

Functional Polymers for Advanced Nanotechnology

Kyung M. Choi

Bell Laboratories, Lucent Technologies, Murray Hill, NJ 07974

We demonstrate a novel chemical approach on the improvements of soft lithography for the nano-resolution integrations by the development of new photopatternable silicon elastomers. We designed a chemical structure of silicon rubbers, which produce stiffer stamps with high physical toughness to satisfy our requirements on lithographic tasks. The new silicon stamps show advanced performances in pattern transfers in the nano-scale soft lithography. Its photopatternable capability was also beneficial to fabricate photopatterned electrometric features.

Key words: Nanotechnology, Nanofabrications, Functional Polymers for nanoapplications, Soft lithography.

INTRODUCTION

The ability to integrate high fidelity patterns using functional polymers enables the fabrication of novel nano- or micro-devices with high performances. The development of new functional polymers/organic materials for nanotechnology applications plays an important role to achieve enhanced performances in devices.

There are a lot of challenges present for chemists and materials scientists in this area to achieve high resolution pattern fabrications by developing new materials; because, nano-technology is a part of the chemical domain, which can create and bring desired functions by modifying molecular structures. It thus requires novel molecular designs of manipulating chemical structures to investigate and explore several aspects that may contribute to the improvements of device performances. Our diverse efforts in this area have brought new advances in device functions by the development of novel materials that are not commonly used to implement complex requirements.

A variety of functional polymers has been designed and synthesized for applications in nanotechnology. One of recent achievements includes the device fabrication by 'soft lithography', which use 'soft' materials, such as silicon elastomers as a stamp material to replicate or transfer small features from the original masks to flexible substrates for applications, for example plastic electronics.

Soft lithography has gotten a great attention to the replication of small features generated on a variety of substrates as a low cost alternative to conventional photolithography.¹⁻¹¹

However, the resolution of current soft lithography limits to nano-regime due to low mechanical moduli of commercial stamps based on silicon elastomers such as Sylgard 184 system. Significant thermal deformation during the curing process also has been a problem to achieve high fidelity pattern fabrications. Since the resolution of this technology significantly relies on mechanical property of stamp materials, we present here chemical strategies to improve resolution in the pattern fabrication by designing a new version of photocurable silicon elastomers, which fulfill our diverse demands and thus to extend current limited soft lithography to advanced levels.

In soft lithography, silicon elastomers such as Sylgard 184 (Dow Corning, MI) are in current use. The structure of those commercial silicon elastomers is based on poly (dimethyl) siloxane (PDMS), which consists of a Si-O-Si polymeric backbone.

The Sylgard 184 system produces a highly stretchable silicon elastomer, which is useful for pattern transfer. Its elastomeric property arises from the repeated Si-O-Si backbone. Due to its excellent electrometric property, it also allows fabrication of mechanically flexible non-planar surfaces by rolling the curved substrates over PDMS stamps in 'roll-to-roll flexible printing fabrication'.⁹

However, we need to improve the resolution of current soft lithography to nano-scaled regimes for fabricating more smaller devices, for example organic thin film transistors, flexible panel display, bio-sensors, and microfluidic devices, by designing more stiffer stamp materials.

RESULTS AND DISCUSSIONS

In this study, the new, stiffer photocurable PDMS system has been developed to satisfy a set of our multiple requirements including enhanced mechanical modulus, high physical toughness, good surface adhesion, photocurability, stress-free system, and low polymerization shrinkage. We demonstrate its improved physical property and soft lithographic performance at the nano-scale in a comparison to conventional thermo-curable PDMS stamps.

Since commercial silicon elastomers often collapse and merge during the lithographic process due to their inadequate mechanical properties, we have developed a new version of PDMS stamps (hv-PDMS), which overcomes some of those difficulties of commercial PDMS stamps. Our strategy in the molecular design of a new version of PDMS prepolymers was motivated by an interpretation that the development of stiffer and photocurable stamps may facilitate fundamental interrogations to extend current soft lithographic technology to an advanced level.

