

# Photolithography with transparent reflective photomasks\*

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A new type of photomask was fabricated by casting a prepolymer of a transparent, elastomeric polymer (polydimethylsiloxane, PDMS) against a Si(100) master whose surface has been patterned with V-shaped trenches or pyramidal pits using anisotropic etching. The PDMS replica, when placed in contact with a film of photoresist and illuminated, acts as a photomask. The sidewalls of the trenches and pits in the silicon master meet with the plateaus in dihedral angles of 54°; as a result, the PDMS replica selectively blocks the incident light in regions where it has sloping features by total internal reflection, and acts as a reflective contact mask for photolithography. The feasibility of this new type of photomask has been demonstrated by the fabrication of micropatterns in photoresist (and in an underlying silicon substrate) with smaller feature sizes and higher complexities than those present on the original chrome mask used in patterning the silicon master. The patterns produced using these elastomeric photomasks can be changed by varying the pressure applied in contacting them. © 1998 American Vacuum Society. [S0734-211X(98)05701-1]

## I. INTRODUCTION

Photolithography is a remarkably efficient technique for mass-producing microstructures.<sup>1</sup> Conventional photomasks used in photolithography are rigid, fused quartz plates covered with patterned microstructures of an opaque material such as chrome. Transparent apertures on the mask define the features of the design: the incident light is selectively blocked through absorption by the opaque material. Excimer laser ablation is another useful route to patterning materials without the use of resists or wet processes.<sup>2</sup> Reflective masks have been used in projection ablation involving high-power excimer laser.<sup>3</sup> The masks were fabricated by depositing an alternating series of thin films of two dielectric materials with different indices of refraction. The thickness of each layer was exactly one quarter of the wavelength of the excimer laser. The interface between layers reflects a specific amount of incident light, and the overall reflectivity is determined by the total numbers of the layers. Although these masks have higher damage thresholds than conventional photomasks, they suffer from the disadvantages of high cost and unique fabrication processes. This article describes the fabrication of a new type of photomask and its application in photolithography. The photomask demonstrated here works by a *different* principle from a chrome mask: the incident light is selectively blocked via total internal reflection. As a result, transparent materials can be used to fabricate reflective photomasks.

The proof-of-concept experiments were carried out with anisotropically etched Si(100) masters.<sup>4</sup> Anisotropic etching of Si(100) itself has the capability to generate complex patterns by starting from simple patterns such as lines, circles, and rectangles. Reflective photomasks were fabricated by replica molding against the etched Si(100) masters using an

organic polymer;<sup>5,6</sup> the one we used for the present work was a prepolymer of polydimethylsiloxane (PDMS), an elastomer optically transparent down to ~300 nm.<sup>7</sup> The elastomeric characteristics provide several advantages to using PDMS reflective photomasks: first, they can easily form conformal contact with substrates and thus allow us to form uniform patterns over large areas. Second, they are flexible and can be used to generate microstructures on curved substrates. Third, they can be deformed in a controlled way by mechanical compression, bending, and stretching to modify the shapes and sizes of features present on the reflective photomask.<sup>5</sup>

We are exploring new microlithographic strategies for carrying out microfabrication by employing elastomeric materials. Based on PDMS stamps embossed with relief on their surfaces, we have developed a number of soft lithographic techniques—microcontact printing ( $\mu$ CP),<sup>8</sup> micromolding in capillaries (MIMIC),<sup>9</sup> microtransfer molding ( $\mu$ TM),<sup>10</sup> and replica molding<sup>5,6</sup>—to fabricate microstructures and nanostructures of various materials on a variety of substrates. We have also demonstrated near field photolithography using a PDMS replica as the phase-shift mask to generate features with sizes of ~90 nm in thin films of photoresist on both planar and curved substrates.<sup>11</sup> Soft lithography, phase-shift lithography, and photolithography with reflective photomasks all benefit from the use of elastomers; they provide alternative approaches for generating microstructures and nanostructures that are increasingly important in many areas of modern technology. We believe that these techniques will find applications in the fabrication of microelectromechanical systems (MEMS),<sup>12</sup> microanalytical systems,<sup>13–15</sup> optical systems,<sup>16,17</sup> sensors,<sup>18</sup> and biosurfaces.<sup>19</sup>

