

Lithographically induced self-construction of polymer microstructures for resistless patterning

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We have discovered and developed a method that can directly pattern polymer microstructures of *arbitrary shapes* without using a resist, exposure, chemical development, and etching. A mask with protruded patterns is placed *a distance above* an initially flat polymer film cast on a substrate. During a heating cycle that raises the temperature above the polymer's glass transition temperature and then cooled back to the room temperature, we found that the polymer was attracted to the mask protrusions on their own, forming the mesas that have a lateral dimension *identical* to that of the mask protrusions, a height equal to the distance between the mask and the substrate, and a relatively steep sidewall. The method, termed lithographically induced self-construction, is important to the fabrication of polymer electronic and optoelectronic devices. © 1999 American Institute of Physics. [S0003-6951(99)01233-4]

Direct patterning of microstructures without using a resist, exposure, development, and etching has a number of advantages, such as reducing fabrication steps, increasing yield, and cutting cost. It is also necessary to the fabrication of many polymeric devices, since most of the polymer materials used for devices can be severely damaged by the common resist solvents, ultraviolet exposure, chemical developers, and etching.¹⁻³ Here, we report a method, lithographically induced self-construction (LISC), that can directly pattern a thermal-plastic polymer without using a resist, exposure, development, and etching.

In LISC, a mask with protruded patterns is placed a certain distance above an initially flat polymer that is cast on a substrate (Fig. 1). During a heating process that raised the temperature above the polymer glass transition temperature and cooled back to the room temperature, the polymer was attracted, against gravitational force and surface tension, to the mask protrusions, but not to the recess areas of the mask, forming the polymer mesas on their own. The mesas have a lateral dimension *identical* to the protruded patterns on the mask, a height equal to the distance between the mask and the substrate, and a relatively steep sidewall. In the following, we will discuss the experiments and a possible explanation for the process.

In our experiments, both the mask and the substrate are made of silicon. The protrusions with a variety of shapes have a height of ~ 300 nm. The polymer is polymethyl methacrylate (PMMA) which was spin-cast on the substrate and was baked at 80°C to drive out the solvent. The molecular weight and thickness is typically 2000 and 100 nm, respectively. The gap between the initially flat polymer film and the mask protrusions ranged from 100 to 400 nm, and was controlled by a spacer. The temperature was cycled from room temperature to 170°C . The heat was from the top and bottom of the sample, making the thermal gradient on the sample very small. A press was used to supply the heat and to hold the gap constant. A surfactant with a low surface energy was

coated on the mask to facilitate the mask-sample separation after LISC. We found that the materials (for the mask and substrate) and the parameters (e.g., the protrusion height, polymer thickness, polymers molecular weight, gap, etc.) are not very critical to LISC at all. LISC can be formed over a wide range of these parameters. The typical diameter of the masks and substrate is larger than 2 cm. The masks are made by photolithography and etching.

Figure 2 shows the optical images of a protruded rectangle on the mask and the PMMA mesa (2 K molecular weight) formed under the protrusion, as well as a tapping mode atomic force microscopy (AFM) image of the PMMA mesa. The optical images clearly showed the PMMA rectangle mesa ($12\ \mu\text{m} \times 24\ \mu\text{m}$) formed under the mask protrusion in LISC has a lateral dimension identical to the mask protrusion. The AFM image showed that the height of the mesa is 200 nm, that is equal to the separation between the substrate and the mask protrusion. The AFM image also shows that the top of the mesa is flat, the mesa sidewall is quite vertical (note that the AFM measurements of the angle between the sidewall and the substrate is limited by the AFM tip). The initial film thickness is 100 nm. The mesa has the round corners similar to the round corner on the mask pattern. Further AFM showed that the polymers in the area surrounding each mesa are depleted almost completely, leaving a residual thickness less than the detection limit of the tapping mode AFM (about 2 nm), which is measured by scratching the area with a metal pin and followed by AFM.

The AFM study reveals two important facts. First, in forming the mesas, the extra polymers were transported from the location near a mask protrusion to the area under the protrusion. Second, the residue polymer surrounding the mesas is less than 2 nm. The first fact implies that the polymer transfer in LISC might impose a limitation on the mesa size and pattern density that can be formed by LISC. However, some strategies (such as using dummy patterns) can be utilized to alleviate the problem. Currently, we have been able to form perfect mesas with areas of $50\ \mu\text{m} \times 50\ \mu\text{m}$. It was found that the polymer can come from at least $50\ \mu\text{m}$ away.