In new molecular design, we inserted urethane functional group to create its physical toughness based on hydrogen bonds between cross-linkers to minimize mechanical failures during lithographic process. Methacrylate group was also used in the modification of PDMS network to bring photocurability since commercial thermocured stamps have shown significant thermal deformations during the thermal cure. We also designed a linear prepolymerized system to reduce polymerization shrinkage. This chemical strategy creates adjustable mechanical properties of stamp materials from 'soft' to 'hard' silicon rubbers.

Usually, the resolution of soft lithographic replicating and micro-contact printing rests on the 'physical toughness', which combines both mechanical stiffness and elasticity. Since the hv-PDMS stamp shows an optimized physical toughness, the new stamp material with good physical toughness may compromise mechanical instability shown in commercial stamps for our lithographic applications.

We also prepared an original master with features of narrow (300 nm line-wide) and tall heights (600 nm thickness) of photoresist. We present examples of hv-PDMS stamp for high fidelity nano-pattern transfer using the master with nano-striped patterns. SEM and AFM analyses follow to analyze the performance.

We carried out 'stamping process' to transfer patterns onto an optical adhesive layer (NOA 72, Norland) using the hv-PDMS mold. Figure 1 shows SEM images of patterns generated on the optical adhesive layer through the stamping process using hv-PDMS stamp. As shown in the Figure 1, those patterns transferred on the optical adhesive represent a high fidelity performance with well-defined and defect-free patterns within a large area. Figure 1 demonstrates a conspicuous advance in its nano-scale

lithographic performance, especially shown in those SEM

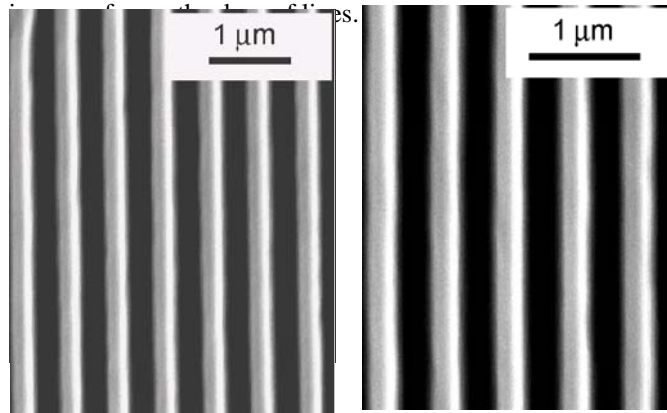


Figure 1. SEM images generated on the NOA optical adhesive layer using the photocurable hv-PDMS mold with a variety of magnifications.

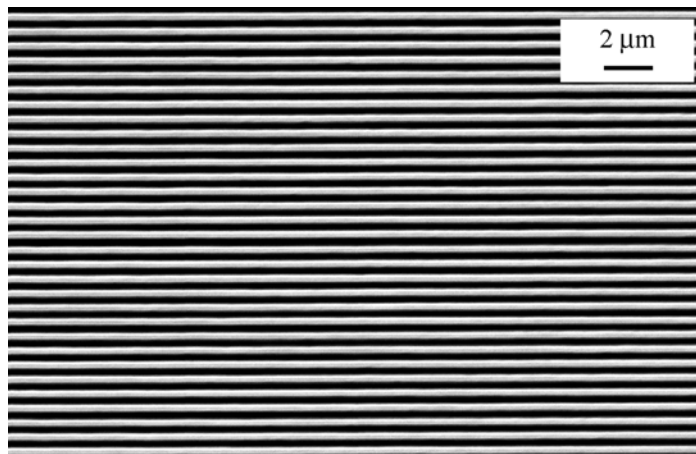


Figure 2. SEM images generated on the NOA optical adhesive using the hv-PDMS mold over a large area with uniform and defect-free feature.

Since our overall efforts toward adjusting mechanical properties of hv-PDMS stamps has resulted in new advances in nano-resolution soft lithography, our molecular design prototype demonstrated in this study will shorten the distance from materials' developments to our lithographic objectives.

We also examined its stamping process over 'a large area lithography' using hv-PDMS stamp, which is shown in Figure 2. As shown in Figure 2, it presents a large-area nano-scaled soft lithography ($\sim 25 \text{ cm}^2$) without showing any significant defects.

