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Unconventional Patterning with A Modulus-Tunable Mold: From Imprinting to Microcontact Printing

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Modulus-tunable ultraviolet (UV) curing molds allow not only physical patterning of imprinting but also chemical patterning of microcontact printing. The mechanical properties of the mold can be tailored by the chain length of an acrylate modulator in the cross-linking reaction. This tunability can be utilized to obtain a proper balance that is needed for a given patterning technique between the rigidity requirement (tensile modulus = 320 MPa) of a mold for patterning a fine structure and the flexibility requirement (tensile modulus = 19.8 MPa) for a conformal contact. Successful low-pressure imprinting of sub-100-nm patterns and microcontact printing of submicrometer patterns verify the suitability of the mold for a wide spectrum of patterning techniques.

Introduction

The ability to fabricate and manipulate nanostructures has played an important role in modern science and technology, especially for electronic, optical, and nanoelectromechanical devices and nanometer-scale biological sensors.^{1,2} While the conventional methods such as photolithography and electron-beam lithography can be used for the fabrication,³ they are too costly to use in many applications. Unconventional methods, on the other hand, could provide simpler and cheaper routes to the fabrication, and a number of methods have been developed since the 1990s. Two representative methods are imprint lithography and soft lithography. Both are parallel processes. Hence, various patterns are simultaneously formed by the physical contact of a hard or soft mold with the targeted substrate.

Nanoimprint lithography is a technique to generate nanostructures by mechanically pressing a rigid master with surface-relief features into a thin thermoplastic polymer film that is then heated above the glass transition temperature of the polymer (T_g), which leads to the physical pattern that has a thickness contrast on the polymer film, i.e., a physical patterning.⁴ Soft lithography is the collective name for microfabrication techniques that involve pattern replication with an elastomeric mold such as poly(dimethylsiloxane) (PDMS).^{5,6} Microcontact printing is a typical process of

soft lithography that defines a pattern by transferring a molecular ink from a patterned PDMS mold to a substrate, which can be termed chemical patterning. The characteristics inherent in these contact-dependent methods give rise to certain limitations and disadvantages. The imprint lithography based on a hard, stiff master mold can provide a resolution down to a several-nanometer scale but it requires very high pressure and an extremely flat surface.⁷ The soft lithography based on a soft mold, typically made of PDMS, does not necessarily require a pressure or a flat surface but its resolution capability is quite limited.^{8–10} In the submicrometer range, the PDMS mold loses its mechanical integrity and deforms into unexpected shapes.^{11,12}

To overcome these problems, several approaches have been taken such as step and flash method¹³ or low-pressure nanoimprint lithography¹⁴ and utilizing a modified PDMS^{15–17} or new materials^{18,19} in soft lithog-

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raphy. Nevertheless, some basic problems still remain, such as the requirement of an expensive quartz mold in the step and flash imprinting, a relatively long processing time in the low-pressure imprinting, and pattern collapse in soft lithography when the features are fine and dense with a high aspect ratio ($AR > 1$). As these problems are inherently related to the mold material, there has been a need for a new mold material that can provide a rigidity high enough for fine and dense features with a high aspect ratio and yet a degree of flexibility for a conformal contact over a nonflat, large area. A new material for such a mold has been presented for sub-100-nm lithography.²⁰ While the material, mold preparation, and the mold replication have been presented previously, the patterning capability of the mold as applied to various patterning techniques has not.

Here, we utilize the mold material for two contrasting lithographic techniques: physical patterning of imprinting that is usually carried out with a hard mold typically made of silicon wafer and chemical patterning of microcontact printing that is usually carried out with an elastomeric soft mold. For the two contrasting methods, the mechanical properties are tuned to each application by choosing a functional modulator that can modulate the chemical structure of the UV-curable mold material. Successful imprinting of 75-nm lines and microcontact printing of 250-nm lines reveal that the mold can be tailored over a wide spectrum of modulus for various patterning needs and techniques.