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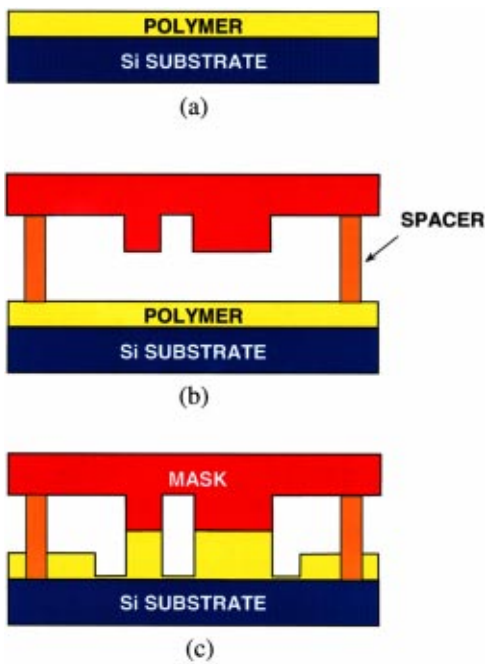


FIG. 1. Schematic of LISC: (a) a thin polymer film cast on a flat silicon substrate, (b) a mask with protruding patterns placed a distance above the polymer film, (c) during a heat-and-cool cycle, the polymer film self-constructs into a mesa under a mask protrusion. The mesa has a lateral dimension identical to that of the mask protrusion, a height equal to the distance between the mask and the substrate, and a steep side wall.

The second fact implies that the thin layer of residue polymer surrounding the mesas can be easily removed in a number of ways, so that each mesa can be electrically isolated from the rest. It is also scientifically intriguing to understand why the residue polymer is less than 2 nm and what is the mechanism of polymer transport.

When a mask has an array of protruded dots, PMMA pillars are formed with one pillar under each dot (Fig. 3). The pillar has a diameter of 1.3 μm , identical to that of the dot on the mask. The initial PMMA film was 105 nm thick, but the PMMA pillars formed in LISC is 350 nm tall. The PMMA has a molecular weight of 15 K. The temperature was cycled to 175 $^{\circ}\text{C}$. At present, the minimum size of the polymer microstructures formed by LISC is limited by the patterns on the mask. There are evidences that submicron structures can be formed by LISC.

To further test the ability of LISC in forming an arbitrary pattern, we created the protrusions of the word ‘‘PRINCETON’’ on a LISC mask. Comparison of PMMA LISC patterns with the mask showed that the polymer mesas formed in LISC duplicate the patterns on the mask very well (Fig. 4). The linewidth and the height of the pattern is 3 μm and 230 nm, respectively. The initial PMMA film thickness is only 100 nm.

Although LISC has demonstrated usefulness in resistless patterning, its principle is still unclear at the moment. We now discuss possible mechanisms for LISC. First, what makes the polymer attracted, against gravitational force and surface tension, to the mask protrusions? Since the distance between the mask and the initially flat polymer is closer in the protrusion area than in the recessed area, the polymers under the mask protrusion should have a larger temperature gradient during heating and an electrostatic interaction with

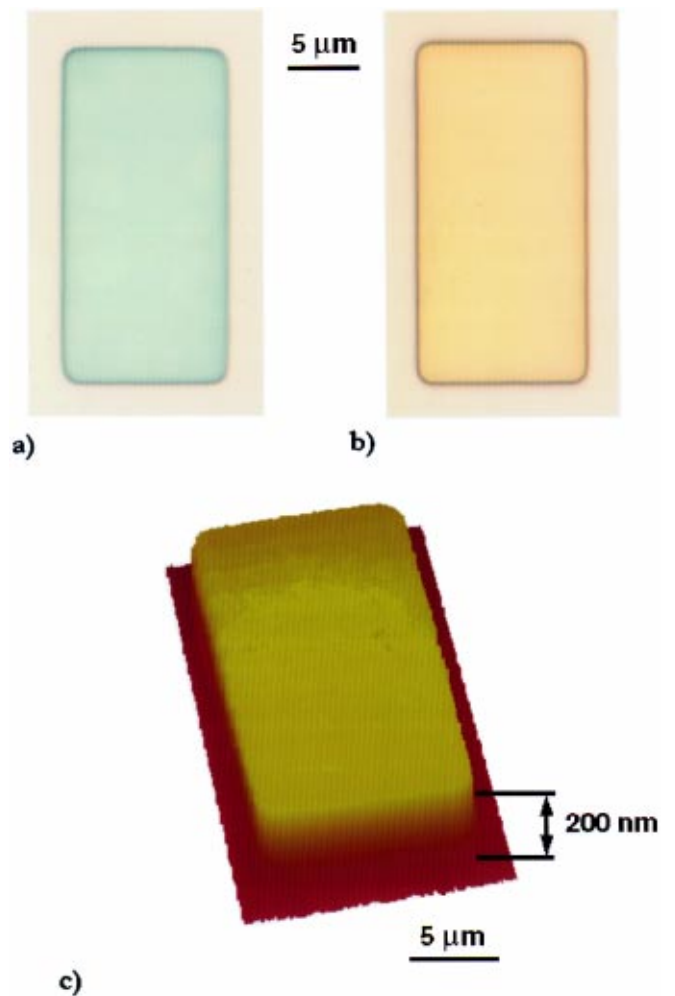


FIG. 2. Optical image of (a) a mask protrusion (12 μm wide and 24 μm long) and (b) the PMMA mesa (2 K molecular weight) formed under the protrusion by LISC, showing the same size as the mask pattern, and (c) AFM image of the mesa. The initial film thickness is 100 nm. The mesa height, equal to the spacing between the substrate and mask, is 200 nm. The round corner is due to the round corner on the mask pattern.