We also provide an additional information of the performance at nano-resolution lithography by AFM technique to determine the results in Figures 1 and 2, in both of line-width and height profiles. Figure 3 shows AFM profiles of nano-lined patterns fabricated on an optical adhesive (NOA) using hv-PDMS stamp.

The top image of Figure 3 shows an AFM line-width profile, which a horizontal distance between two red-arrows was observed to be 603 nm; it also corresponds to the 300 nm line-width on the original master. We also carried out a height profile evaluation to verify the thickness of the three-dimensional patterns; as shown in the right AFM image of Figure 3, it reveals a thickness of ~ 600 nm. These numbers also agree with those of the original master.

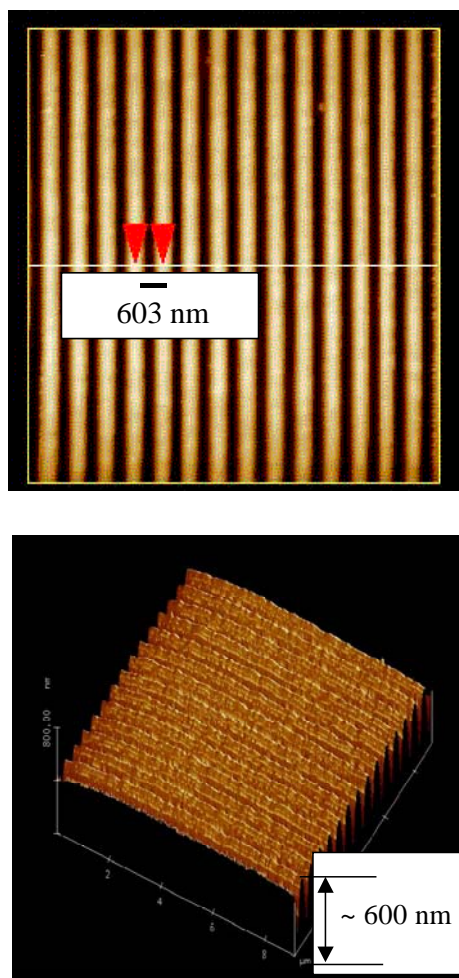


Figure 3. AFM analysis; the width (a) and height (b) profiles of nano-lined patterns generated on a thin layer of the NOA optical adhesive using the $h\nu$ -PDMS.

We demonstrate here that the adjusting physical toughness of $h\nu$ -PDMS stamp was directly beneficial to the reduction of mechanical failures during the pattern transfers and thus it produces an improved performance in nano-resolution soft lithography, which can't be easily achieved from conventional stamps.

Additionally, we also carried out photopatterning process using the $h\nu$ -PDMS prepolymers for functional patterning task. Since most commercial stamps are thermocurable, which results in significant deformations during the cure, those new stamp materials with photocurable capability are

beneficial to extend our applications in fabrications. Figure 4 shows the result of 'elastic photopatterns' generated on a silicon wafer using the newly designed PDMS prepolymers.

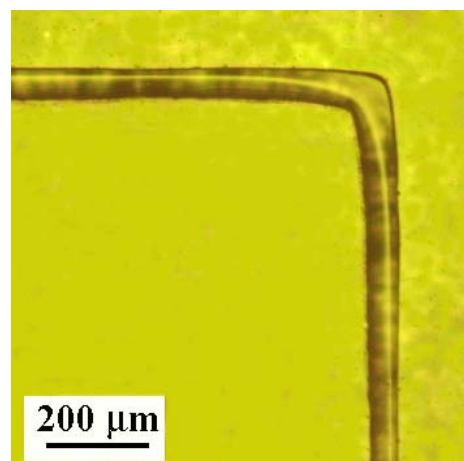


Figure 4. A microscopic image of curved pattern fabricated using photocurable $h\nu$ -PDMS polymer.