Experimental Section

Fabrication of UV-Curable Mold. The UV-curable mold material consists of a functionalized prepolymer with acrylate group for cross-linking, a monomeric modulator, a photoinitiator, and a radiation-curable releasing agent for surface activity.²⁰ Depending on the choice of the modulator that is discussed in the next section, the mold can be prepared as a hard or soft one as shown in Figure 1. To prepare the mold material, the monomeric modulator was added to the urethane acrylate prepolymer (Ebecryl 265, SK-UCB Co., Korea) in a weight ratio of 0.35 to 1. Subsequently, photoinitiators of Irgacure 184 (1-hydroxycyclohexylphenylketone, Ciba Specialty Chemicals, Switzerland) and Darocur 1173 (2-hydro-2-methyl-1-phenyl-1-propane, Ciba) were added to the mixture at 1.5 and 1.5 wt %, respectively. To promote the releasing property of the mold from the master, a reactive releasing agent, Rad 2200N (TEGO Chemie Service, Germany) at a loading level of 1 wt %, was blended with the prepared mixture. This additive has not only polyether or alkyl pendants for mixing compatibility with the prepolymer and modulator but also a reactive acrylate group for the radiation curability. Therefore, the agent that participates in the curing reaction serves the purpose of lowering the surface energy (surface tension ≈ 23.0 dyn/cm)²¹ without causing any pattern deformation or swelling problems.

Then, the liquid mixture was drop-dispensed onto a master pattern, as shown in Figure 1a for a film-supported mold or film mold. A flexible and transparent polyethyleneterephthalate (PET) film was brought into contact with the liquid mixture. Subsequently, it was exposed to UV ($\lambda = 250\text{--}400$ nm) for a few tens of seconds through the transparent backplane (dose = 100 mJ/cm²). After the UV curing, the mold

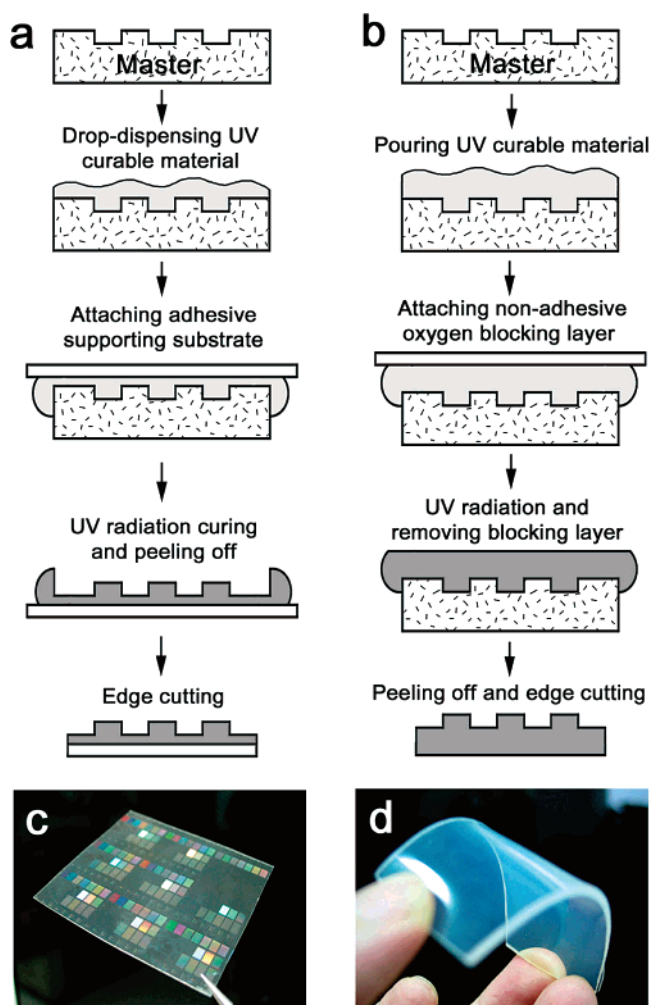


Figure 1. Schematic illustration for the fabrication of UV-curable molds and examples of the prepared molds. The lighter shaded parts represent the uncured liquid and the darker ones represent the cured mold. (a) Procedure for making a film-supported type mold. (b) Procedure for making a single block type mold. (c) Example of hard mold resulting from the procedure (a). (d) Example of the soft mold resulting from the procedure (b).

