APPLIED PHYSICS LETTERS VOLUME 78, NUMBER 16 16 APRIL 2001

Fabrication of arrays of two-dimensional micropatterns using microspheres as lenses for projection photolithography

Ming-Hsien Wu and George M. Whitesides[a)]
Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge, Massachusetts 02138

(Received 25 September 2000; accepted for publication 28 December 2000)

This letter demonstrates the use of an array of transparent microspheres in forming repetitive, micrometer-scale patterns in photoresist, starting from masks with centimeter-scale patterns. A transparent microsphere with diameter $d > 1.5$ μm acts as a lens and reduces centimeter-scale images into micrometer-scale images on its image plane. A planar array of microspheres projects the image of an illuminated mask onto a corresponding array of micropatterns on their common image plane. We have prepared arrays of polystyrene microspheres ($d = 1.5$–10 μm) embedded in a transparent membrane to generate repetitive patterns in photoresist, and have transferred the resulting patterns into metal films by liftoff. The optical system of this technique is related to that used in conventional projection photolithography, but differs in that the lens that accomplishes size reduction is positioned within 10 μm of the photoresist. The microspheres generate uniform patterns over an area of ~ 2 cm^2, using a mask with area $\sim 25 \times 25$ cm^2 illuminated with a white light source. This method can generate submicron features either within a micropattern or between neighboring patterns. [DOI: 10.1063/1.1351525]

Transparent microspheres act as microlenses, and their optical performance can be approximately described by geometric optics.[1–6] Here we describe a strategy for generating arrays of small, repeating features using a form of photolithography in which a common image is projected onto a layer of photoresist using an ordered array of transparent microspheres positioned close to the photoresist.[1,2,7] This technique can generate arrays of patterns with features smaller than 200 nm. It is remarkable in that it accomplishes a size reduction of $\sim 10^3$ in a single step, albeit with significant aberration in the pattern. It can eliminate a stepper in certain circumstances, and should be useful for the production of simple repetitive micropatterns.

The key elements of this procedure are a planar array of microlenses (transparent microspheres with diameter $d = 1.5$–10 μm) held at an appropriate distance (approximately d, for the systems described here) from the photoresist, and a common pattern element (with features with millimeter to centimeter dimensions) that is imaged into the photoresist by each of these lenses. Microspheres are readily available in a wide range of sizes and materials. We have used precision polystyrene (PS) microspheres (refractive index $n_s = 1.59$, Polysciences, Inc, Warrington, PA). We used poly(dimethylsiloxane) (PDMS $n_m = 1.40$) membranes to position the spheres. The arrays that we have used for demonstrations are two-dimensional crystals of these spheres embedded in PDMS membranes.

The focal length of a microsphere embedded in a homogeneous medium depends on n_s, n_m, the diameter of the sphere, and the incident wavelength. It is nonlinearly proportional to the diameter. For $n_s = 1.59$, $n_m = 1.4$, and $d = 6$ μm, the focal length is ~ 6 μm. The sphere must therefore be positioned accurately, and close to the photoresist, to perform as imaging lenses. We fabricated the required arrays using the procedure shown in Fig. 1.

The PDMS optical elements containing arrays of microspheres were prepared on silicon wafers passivated with a thin film of a polyfluorosilane (tridecafluoro-1,1,2,2-tetrahydrooctyltrichlorosilane, United Chemical Technologies, Inc., Bristol, PA). We spin-coated the passivated silicon wafer with a thin film of PDMS diluted in heptane (PDMS: heptane = 1:5.1 by volume for 3 μm PS spheres). This solu-

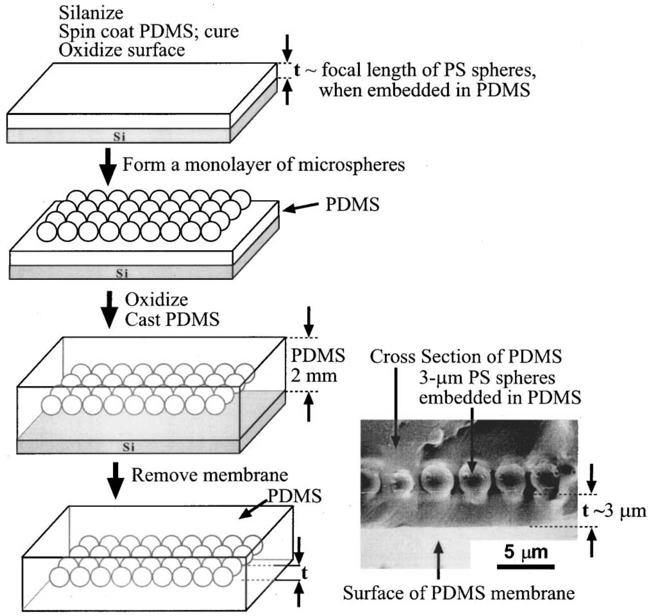

FIG. 1. The figure illustrates the procedure for the preparation of PDMS membranes containing monolayers of microspheres. The two layers of PDMS sandwiching the spheres are prepared under the same conditions, using a ratio of prepolymer: curing agent = 10:1. The SEM picture shows a cross section of a PDMS membrane with embedded 3 μm PS spheres.