## II. EXPERIMENTAL DETAILS

### A. Materials and substrates

Microposit 1805 photoresist was obtained from Shipley (Malborough, MA). Polydimethylsiloxane (Sylgard 184) was

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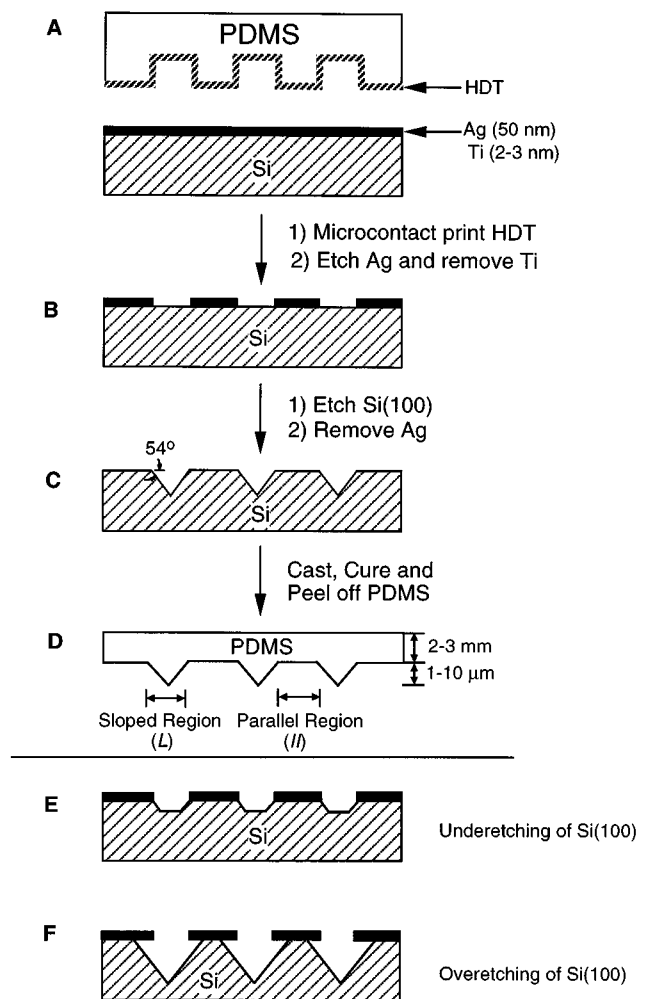


FIG. 1. (A–D) Schematic procedure used for fabrication of reflective PDMS photomask. (E, F) Schematic illustration of underetching and overetching of Si(100).

obtained from Dow Corning (Midtown, MI). Thermally curable epoxy (F113) was obtained from TRA-CON (Medford, MA). Ag (99.999%) and Ti(99.99%) were obtained from Aldrich. Hexadecanethiol (HDT) was obtained from Aldrich and was purified under nitrogen by chromatography. Si(100) wafers (Cz, phosphorous-doped, test grade, SEMI Std. flats, covered by native or thermal oxide) were obtained from Silicon Sense (Nashua, NH). Silver films (50 nm thick) were prepared by e-beam evaporation onto Si wafers that had been primed with Ti (2.5 nm thick).

## B. Fabrication of reflective masks

Figures 1A–1D outline the procedure used to fabricate reflective photomasks. A PDMS stamp with patterned relief structures on its surface was fabricated by casting a prepolymer of PDMS against a master (a patterned film of photoresist on silicon). After curing at  $\sim 65^\circ\text{C}$  for 3 h, the stamp was peeled off carefully from the master. The PDMS stamp was then inked with a solution ( $\sim 2\text{ mM}$ ) of HDT in ethanol, and brought into contact with the surface of the silver for  $\sim 10\text{ s}$  to form patterned self-assembled monolayers (SAMs)