was peeled off. The backplane film for the hard mold in Figure 1c is a 188- μm -thick adhesive PET film (PET primed with polyurethane, SKC Co., Korea) that allows a degree of flexibility. The mold fabrication procedure for a soft block-type mold is shown in Figure 1b. To prevent radical scavenging by the oxygen in open environment, a nonadhesive PET film as an oxygen blocking layer was used. After curing for about 10 min, the PET film was removed and the block mold was peeled off from the master. The cured mold can be used repeatedly for the patterning without any deformation problem of the mold if there is no contamination from the experimental environment.

Pattern Formation by Imprinting. For imprinting, cleaned silicon substrates were spin-coated with polystyrene (PS, $M_n = 404\,200$ g/mol, $M_w/M_n = 1.05$, Polymer Source Inc., Canada) in toluene. The samples were, in turn, baked in a vacuum at 100 °C for 2 h to remove any residual solvent in the PS film. A UV-cured mold was then placed on the polymer and a piece of thick paper was placed on the mold as a buffer layer for an even distribution of pressure. While maintaining the temperature above T_g of PS (100 °C), typically 120 °C, a pressure of 3–4 bar (0.3–0.4 MPa) was applied by putting a steel block on the sample surface for 20 min for the imprinting. The imprinted patterns were examined by scanning electron microscopy (SEM, XL30FEG, Philips Electron Co., Nether-

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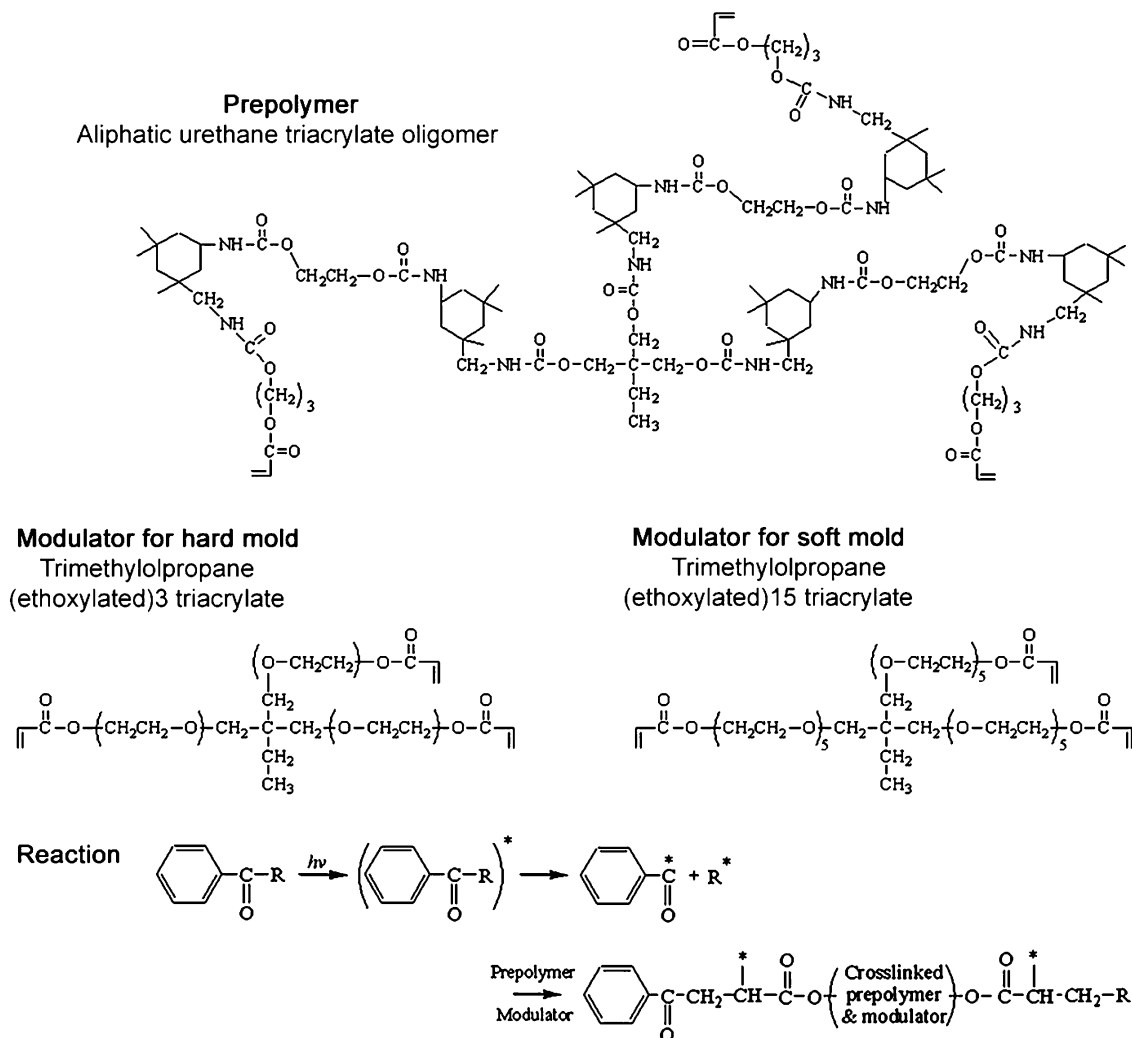


