ADVANCED MATERIALS

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Rapid Prototyping of Complex Structures with Feature Sizes Larger Than 20 μm**

By *Dong Qin, Younan Xia*, and *George M. Whitesides**

Although the focus of most research in microfabrication has been microelectronics,[1] a number of new areas of application are now developing. These include microelectrical mechanical systems (MEMS),[2] microanalytical systems,[3–5] combinatorial arrays,[6] supports for attached cell culture,[7,8] and optical systems.[9,10] These applications require features with sizes in the range of 1–100 μm, rather than those in the 0.1–1 μm range now required in microelectronics. Much of the work in fabrication of larger structures uses photolithography, even though the sophistication of this technique may be overkill for applications less demanding than those in microelectronics. Photolithography is an extremely useful method for generating patterned relief structures in photoresist films with feature size 0.5 μm , but it is not well suited as a technique for rapid fabrication of structures with large features (typically > 20 μm), and especially not by laboratories not intimately connected to facilities for conventional microfabrication.

Photolithography is carried out by projecting a pattern embodied in an opaque material (normally a thin chromium film- a "chrome-mask") supported on a transparent support into a film of photoresist. Chrome-masks are commercially available from custom fabricators, but the time required for vendors to produce a chrome-mask from a design presented in a CAD file can be weeks to months, and is expensive (~$ 300 per square inch for features larger than 20 μm, and ~$ 1500 per square inch for features between 1 μm and 20 μm). The time, expense, and unfamiliar manipulations involved in generating chrome-masks has presented a significant barrier to the use of photolithography and microfabrication by chemists and biologists, and has slowed the rate of use of microfabrication in these fields.

We wished to have a system that would enable us to carry out microfabrication in the range of relatively large feature sizes (≥20 μm) rapidly and at low cost, in order to prototype MEMS and microanalytical systems. In this paper, we describe such a method: the patterns are designed using a personal computer, and printed out on transparent films of polymers using a commercial image-setting system. Using this method, photolithographic masks–transparent polymeric films patterned with microstructures of black, solid ink–can be made in a few hours at acceptably low cost (~$ 1 per square inch). These masks do not have the durability and dimensional stability required for use in the manufacturing of microelectronic devices, but they are ideal for the rapid production of limited numbers of prototype microfluidic, micro-sensor and optical structures. Coupled with microcontact printing (μCP),[11–14] micromolding in capillaries (MIMIC)[15–17] and microtransfer molding (μTM),[18] in which the patterned photoresist is used to produce an elastomeric polydimethylsiloxane (PDMS) stamp, this method of rapid prototyping makes it possible to produce substantial numbers (> 10^3) of simple microstructures rapidly and inexpensively. In these methods, the actual fabrication is carried out by the PDMS stamp, and the photolithographically patterned structures in photoresist are used only to make these stamps.

The patterned polymer films described here also have two other attractive features not offered by chrome-masks: i) they are flexible, and can be used to pattern non-planar substrates. ii) They are thin and can be stacked on top of one another to generate new types of patterns in certain types of fabrication.

Figure 1 outlines the procedure used to generate patterned structures of black ink on transparent polymer films, and the subsequent uses of these patterned films as masks in photolithography. Patterns were drawn using computer programs such as Freehand® or AutoCAD® and directly printed onto polymer films using a commercial laser-assisted image-setting system (Herkules PRO, 3387 dpi, Linotype-Hell Company, Hauppauge, NY).[19] These patterned films were then used as photolithographic masks in three different configurations: 1) singly, in conventional 1:1 projection photolithography to form relief structures in photoresist films (Microposit 1813, Shipley, MA) supported on planar substrates (Si/SiO_2, glass and metals); 2) in stacks of two films in planar lithography, to generate patterns that could not be made using a single mask; and 3) bent around curved substrates, to fabricate relief structures in non-planar photoresist films.

Figure 2 gives several typical examples of relief patterns and structures formed in photoresist films using this procedure. The time required to start with the CAD file, carry out the high-resolution printing, and use the printed transparency to produce a relief structure in photoresist was ~5 h. Formation of a PDMS stamp from this master relief structure and initial stamping or replication required another ~2 h. Figure 2A and 2B show SEM images of patterns interesting as possible negative Poisson ratio materials.[20] Figure 2C shows an SEM image of a pattern produced by stacking two polymer masks, with each mask having a pattern of parallel lines on its surface (patterns with different shapes could be easily fabricated by changing the relative orientation between the lines on these two masks). Figure 2D shows an optical micrograph of parallel lines

[*] Prof. G. M. Whitesides, Dr. D. Qin, Y. Xia
Department of Chemistry, Harvard University
12 Oxford Street, Cambridge, MA 02138 (USA)

[**] This work was supported in part by ONR and ARPA. This work made use of MRSEC Shared Facilities supported by the National Science Foundation under Award Number DMR-9400396. D. Q. would like to thank Drs. Nicholas Willmore and Andrew Zhuk for their assistance. The designs in Figure 2A and 2B were due to Professor Ihan Aksay; the CE design in Figure 4A to Dr. J. Michael Ramsey; and the SAW device design in Figure 4D to Professor Michael Grunze. We thank them for their assistance.