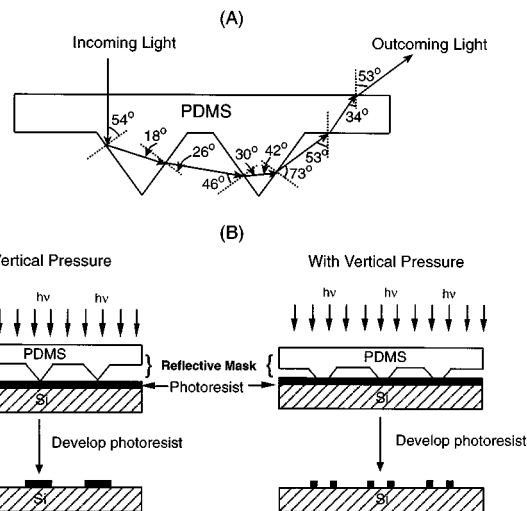


FIG. 2. Schematic diagram for (A) operational mechanism of a reflective photomask and its application (B, C) in photolithography.

of hexadecanethiolate. A pattern of silver was obtained after selective removal of silver unprotected by SAMs in an aqueous ferricyanide etchant containing  $\text{K}_2\text{S}_2\text{O}_3$  (0.1 M),  $\text{K}_3\text{Fe}(\text{CN})_6$  (0.01 M), and  $\text{K}_4\text{Fe}(\text{CN})_6$  (0.001 M).<sup>20</sup> The exposed Ti, after etching of the silver, was dissolved in an aqueous HF solution ( $\sim 1\%$ ). The pattern of silver was further used as the secondary mask in the anisotropic etching of Si(100) in an aqueous solution containing KOH and *i*-propanol (400 mL of  $\text{H}_2\text{O}$ , 92 g of KOH, and 132 mL of *i*-propanol, heated at  $70^\circ\text{C}$ ).<sup>20</sup> The profile of the relief structures etched in a Si(100) wafer can be precisely controlled by changing etching conditions (for example, the temperature and the duration of the etching).<sup>4</sup> The surface of the etched Si(100) wafer was made hydrophobic by treatment with a perfluorosilane (a solution of  $\text{C}_6\text{F}_{13}(\text{CH}_2)_2\text{SiCl}_3$  in hexane,  $\sim 1\%$ ) and then served as the master to cast PDMS reflective photomasks used in photolithography.

## C. Instrumentation

Scanning electron microscope (SEM) images were taken on a JSM-6400 JEOL scanning electron microscope with an accelerating voltage of 15 kV. Polymeric microstructures were sputtered with gold ( $\sim 100\text{ nm}$  thick) using an argon plasma sputter (Hummer II, Technics Inc.) before imaging by SEM. Atomic force microscope (AFM) images were taken with non-contact mode using Topometrix TMX 200 (Mountain View, CA).

## III. RESULTS AND DISCUSSION

### A. Photolithography with reflective photomasks

Figure 2(A) illustrates the mechanism of operation of a transparent, reflective photomask. When light (350–400 nm) is illuminated in the regions with sloping features, the incident angle of light is  $54^\circ$  at the PDMS/air interface, which is larger than the critical angle of  $47^\circ$  [determined by the refractive indices of PDMS ( $n \approx 1.43$ ) and air ( $n \approx 1.00$ )] for

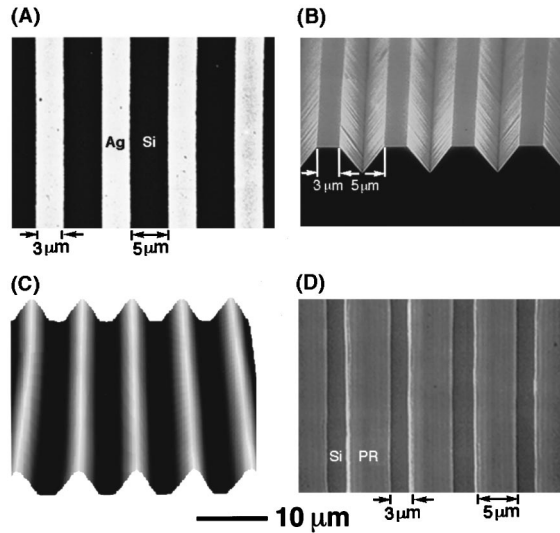


FIG. 3. (A) A SEM image of a test pattern of Ag on Si(100)/SiO<sub>2</sub> fabricated by  $\mu$ CP and selective wet etching; (B) a SEM image of the pattern formed by anisotropic etching of silicon in (A), followed by removal of the silver mask; (C) an AFM image of a PDMS replica cast from the etched Si master in (A); (D) a SEM image of patterns of photoresist (PR) on a Si/SiO<sub>2</sub> substrate generated using photolithography with a reflective PDMS mask cast from the Si master in (B).