Figure 2. Preparation of modulus-tunable UV-curable mold and reaction route. In the reaction route, initiators react with the acrylate group in the prepolymer and the modulator, which results in a cross-linked structure for the mold.

lands) and atomic force microscopy (AFM, Dimension 3100, Digital Instrument, Woodbury, NY) in the tapping mode.

Pattern Formation by Microcontact Printing. For microcontact printing, a gold-coated silicon wafer was prepared for the substrate by depositing a 3-nm-thick layer of titanium as an adhesion layer, followed by depositing an 80-nm-thick gold layer by thermal evaporation. After the deposition, the gold coated samples were kept in a vacuum chamber and taken out right before the printing. For the printing, the soft PUA mold was soaked in a 0.5 mM hexadecanethiol (HDT, Aldrich, Milwaukee, WI) solution in ethanol for 1 h and then dried for 10 min under nitrogen atmosphere. Then the HDT-treated soft mold was brought into contact with the surface of the gold for 30 s. Although the mold was flexible enough for conformal contact, spontaneous wetting on the surface as with soft PDMS did not take place. Therefore, a low-pressure less than 0.1 bar (0.01 MPa) was applied to ensure intimate contact. A soft PDMS block was used as a buffer layer on the PUA mold for an even distribution of pressure.¹⁴ For the gold etching, the conventional CN^-/O_2 aqueous solution (1 M of KOH, 0.1 M of KCN, with vigorous stirring for oxygen supply) was used.^{22,23} Typical etching time was 20 min, and the etched samples were washed with water, followed by drying with nitrogen. Then the etched patterns were examined by SEM and AFM.

Results and Discussion

Figure 2 gives the chemical formulas of the species involved in the material for modulus tunability and the reaction routes to the prepared mold material. To obtain a balance between rigidity and flexibility, a triacrylate in the form of cycloaliphatic urethane triacrylate oligomer (Ebecryl 265) was chosen as the prepolymer. A high-molecular-weight structure provides a good elongation property while the cycloaliphatic backbone gives a high degree of mechanical stiffness.²⁴ A radiation-curable monomeric modulator plays a key role in preparing the mold material. Mixing the monomeric modulator with the prepolymer of a molecular weight on the order of several thousands results in a reduction of viscosity that allows the mixture to fill very fine structures of sub-100-nm channels or holes. More importantly, the modulator allows one to change the chain length or cross-linking density, which leads to a change in the mechanical properties.²⁵ Figure 2 shows two monomeric triacrylates for tuning the modulus. The backbone of the cured mold is poly(urethane acrylate) and thus the mold may be called PUA mold.

