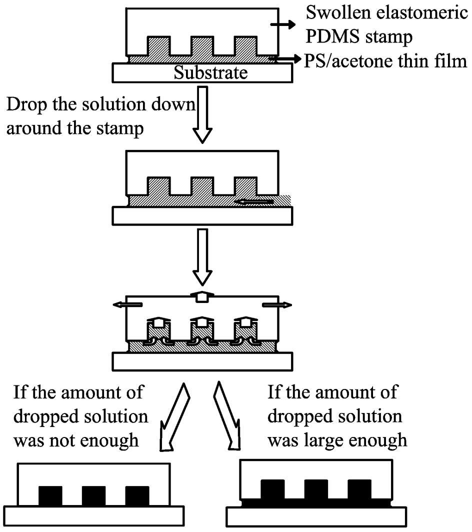

FIG. 3 The sketch of MIMIC using swollen stamp.

SES depends on both the added amount of polymer solution and the drying process.

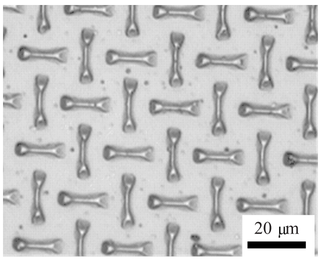

FIG. 4 Micro-patterns of produced PS resulting from some irregular deformation in MIMIC using swollen stamp.

B. Shrinkage of swollen elastomeric stamp

Some distorting micro-patterns could be observed in the area with micro-pattern, particularly in the region near the edge which is shown in Fig.4. Obviously it resulted from the difference of stamp shrinkage for varying acetone evaporation rates in different places. The mechanism could be analyzed as the following steps (Fig.5): The inhomogeneous pressure on the swollen PDMS stamp resulted in varying thickness in the layer of PS solution under the PDMS stamp. This should be avoided but doing so is hard to realize at present. Where the PS liquid layer is thinner, sunken micro-cubic poles formed between the PDMS stamp and the substrate glass,and they could not get any additional solution supply because the PDMS stamp was in tight contact with the substrate glass and formed a closed space, which resulted in the shrinkage of PDMS and negative pressure in the sunken micro-cubic poles. The negative pressure in the sunken dot brought on collapse of the micro-square, followed by the collapse of the nearest neighbor micro-cubic poles one by one. The collapse of partial micro-cubic poles led to the lower efficiency of MIMICSES. After changing the solvent or improving the swelling degree of the stamp by montmorillonite [5], MIMICSES will have potential application in microfabrication technology.

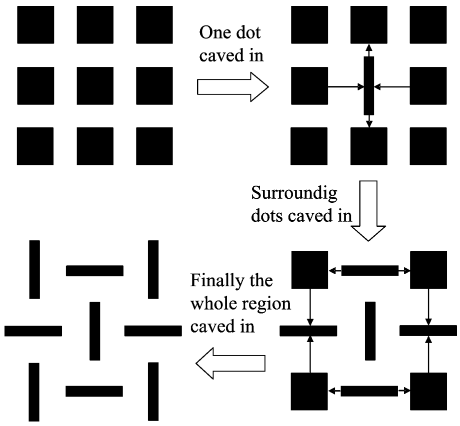

FIG. 5 Possible mechanism of irregular deformation in micro-pattern using swollen stamp.

IV. CONCLUSION

In this work, a new MIMIC technique, called "micromolding in capillaries by swollen elastomeric stamp" (MIMICSES) was introduced. In MIMICSES the polymer micro-patterns can be controlled by changing the amount of polymer solution. At the same time, the external pressure can induce the forming of some regular micro-patterns in MIMICSES. The MIMICSES method offers a new technique of polymer micro-patterning and needs to be developed further in subsequent research.

V. ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (No.20374049) and the Specialized Research Fund for the Doctoral Program of Higher Education (20040358018).

[1] Y. N. Xia, J. A. Rogers, K. E. Paul and G. M. Whitesides, Chem. Rev. **99**, 1823 (1999).
[2] J. P. Liu and P. S. He, Chin. J. Chem. Phys. **17**, 215 (2004).
[3] X. S. Wu, L. J. Pan, G. Zou, J. P. Liu and P. S. He, Chin. J. Chem. Phys. **17**, 641 (2004).
[4] B. K. Jin and P. S. He, Chin. J. Chem. Phys. **18**, 439 (2005).
[5] B. K. Jin, X. S. Wu, D. Z. Chen and P. S. He, Chem. J. Chin. Univ. **24**, 1142 (2003).
[6] X. Yan, J. M. Yao, G. Lu, X. Chen, K. Zhang and B. Yang, J. Am. Chem. Soc. **126**, 10510 (2004).
[7] X. Yan, J. M. Yao, G. Lu, X Li, J. H. Zhang, K. Han and B. Yang, J. Am. Chem. Soc. **127**, 7688 (2005).

ISSN 1003-7713/DOI:10.1360/cjcp2006.19(6).527.3