total reflection. This light is totally reflected from the PDMS/air interface and finally refracted out of the PDMS block [Figure 2(A)]. As a result, no light is transmitted through these regions with sloping features on the PDMS replica. Figure 2(B) shows the use of PDMS replica as the reflective photomask in photolithography for generating patterns in a thin film of positive-tone photoresist. The deformation at the tips of the V-shaped teeth on the PDMS replica is not sufficient to allow the light to transmit through onto the photoresist, but it does so if a vertical pressure is applied onto the PDMS replica [Figure 2(C)]. The patterns produced using these elastomeric photomasks can, therefore, be modified in shape and size by changing the applied pressure.

Figure 3 shows an example in which the test pattern on the starting stamp for  $\mu$ CP consisted of parallel lines. Figure 3(A) shows a SEM image of the silver pattern generated by  $\mu$ CP, followed by selective etching in an aqueous solution of ferricyanide. Figure 3(B) gives a cross-sectional SEM image of the etched Si(100) substrate (the silver mask has been removed by immersion in an aqua regia solution). Figure 3(C) shows the AFM image of a PDMS replica cast from the etched Si master shown in Figure 3(B). Figure 3(D) shows a SEM image of patterns in a photoresist film (supported on Si/SiO<sub>2</sub>) generated using photolithography with the PDMS replica as the reflective photomask.

### B. Fabrication of patterns with reduced feature sizes

We have demonstrated previously that a combination of anisotropic etching of Si(100), casting PDMS stamps from the etched silicon, and microcontact printing provides a convenient method for reducing feature sizes; a reduction factor of more than 5 has been achieved.<sup>21</sup> Here, photolithography

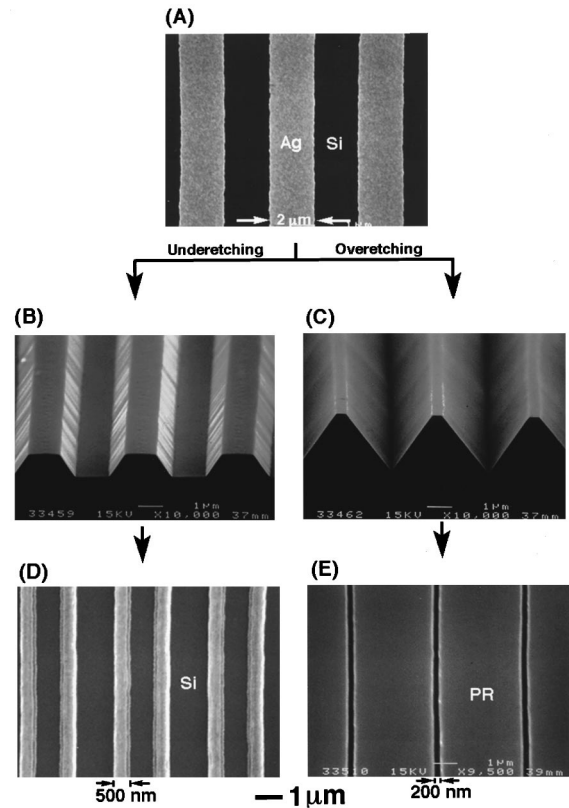


FIG. 4. (A) A SEM image of a silver pattern on Si(100)/SiO<sub>2</sub>, generated using a combination of  $\mu$ CP and selective etching; (B, C) cross-sectional SEM images of patterns formed by anisotropic etching of silicon in (A) for 10 min and 30 min, respectively; (D, E) SEM images of patterns of photoresist on Si/SiO<sub>2</sub> fabricated using photolithography with reflective PDMS masks molded from Si masters shown in (B) and (C), respectively.