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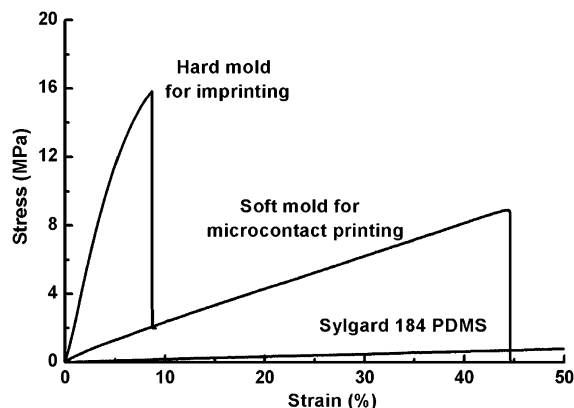


Figure 3. Tensile stress–strain relationship of three materials from the UTM analysis.

Table 1. Comparison of Tensile Modulus and Elongation at Break for Three Materials

material	tensile modulus (MPa)	elongation at break (%)
hard PUA mold for imprinting	320	9
soft PUA mold for contact printing	19.8	45
Sylgard 184 PDMS	1.6	146

For a relatively hard PUA mold that is needed for imprint lithography, which is a film type mold as shown in Figure 1c, trimethylpropane (ethoxylated)3 triacrylate (M310, Miwon Co., Korea) was chosen as the modulator since its relatively short chain length would lead to a dense cross-linking. For a soft PUA mold to be used for microcontact printing, which uses a block type mold as shown in Figure 1d, trimethylpropane (ethoxylated)15 triacrylate (M312, Miwon Co., Korea) was chosen because of its high content of ether linkage. The long ether linkage can have a high degree of rotational movement that allows stretching. As shown in Figure 1d, therefore, the 2-mm-thick soft block mold can be bent or deformed freely and yet it still maintains the pattern shape and enables a conformal contact with other surfaces.

The mechanical properties of the two types of PUA molds, hard and soft, were determined by universal testing machine (UTM, LR10K, Lloyd Instruments, England) with the molds prepared in the form of non-patterned sheets for the tensile modulus and elongation at break. The tensile modulus can be obtained from the slope of stress–strain curve in the linear region, and the elongation at break can be obtained from the value of the strain at which fracture occurs, which corresponds to the abrupt decrease in the stress.²⁶ Testing was carried out under ASTM D638 mode²⁷ and the stretching rate was 5 mm/min. Typical sample dimension was $9.53 \times 3.18 \times 0.3$ (length \times width \times thickness, mm). The measured strain–stress curves are shown in Figure 3. For comparison, the conventional Sylgard 184 PDMS was also tested and the results are summarized in Table 1. The modulus can also be tuned by changing the amount of the modulator in the mold material or by mixing the two modulators.

The mechanical properties in Table 1 suggest that the mold can be used for various patterning techniques. As shown in the table, the usual PDMS of Sylgard 184 has a good elongation property that allows excellent processing characteristics such as spontaneous wetting. On the other hand, the modulus is too low to support the mold structure in submicrometer range, typically for dense or high-aspect-ratio patterns. To enhance the mechanical integrity and thereby extend the patterning capability to smaller feature sizes, a modified hard PDMS¹⁵ (tensile modulus = 8.2 MPa, elongation at break = 7%)²⁸ has been introduced. Comparison of the mechanical properties of the soft PUA mold in Table 1 and those of the hard PDMS mold suggests that the microcontact printing could be extended to a smaller feature size with the soft PUA mold than is possible with the hard PDMS mold. Also, the conformal contact should be better because the soft PUA is much more flexible, despite its higher tensile modulus, due to its higher elongational property than that of hard PDMS. On the other hand, the high modulus of the hard PUA mold in Table 1 implies that the mold could withstand the pressure applied for imprinting. These mechanical properties in turn suggest that the hard PUA mold could be utilized for the physical patterning by imprinting and the soft PUA mold could be used for the chemical patterning by microcontact printing.