[a)] Author to whom correspondence should be addressed; electronic mail: gwhitesides@gmwgroup.harvard.edu.

0003-6951/2001/78(16)/2273/3/$18.00

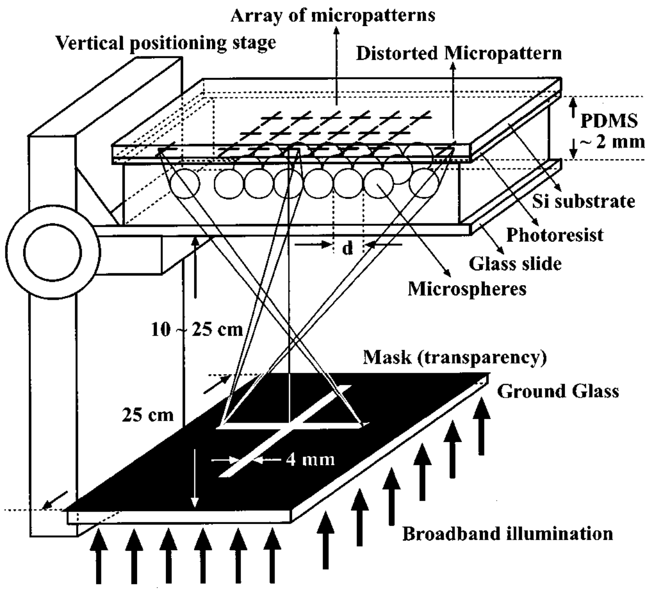

FIG. 2. The figure illustrates the simple optical system for the photolithographic technique. The ground glass is placed on top of the lamp to make the illumination uniform. For a fixed mask, the size of the micropattern projected by each microsphere basically depends on the distance between the sphere and the mask. The larger the distance, the smaller the micropattern. This distance can be changed by tuning the vertical positioning stage.

tion yielded a PDMS film with thickness of ~3 μm after curing. This value is approximately equal to the focal length of the spheres in this medium. The silanization prevented adhesion of the PDMS to the wafer. To crystallize microspheres on the PDMS thin film, we oxidized the PDMS film in an oxygen plasma cleaner for 10 s to render its surface hydrophilic. We placed a dilute aqueous suspension of microspheres on the oxidized surface. Slow evaporation of the water generated polycrystalline monolayers of microspheres.[8] We exposed the PDMS thin film and the arrays of crystallized spheres to an oxidizing plasma for 10 s to produce a layer of oxides on the surface. This oxide layer adheres well to a second, thicker film (~2 mm) of PDMS cast over the thin film to form a flexible membrane. All the microspheres remained embedded in the membrane after we removed the cured membrane from the surface of the wafer. We used this procedure to produce membranes with areas of 2×2 cm^2. Figure 1 shows the fabrication procedure and the cross sectional view of a PDMS membrane with 3 μm PS spheres embedded in the surface.

This technique requires only a minimal optical system for the photolithography (Fig. 2). An optical projector (an overhead transparency projector) or a halogen lamp is used as a broadband light source. The pattern to be used was printed onto a transparency using a desktop printer. We placed the transparency mask on top of the light source. The membrane was positioned at about 15–25 cm above the mask. To perform photolithography, we placed the membrane in conformal contact with a photoresist-coated substrate (photoresist: Shipley 1805).[9,10] For a resist layer with a thickness of ~200 nm, the exposure takes about 1–4 min, depending on the light source, the pattern on the mask, and the distance between the membrane and the mask. After exposure, the membrane was peeled from the resist, and the resist was developed in a solution of sodium hydroxide.