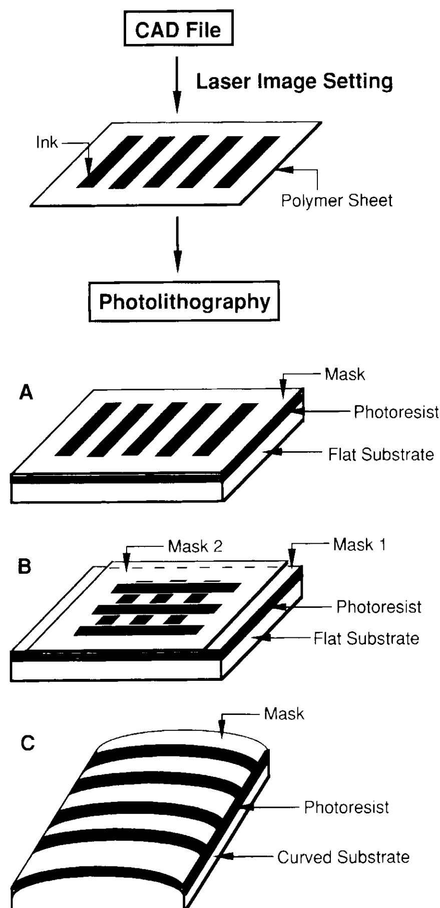

Fig. 1. A schematic outline of the procedure for generating patterns of a black, solid ink on transparent films of polymers, and the subsequent uses of these films as masks in photolithography. Both positive and negative masks can be generated from a CAD file.

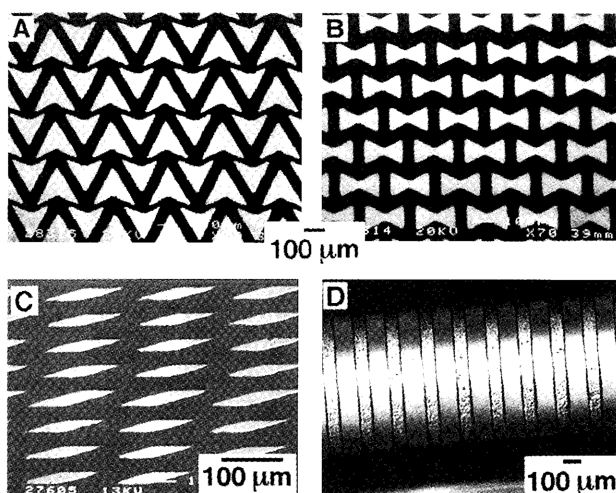

Fig. 2. A,B) SEM images of relief patterns generated in photoresist films using a single layer of printed polymer film as mask; C) SEM image of a relief pattern formed in a photoresist film using two stacked layers of printed polymer film; and D) optical micrograph of parallel lines formed in photoresist film coated on a capillary (~500 μm radius of curvature; the patterns covers 40 % of the circumference of the capillary). In A–C, the dark regions are photoresist; the bright regions are Si/SiO_2, exposed after removing exposed phototoresist.

formed in photoresist film coated on a glass capillary having a radius of curvature of 500 μm.

Elastomeric PDMS stamps cast from these relief structures in photoresist films could be used in μCP to fabricate patterned microstructures of coinage metals.[11–14] Figure 3

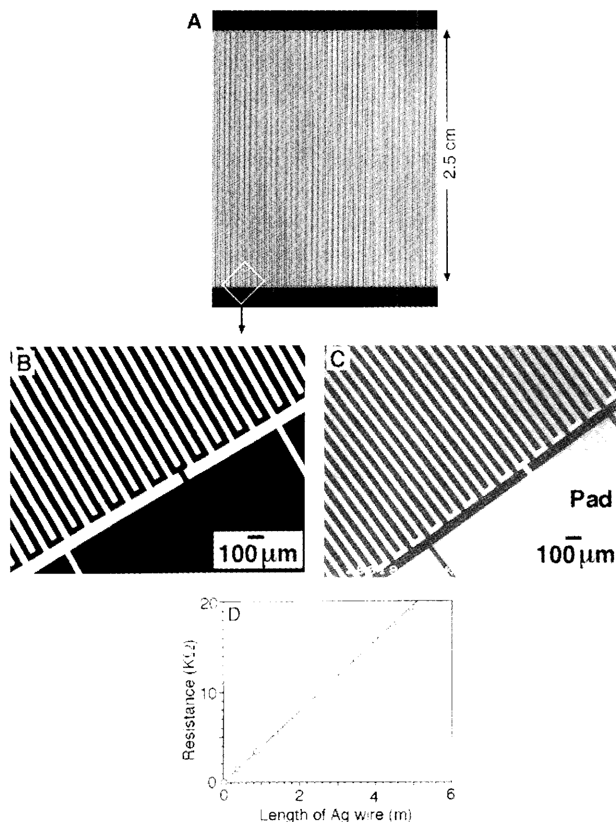

Fig. 3. A) The pattern used to generate a 5 m-long wire for continuity testing; B) an optical micrograph of a portion of the printed polymer film that served as the photolithographic mask; C) an SEM image of a portion of the continuous silver wire (~50 μm in wide and 100 nm thick) generated using this pattern (see text); and D) the dependence of measured resistance (two-probe method) on Ag wire length.