Shown in Figure 4 are the patterning results obtained by imprint lithography with the hard PUA mold. Not only a high-aspect-ratio (>4) pattern (in Figure 4a) but also a sub-100-nm dense pattern (in Figure 4b) was successfully transferred to the polymer film. High-aspect-ratio structure is technologically important because it can provide a high etching selectivity during the pattern transfer to the substrate. In Figure 4a, the patterned polymer has a wider line width than that of the master pattern because of the discordance between the top and bottom widths in the master pattern. In addition, the applied pressure of 3–4 bar was not high enough for complete filling of the channel because of the pressure rising in the compressed region of the void part in the channel such that the resulting pattern height (about 250 nm) is smaller than that of the master pattern (400 nm). Figure 4b shows the patterning result of a 75-nm polarizer pattern (Moxtek Inc., Orem, UT). The sectional AFM micrograph in Figure 4c shows that the pattern height reaches up to about 40% of the master pattern height. A high-aspect-ratio tapping mode tip (AR10-NCH, Nanosensors, Phoenix, AZ) was used to eliminate the tip effects in the AFM analysis. The lower relative pattern height in Figure 4b than that in Figure 4a (60% vs 40%) may have to do with the difference in the mass transfer into the channel due to the pattern density. The more sparsely spaced pattern in Figure 4a (line width/space = 1:2.5) would have more mass to draw from the space region than the more densely spaced pattern in Figure 4b (line/space = 1:1).

It is notable that the hard PUA mold allows for a low-pressure imprinting just as a flexible Teflon mold does.¹⁴ The applied pressure of 3–4 bar contrasts the high pressure in excess of 100 bar needed in the conventional nanoimprint lithography. The mold prepared in the

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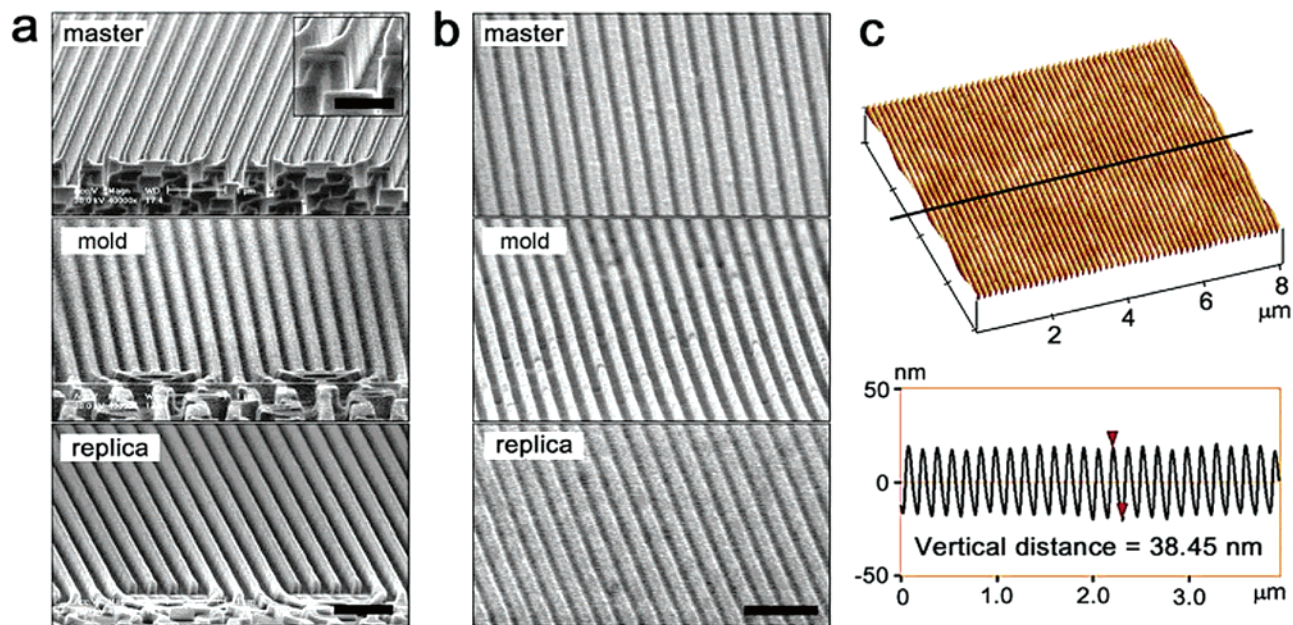