with PDMS reflective masks replicated from etched Si(100) masters provides another approach. By changing the duration time of etching and/or the temperature of the etching solution, we can precisely control the profiles and dimensions of grooves etched into the surface of a Si(100) substrate, and therefore manipulate the sizes and patterns of features generated in the silicon master, PDMS replica, and the film of photoresist. Figure 4 shows two typical examples—underetching (Figure 4B) and overetching (Figure 4C)—of Si(100), and demonstrates the capability to reduce the size of the features in a controlled way. Figure 4(A) shows the SEM image of a test pattern of silver that was fabricated using  $\mu$ CP, followed by selective etching of silver. Figures 4(B) and 4(D) show cross-sectional SEM images of Si(100) substrates that were etched for  $\sim$ 10 min (underetching) and  $\sim$ 30 min (overetching), respectively. Figures 4(C) and 4(E) are SEM images of corresponding patterns generated in thin films of photoresist using photolithography. Note that underetching [Figure 4(B)] allows the generation of patterns with smaller feature sizes and doubled density [Figure 4(C)] than those shown in Figure 4(A). On the other hand, overetching [Figure 4(D)] enables us to reduce the lateral dimension of the plateau from  $\sim$ 2 to  $\sim$ 0.2  $\mu$ m. These two

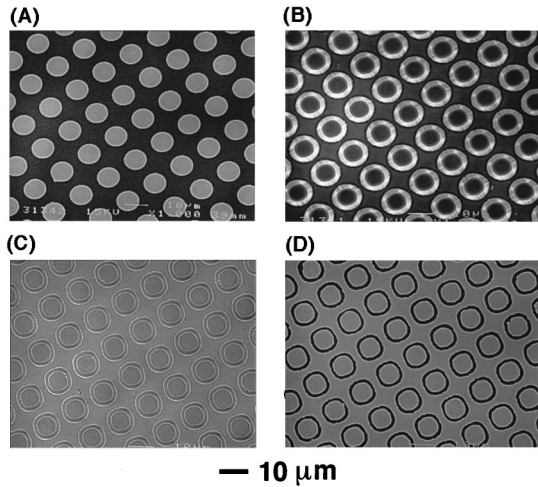


FIG. 5. SEM images of (A) a circle pattern in silver on Si/SiO<sub>2</sub>, generated by  $\mu$ CP and selective etching of Ag; (B) the pattern formed by anisotropic etching of silicon in (A), followed by removal of the silver mask; (C) the pattern of photoresist on a Si/SiO<sub>2</sub> substrate generated using reflective mask cast from master shown in (B); (D) the pattern of silver on Si/SiO<sub>2</sub>, fabricated by  $\mu$ CP with a PDMS stamp cast from the master of (C) and selective etching of Ag.

procedures provide a convenient route to patterned features with sizes of  $\sim 500$  nm by starting from a chrome photomask with feature sizes  $\geq 2$   $\mu$ m.

### C. Fabrication of relatively complex patterns from simple patterns

Photolithography using a reflective photomask also allows the generation of micropatterns with higher complexities than those present on the original chrome mask. Figure 5 shows an example. We started with circles of silver generated using  $\mu$ CP, followed by selective etching of silver [Figure 5(A)]. The silver was then used as a secondary mask in selective etching of the Si(100)/SiO<sub>2</sub> [Figure 5(B)]. A PDMS replica was fabricated by casting against the etched Si master. Using this PDMS replica as a reflective photomask, we generated donut-shaped microstructures in photoresist [Figure 5(C)], which then served as the master to cast a new PDMS stamp. This PDMS stamp was used for  $\mu$ CP on silver to generate the pattern shown in Figure 5(D). This overall process has the effect of converting the test pattern of circles in the first PDMS stamp used for  $\mu$ CP into a more complex pattern in the second.