In conclusion, we developed a new class of photocurable silicon elastomers by molecularly inserting a rigid, photocurable pendant groups into the PDMS polymeric network for use advanced soft lithography at the nano-scale resolution. Its adjustable physical property was directly beneficial to the performance for the case of the nano-features with high aspect ratios which is one of the most challenging 'nano-patterning' tasks in an advanced soft lithography. Those specific advantages obtained from the new molecular design also encourage us to explore functional photopatterning at the nano-scale resolution.

REFERENCES

- [1] (a) T. Thorsen, R. W. Roberts, F. H. Arnold, S. R. Quake, *Phys. Rev. Lett.* **86**, 4163, 2001. (b) T. Thorson, S. J. Maerkl, S. R. Quake, *Science* **298**, 580, 2002. (c) J. P. Rolland, R. M. Van Dam, D. A. Schorzman, S. R. Quake, J. M. DeSimone, *J. Am. Chem. Soc.* **126**, 2322, 2004.
- [2] (a) X. Duan, C. Niu, V. Sahi, J. Chen, J. W. Parce, S. Empedocles, J. L. Goldman, *Nature* **425**, 274, 2003. (b) H. Sirringhaus, T. Kawase, R. H. Friend, T. Shimoda, M. Inbasekaran, W. Wu, E. P. Woo, *Science* **290**, 2123, 2000.
- [3] (a) K. M. Choi, K. J. Shea, *Photonic Polymer Systems, Fundamentals, Methods, and Applications*. Edited by D. L. Wise et. al. World Scientific Publishing Co. Pte. Ltd. **49**, Chapter 12, 1998. (b) P.G. Conrad, P. T. Nishimura, D. Aherne, B. J. Schwartz, D. Wu, N. Fang, X. Zhang, J. M. Roberts, K. J. Shea, *Adv. Mater.* **15**, 1541, 2003.
- [4] (a) K. Keren, R. S. Berman, E. Buchstab, U. Sivan, E. Braun, *Science* **302**, 1380, 2003. (b) M. Lefenfeld, G. Blanchet, J. A. Rogers, *Adv. Mater.* **15**, 1188, 2003.

[5] (a) Y. Xia, G. M. Whitesides, *Angewandte Chemie* 37, 550, 1998. (b) R. J. Jackman, S. T. Brittain, A. Adams, M. G. Prentiss, G. M. Whitesides, *Science*, 280, 2089, 1998. (c) Y. Xia, J. A. Rogers, K. E. Paul, G. M. Whitesides, *Chem. Rev.* 99, 1823, 1999. (d) P. Yang, G. Wirnsberger, H. C. Huang, S. R. Cordero, M. D. McGehee, B. Scott, T. Deng, G. M. Whitesides, B. F. Chmelka, S. K. Buratto, G. D. Stucky, *Science* 287, 465, 2000.

[6] (a) J. A. Rogers, Z. Bao, K. Baldwin, A. Dodabalapur, B. Crone, V. R. Raju, V. Kuck, H. Katz, K. Amundson, J. Ewing, P. Drzaic, *Proc. Natl. Acad. Sci. U.S.A* 98, 4835, 2001. (b) J. A. Rogers, *MRS Bulletin* 26, 530, 2001.

[7] (a) J. A. Rogers, *Science* 291, 1502, 2001. (b) V. Sundar, J. Zaumseil, J. V. Podzorov, E. Menard, R. L. Willett, T. Someya, M. E. Gershenson, E. Michael, J. A. Rogers, *Science* 303, 1644, 2004.

[8] (a) S. R. Forrest, *Nature* 428, 911, 2004. (b) S. Moeller, C. Perloy, W. Jackson, C. Taussig, S. R. Forrest, *Nature* 426, 166, 2003.

[9] (a) C. J. Love, J. R. Anderson, G. M. Whitesides, *MRS Bulletin* 26, 523, 2001. (b) H. Schmid, B. Michel, *Macromolecules* 33, 3042, 2000.

[10] (a) K. M. Choi and J. A. Rogers, *J. Am. Chem. Soc.* 125, 4060, 2003. (b) K. M. Choi, *J. Phys. Chem.* 109, 21525, 2005.

[11] T. W. Odom, C. J. Love, D. B. Wolfe, K. E. Paul, G. M. Whitesides, *Langmuir* 18, 5314, 2002.