Figure 4. Imprinting results with UV-cured hard PUA mold. (a) SEM images for a high-aspect-ratio pattern (master: 100 nm (line) \times 250 nm (space) \times 400 nm (depth), 1 cm \times 1.5 cm (area)). From the top down, the master, the UV cured mold, and the imprinted polystyrene pattern using the UV cured mold. Bar scale is 1 μ m. Inset in the master image (bar scale is 500 nm) shows a magnification for a clear view of the pattern shape. (b) SEM images for a sub-100-nm pattern (master: 75 nm (line) \times 75 nm (space) \times 100 nm (depth), 0.7 cm \times 0.7 cm (area)). Bar scale is 500 nm. (c) Three-dimensional (top) and cross-sectional (bottom) AFM images for the patterned polymer in (b). Z scale in the top image is 300 nm.

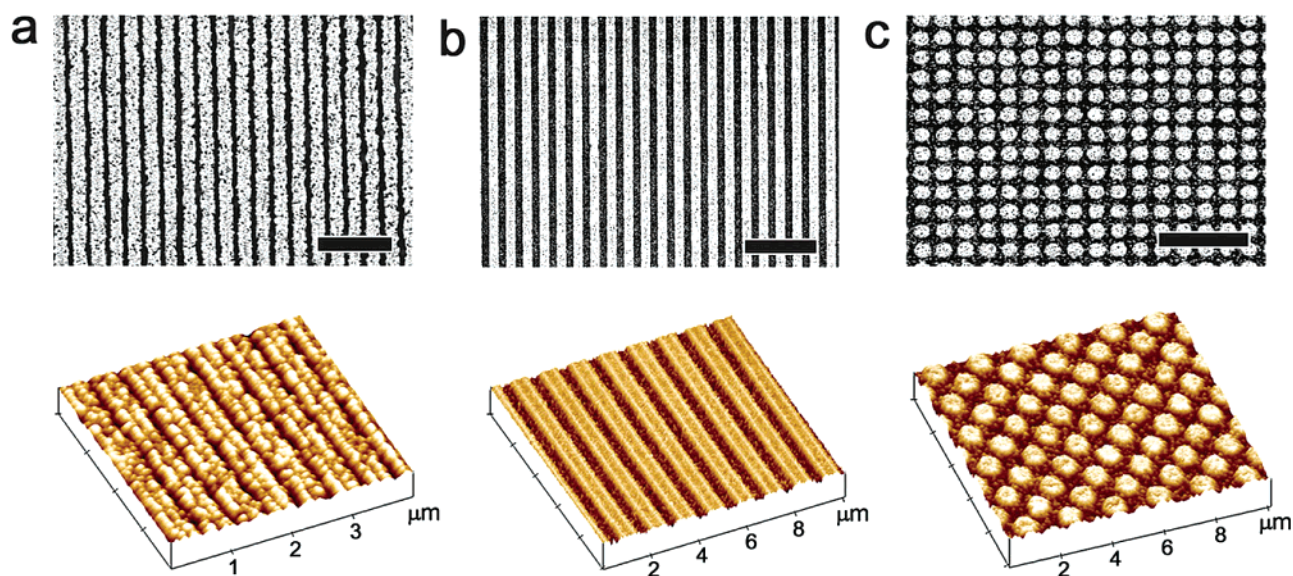


Figure 5. SEM (top) and AFM (bottom) micrographs for the patterning results by microcontact printing method. Z scale in all AFM images is 500 nm. (a) Gold line pattern with 500 nm period (stamping mold: 250 nm (line) \times 250 nm (space) \times 400 nm (depth), 1.2 cm \times 2 cm (area)). Bar scale in the SEM image is 2 μ m. (b) Gold line pattern with 1.2 μ m period (stamping mold: 700 nm (line) \times 500 nm (space) \times 1000 nm (depth), 2 cm \times 2 cm (area)). Bar scale in the SEM image is 5 μ m. (c) Gold dot pattern with 1.2 μ m period (stamping mold: 750 nm (dot) \times 450 nm (spacing) \times 400 nm (depth), 1.2 cm \times 2 cm (area)). Bar scale in the SEM image is 5 μ m.

form of a film, and some degree of flexibility inherent in the mold material provide the necessary flexibility for the low-pressure imprinting. This low-pressure condition makes it possible for the mold to maintain its mechanical integrity during the imprinting process.

Figure 5 shows the results of the gold surface patterned by microcontact printing with the soft PUA mold. In microcontact printing, the swelling characteristics of the mold are important because the inking material is transferred to the mold as a solution and the solvent can induce unexpected deformation of the mold. To

check the effect of solvent swelling, a soft block type mold was immersed in pure ethanol for 3 h and then weighed for the mass difference by swelling. Only a 0.4 wt % increase in the weight was observed, which would have little effect on the pattern deformation by swelling. This slight solvent retention was rather helpful for preserving the HDT on the mold surface and continuous release of HDT during the contact.

Although there are some defects and deterioration along the edges as revealed in Figure 5, the pattern transfer by the printing was successfully demonstrated