Figure 6 illustrates another example of this ability of the system to increase the complexity of a starting pattern. Figure 6(A) shows a SEM image of a star pattern in silver generated by  $\mu$ CP, followed by selective etching. Figure 6(B) is a SEM image of the anisotropically etched Si(100) that subsequently served as the master to fabricate the PDMS reflective photomask. The SEM image shows that the hexagonal pattern of Figure 6(A) is transformed into a different symmetry and structure as a result of the anisotropy of the etching processes in Si(100). Figure 6(C) shows a SEM image of patterns generated in the film of photoresist using a PDMS reflective mask cast from the Si master shown in

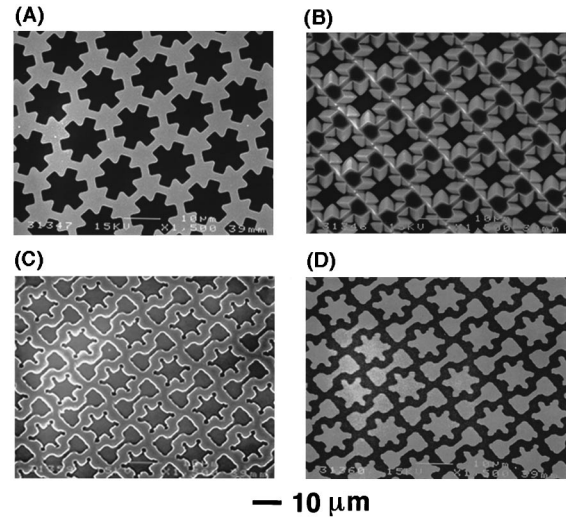


FIG. 6. SEM images of (A) a star pattern in silver on Si/SiO<sub>2</sub> generated by  $\mu$ CP and selective etching of Ag; (B) the pattern formed by anisotropic etching of silicon in (A), followed by removal of the silver mask; (C) the pattern of photoresist on a Si/SiO<sub>2</sub> substrate generated using reflective mask cast from master shown in (B); (D) the pattern of silver on Si/SiO<sub>2</sub>, fabricated by  $\mu$ CP with a PDMS stamp cast from the master of (C) and selective etching of Ag.

Figure 6(B). Figure 6(D) shows a SEM image of silver patterns generated by  $\mu$ CP with a PDMS stamp cast from the photoresist master shown in Figure 6(C), followed by selective etching. Note that the symmetry of the original star pattern [Figure 6(A)] has been reduced from C<sub>6</sub> to C<sub>2</sub> [Figure 6(D)] in this process.

### D. Fabrication of patterns with doubled density of features

By controlling the etching conditions for Si(100), we can easily double the density of periodic lines. For example, in Figure 7, two sets of continuous lines of silver [Figure 7(A)] were used as secondary masks to generate anisotropically etched Si(100) master [Figure 7(B)]. Photolithography with the PDMS reflective mask cast from the Si master generated four sets of continuous lines in the thin film of photoresist [Figure 7(C)]. The complexity of the microstructures also increased correspondingly. The entire process could be repeated to increase the density of features further. Imperfections (for example, at the turning points of the lines) often occur in this process as a result of the anisotropy in the etching of Si(100).

### E. Fabrication of patterns with a gradient in size

By carrying out the molding with mechanical deformation,<sup>5</sup> we have been able to fabricate patterns with a gradient in size over distances of  $\sim 1$  cm. We started with a silicon master having an array of square pyramidal pits etched into its surface. A PDMS replica was fabricated from this master. In the procedure used to generate gradient structures, the PDMS replica was sandwiched between two glass slides, one of which—the slide that touched the relief fea-