the mask stronger than the polymer under the recessed area. Both temperature gradient (which causes a surface tension gradient) and the electrostatic force could be important to push the polymer up. Yet the exact role of each force is not clear.

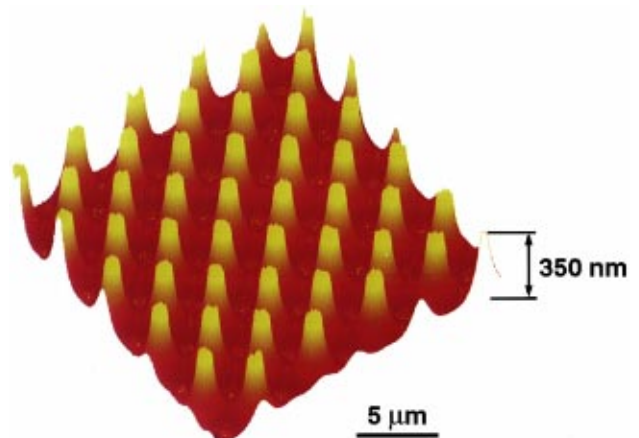


FIG. 3. AFM image of the PMMA pillars (15 K molecular weight) formed by LISC. Each PMMA pillar is formed under each dot protrusion on the mask. The pillar has a diameter of 1.3 μm , identical to that of the dot on the mask. The initial PMMA film was 105 nm thick, but the PMMA pillars formed in LISC are 350 nm tall.

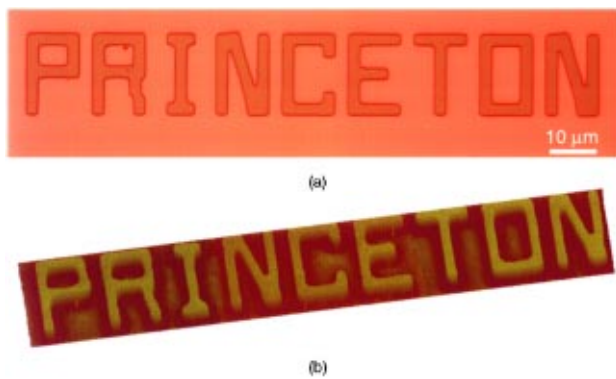


FIG. 4. (a) Optical image of protruded pattern of PRINCETON on the mask, and (b) AFM image of the PMMA LISC patterns (2 K molecular weight) formed underneath the mask pattern. The LISC pattern duplicates the lateral dimension of the mask pattern. The linewidth and the height of the PMAA pattern is $3\ \mu\text{m}$ and 230 nm, respectively. The initial PMMA film thickness is 100 nm.

Second, what is the mechanism that makes the polymer mesa have the same lateral shape as that of the mask protrusion, rather than spread over the entire mask? We suspect that this might be due to the pinning of the triple-phase (liquid–solid–vapor) line at the edge of the mask protrusion.

Third, what are the major differences between LISC and lithographically-induced self-assembled (LISA)—another interesting phenomenon that we observed recently?⁴ In LISA, an array of periodic polymer pillars was formed under a single mask protrusion, instead of a single polymer mesa with the same lateral dimension as the mask protrusion is

formed as in LISC. The key to have a LISC rather than LISA is to reduce the difference of the surface tensions of the polymer and the mask. When the difference is small enough, each polymer pillar formed in the initial phase of LISC will spread and merge with other pillars to form a single mesa under each mask protrusion. The surface tension difference can be reduced by either using a different surfactant on the mask or increasing the processing temperature (which would reduce the polymer surface tension).

Finally, LISC is also fundamentally different from nanoimprint lithography, where a mold is pressed into a polymer melt, and a polymer is mechanically deformed into the shape of the mold.⁵ To observe LISC, the mask must initially be kept a distance away from the polymer film.

In summary, we have discovered and developed a method in forming polymer microstructures without using resists, exposures, developers, and etchings. Practically, the method may find applications in the fabrications of polymer electronic and optoelectronic devices. Scientifically, the method offers understanding of interplay of different forces at micron and nanometer scales.

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