even for the densely spaced submicrometer pattern (250-nm line and space pattern in Figure 5a). There have been a number of results for nanoscale patterning by microcontact printing method, but they were mostly for sparsely separated and isolated patterns.^{29–33} Only recently has there been a successful patterning by the microcontact printing for a 300-nm line and space pattern with a UV-curable PDMS mold.²⁸ However, the conventional PDMS and other materials^{16–19} fail to maintain the mechanical integrity during the contact process when the pattern is densely spaced, which leads to a pattern collapse or nonselective diffusion of self-assembled monolayer material to the gold surface.³⁴ There also exists a diffusion problem in our results in Figure 5. When compared with the pattern dimensions of the molds given in Figure 5, the patterned lines show an increase in the line width at a level of 30–40 nm. The significance of the results, however, lies in the fact that there is a distinct separation between lines, which reveals that a definite contact was made between the mold pattern and the gold surface without any deformation problem. The mold deformation that may occur during the microcontact printing can easily be quantified using a criterion reported in the literature.³⁵ For

high-aspect-ratio patterns, deformation of a mold is usually due to buckling of the mold pattern. According to the criterion, a pressure of 6.7 bar is the minimum pressure leading to the buckling even for the harshest condition of our soft PUA mold (the high-aspect-ratio mold used in Figure 4(a), tensile modulus = 19.8 Mpa), which is much larger than our experimental pressure of 0.1 bar. This result shows that there would not be any deformation problem in the microcontact printing. Nevertheless, our attempt to print 100-nm and sub-100-nm patterns failed because of the diffusion problem, which was verified from the nonetched stamped region. A superior inking material such as eicosanethiol³⁵ or dendrimer-based inks^{36,37} that reduce the diffusion effect may resolve the resolution problem.

Conclusions

We have shown tunability of mechanical properties of poly(urethane acrylate) mold. These properties can be tuned to a given patterning method simply by changing a monomer modulator and/or varying the amount of the modulator in the mold material. The tunability to a given patterning technique has been demonstrated with two contrasting methods: physical patterning by imprinting and chemical patterning by microcontact printing. A proper balance between the mold rigidity required for patterning a very fine and dense structure and the flexibility needed for a conformal contact with the substrate is at the core of the successful applications.

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