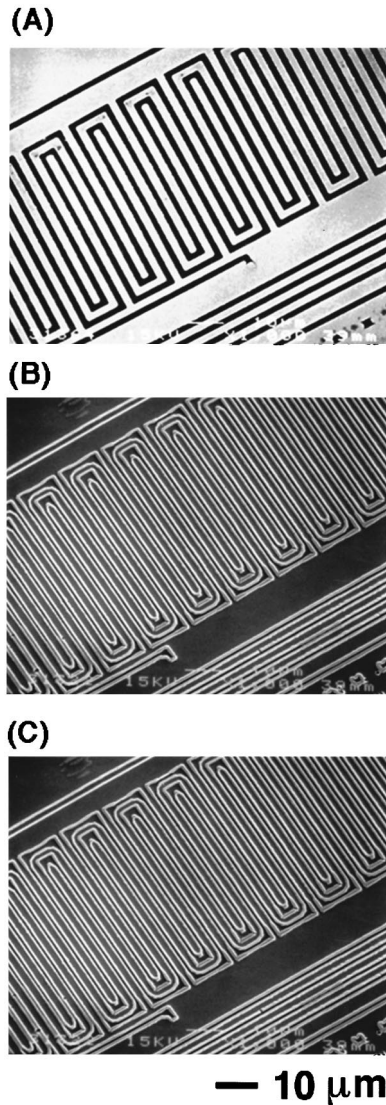


FIG. 7. SEM images of (A) a pattern in silver on Si/SiO<sub>2</sub>, generated by  $\mu$ CP and selective etching of Ag; (B) the pattern formed by anisotropic etching of silicon in (A), followed by removal of the silver mask; (C) the pattern of photoresist on a Si/SiO<sub>2</sub> substrate generated using reflective mask cast from the master shown in (B).

tures on the PDMS—had been coated with a thin layer of an epoxy prepolymer. The sandwich was compressed asymmetrically by applying different pressures to the two ends of the glass slides. The tips of the square pyramids on the PDMS master deformed when they were compressed. After curing the prepolymer thermally, the resulting epoxy replica was used as a new master to cast a PDMS stamp to be used as the reflective photomask in photolithography. Figure 8 shows SEM images of microstructures taken from different areas of a patterned film of photoresist. The thickness of lines of the squares decreases continuously from  $\sim 4$  to  $\sim 2$   $\mu\text{m}$  over a distance of  $\sim 1$  cm.

### F. Limitations

The very high anisotropy of etching along different crystallographic directions of single crystal silicon limits the ap-

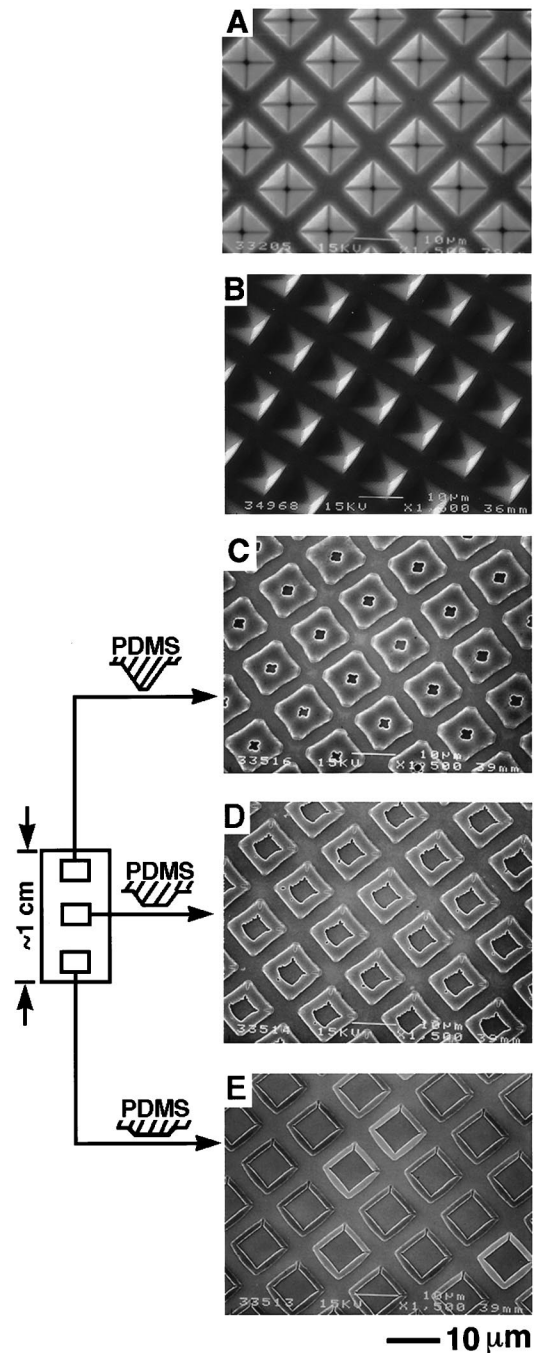


FIG. 8. SEM images taken from different areas of sample that was fabricated with a reflective PDMS mask having a gradient in feature size.