shows an example–a continuous silver wire 5 m long on Si/SiO_2 (2 μm thermal oxide). Figure 3A is the pattern used to fabricate this wire;[21] Figure 3B is an optical micrograph of a portion of the printed polymer film produced using this pattern; and Figure 3C shows an SEM image of a portion of the silver wire. This wire was fabricated using μCP with a PDMS stamp cast from the photoresist pattern generated using this printed polymer film, followed by selective removal of Ag unprotected by hexadecanethiolate SAMs by etching in an aqueous ferricyanide solution.[14] Exposed Ti was dissolved subsequently in an aqueous HF solution (~2 %).[22] This silver wire was continuous; its resistance depended linearly on length (Figure 3D), with a resistivity ~2 μΩ cm (the value for bulk silver is 1.6 μΩ cm[23]).

We have demonstrated the flexibility of this procedure by fabricating structures representative of those used in microanalytical systems: for example, a miniature capillary

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electrophoresis (CE) channel[24] and a surface acoustic wave (SAW) device.[25] Figure 4A shows a schematic design

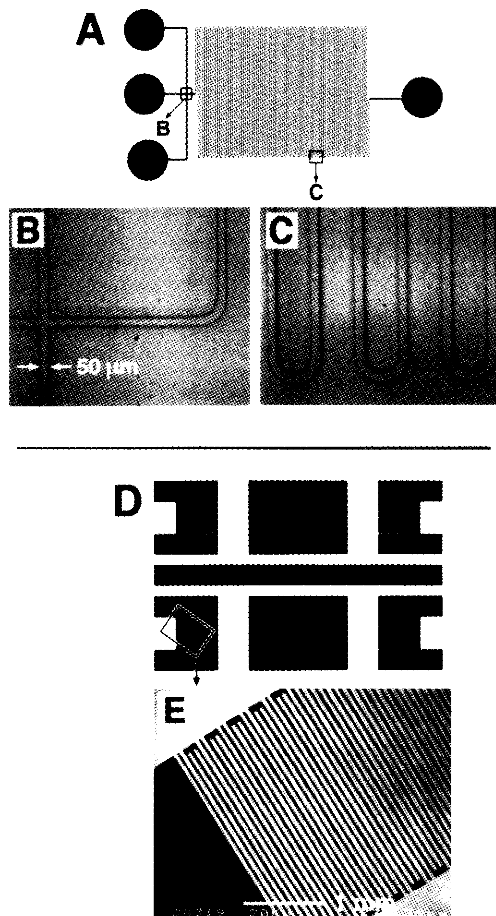

Fig. 4. A) The designed pattern used in microCE; and B,C) optical micrographs of two selected areas of the pattern that was etched into a glass slide. D) The designed pattern used in a SAW device; and E) an SEM image of a portion of the pattern generated in silver on Si/SiO_2. In E, the bright regions are Ag; the dark regions are Si/SiO_2 where exposed Ag has been removed using aqueous ferricyanide etchant. For both samples, the photoresist masks were striped-off after etching of glass or silver.

of the pattern used in the microCE system. Figures 4B and 4C show optical micrographs of two areas of the pattern that had been etched into a glass slide (~10 s in an aqueous ~2 % HF solution), using the patterned photoresist film as mask; the depth of the channel in the glass was ~1 µm. Figure 4D illustrates the pattern used for the SAW device, and Figure 4E shows the SEM image of a portion of this device (made of silver on Si/SiO_2) that was fabricated by selective etching in an aqueous ferricyanide solution with the patterned photoresist film as mask.[14]

At present, the smallest features that can be generated directly using this procedure are ~20 µm, a size that is limited by the resolution (3387 dpi) of the image-setting system. It will be possible to generate features with smaller sizes by using image-setting systems with higher resolution.[26] Even with masks made by the current image-setting system, however, we were able to generate micrometer-sized features by using some of the techniques for size reduction reported previously.[27,28]

The procedure described here combines high-resolution, CAD-based printing, 1:1 projection photolithography, and soft microlithographic techniques (µCP, MIMIC, µTM) into a convenient and economical system for rapid prototyping of complex patterns and structures with modest feature sizes (≥20 µm). We believe that this combination paves the way for much expanded use of microfabrication in laboratories of chemistry, biology and other areas that do not have routine access to sophisticated microfabrication facilities, or extensive familiarity with the operation of these facilities.

Received: May 29, 1996
Final version: July 10, 1996

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