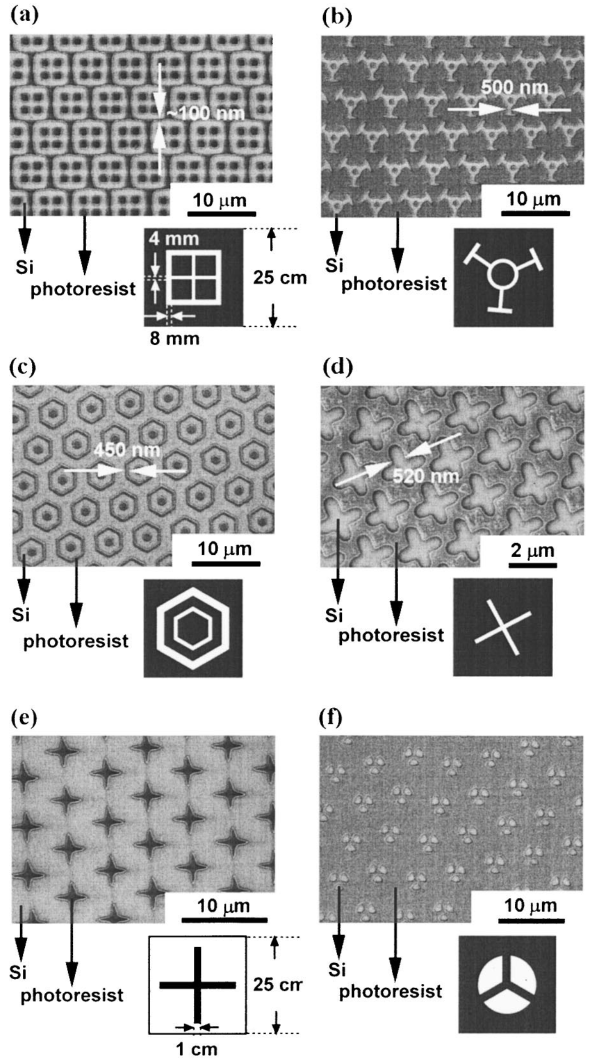

FIG. 3. SEMs show patterns in 220 nm thick photoresist generated by PS spheres with the corresponding masks shown below each SEM micrograph. (a)–(c): patterns produced by 6 μm spheres. (d): a simple pattern generated by 2 μm PS spheres. The linewidth of the patterns on the masks for (a)–(d) is ~4–8 mm. (e) and (f): patterns produced by negative masks. The linewidth of the patterns on the masks is 1 cm.

Figure 2 indicates that the spheres located on the boundary region of the membrane received illumination different from that received by the spheres in the central region. This difference in illumination results in variation of the micropatterns at different radial positions of the substrate. The micropatterns on photoresist is uniform with low variation on the central part of the substrate, while the micropatterns outside of this region are skewed. With an optical projector (area of illumination $\sim25\times25$ cm^2) as the light source, we can generate uniform micropatterns over a circular region with a diameter about 0.5–2 cm. This area of high and uniform definition is basically determined by two factors: (i) the mask distance (the distance between the mask and the spheres), and (ii) the size and shape of this pattern. The greater the mask distance, or the larger and simpler the pattern on the mask, the larger the area of uniform patterning.

Since crystallized PS microspheres are dense arrays of microlenses, they produce dense micropatterns on photoresist and the periodicity of micropatterns equals the size of spheres. Figures 3(a)–3(c) shows the scanning electron mi-

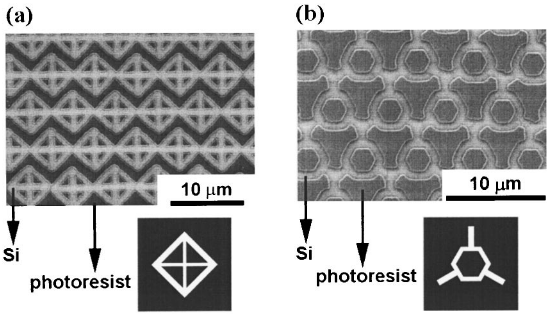

FIG. 4. SEMs show interconnected micropatterns in 220 nm thick photoresist generated by 6 μm PS spheres; the corresponding masks are shown below each SEM picture.

croscopy (SEM) pictures of representative micropatterns on photoresist generated by 6 μm PS spheres with the corresponding masks shown below each SEM micrograph. Each pattern on the mask is about 10–20 cm in length with a linewidth of ~4 mm. With careful control of exposure, we can generate features having dimensions <200 nm either between or within an exposed region [Fig. 3(a)]. Spheres as small as 2 μm project simple patterns onto photoresist. Figure 3(d) shows an array of crosses produced by 2 μm spheres.