plication of the current procedure to specific types of patterns. As the pattern on the original chrome mask is made more complex, it becomes increasingly difficult to obtain well-resolved patterns during Si etching. Figure 9 shows one such example. In this case, the original pattern is taken from a microelectronic circuit and has a variety of microstructures with different feature sizes and shapes [Figure 9(A)]. The patterned microstructures generated in the thin film of photoresist [Figure 9(C)] indicate that all the detail on the etched Si(100) surface [Figure 9(B)] can be reproduced, but much of the information in the original pattern was lost during the

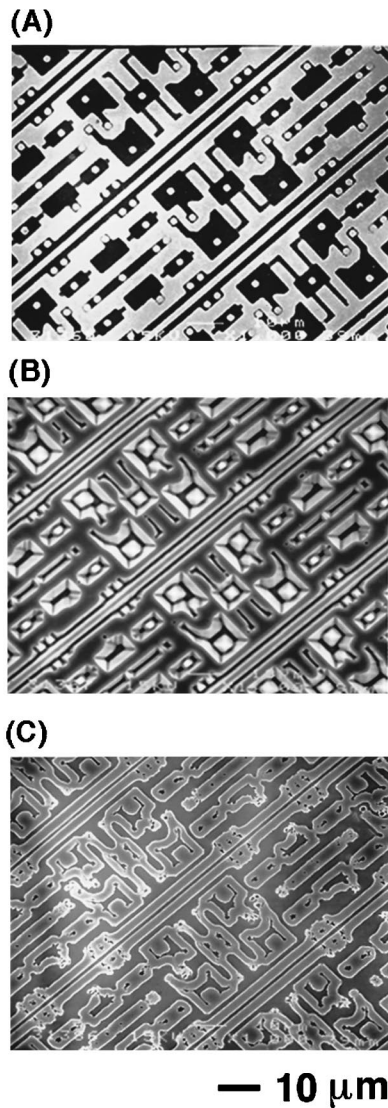


FIG. 9. (A) A SEM image of a complex pattern (taken from a microelectronic circuit) in Ag on Si(100)/SiO<sub>2</sub>, generated by  $\mu$ CP and selective etching of Ag. (B) A SEM image of the pattern formed by anisotropic etching of the structure in (A), followed by removal of the silver mask. (C) A SEM image of patterns of photoresist on a Si/SiO<sub>2</sub> substrate generated using a reflective mask fabricated by molding from the master shown in (B).

etching of Si(100). The pattern of Figure 9(A) was not *intended* to be used with this kind of procedure, and designs that conformed to (or took advantage of) the anisotropy in etching characteristic of Si(100) would give much better results. It is clear, however, that designing, patterning, molding of PDMS, and photoexposure must be considered as a system, since they are closely connected.

#### IV. CONCLUSIONS

In summary, we have demonstrated a new strategy for fabricating photomasks to be used in photolithography. This new type of photomask was fabricated by molding against a

Si(100) master with an array of V-shaped trenches or cavities anisotropically etched in its surface. Internal reflection occurs at the edges of these features present on the PDMS replica and incident light is selectively blocked in these regions. This procedure provides a simple method for manipulating the sizes and shapes of features present on a chrome mask. Using this method, we have been able to generate (1) microstructures with smaller feature sizes and higher complexities than those present on the original chrome mask; and (2) patterns with a gradient in size. The high anisotropy of etching along different crystallographic directions of Si(100) limits the application of the current procedure to specific types of patterns, that is, patterns with simple designs (lines, circles, squares) and uniform feature sizes. We believe that photolithography with transparent reflective photomasks will be useful for optical systems (such as chirped diffraction gratings and diffraction-based sensors), microelectrode arrays, and patterns for cell culture.

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