The masks shown in Figs. 3(a)–3(d) are positive masks, which consist of narrow straight or curved transparent slits. Masks that consist of the reverse patterns—opaque lines in a bright field—are negative masks. Figures 3(e) and 3(f) show representative micropatterns produced by negative masks. Micropatterns produced by negative masks show more distortion than those produced by positive masks.

When the mask distance is reduced, the micropatterns become larger. With appropriate orientation of the membrane and the mask and a shorter mask distance, the spheres can produce interconnected patterns on photoresist. Figure 4 illustrates interconnected patterns produced by the masks shown below each SEM micrograph.

Compared with conventional photolithography,[11] the method described in this letter has several advantages: it offers a size reduction of features by factors of >1000 in a single exposure, and produces submicron features starting from a pattern on a transparency with millimeter-size features. Since a millimeter-scale modification of the pattern on the transparency results in a nanometer-scale change on the micropatterns, we can easily and quickly adjust the micropatterns at nanoscale by modifying the pattern on the transparency. Conventional photolithography cannot directly reduce a centimeter-size pattern to a micrometer-size pattern and it cannot easily modify a micropattern at the nanometer scale. It requires complicated facilities and the use of expensive chrome masks with micrometer-size features. Another advantage of this technique is the reduced sensitivity of the lithographic process to the surface flatness of photoresist, since the elastomeric membrane conforms to the surface of photoresist. This method also has disadvantages: it produces only repetitive simple patterns, and the patterns produced are not entirely uniform, since microlenses on different positions receive different illumination during exposure. The use of ball lenses also introduces substantial aberrations into the image. Although the aberrations result in a difference of shapes between the planned pattern and the generated micropatterns, we can minimize this difference using a mask with a modified pattern.

This technique offers a low-cost route for generating high-density arrays of simple patterns with submicron linewidths. These patterns have characteristics appropriate for a number of applications: for example, in frequency-selective surfaces,[12,13] photonic crystals,[14,15] information storage devices, and flat panel displays.[6]

The authors would like to thank K. E. Paul and Dr. Olivier Schueller for the discussion of crystallization of microspheres, and Professor Younan Xia for a preprint describing his related work.[2] This research was supported by Defense Advanced Research Projects Agency/Air Force Research Laboratory/Space and Naval Warfare Systems Center, San Diego.

[1] S. Hayashi, Y. Kumamoto, T. Suzuki, and T. Hirai, J. Colloid Interface Sci. **144**, 538 (1991).
[2] Y. Lu, Y. Yin, and Y. Xia, Adv. Mater. **13**, 34 (2001).
[3] M. Sasaki, T. Kurosawa, and K. Hane, Appl. Phys. Lett. **70**, 785 (1997).
[4] M. E. Friese, A. G. Truscott, H. Rubinsztein-Dunlop, and N. R. Heckenberg, Appl. Opt. **38**, 6597 (1999).
[5] J. P. Brody and S. R. Quake, Appl. Phys. Lett. **74**, 144 (1999).
[6] M. Ida, B. Montmayeul, and R. Meyer, Euro Display '96 (1996), p. 177.
[7] R. Völkel, H. P. Herzig, P. Nussbaum, P. Blattner, R. Dändliker, E. Cullmann, and W. B. Hugle, Microelectron. Eng. **35**, 513 (1997).
[8] N. D. Denkov, O. D. Velev, P. A. Kralchevsky, I. B. Ivanov, H. Yoshimura, and K. Nagayama, Langmuir **8**, 3183 (1992).
[9] J. A. Rogers, K. E. Paul, R. J. Jackman, and G. M. Whitesides, Appl. Phys. Lett. **70**, 2658 (1997).
[10] J. A. Rogers, K. E. Paul, R. J. Jackman, and G. M. Whitesides, J. Vac. Sci. Technol. B **16**, 59 (1998).
[11] W. M. Moreau, *Semiconductor Lithography* (Plenum, New York, 1989), Chap. 8.
[12] D. M. Byrne, A. J. Brouns, F. C. Case, R. C. Tiberio, B. L. Whitehead, and E. D. Wolf, J. Vac. Sci. Technol. B **3**, 268 (1985).
[13] M. D. Morgan, W. E. Horne, V. Sundaram, J. C. Wolfe, S. V. Pendharkar, and R. Tiberio, J. Vac. Sci. Technol. B **14**, 3903 (1996).
[14] J. D. Joannopoulos, R. D. Meade, and J. N. Winn, *Photonic Crystals: Molding the Flow of Light* (Princeton, New Jersey, 1995), Chap. 5.
[15] V. Berger, O. Gauthier-Lafaye, and E. Costard, Electron. Lett. **33**, 425 (1997).