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Generation of submicrometer structures by photolithography using arrays of spherical microlenses

Ming-Hsien Wu, Cheolmin Park, and George M. Whitesides *

Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA 02138, USA

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Abstract

This paper describes the fabrication of arrays of spherical microlenses by self-assembly of microspheres and the use of these arrays for nearfield photolithography to generate repetitive microstructures in photoresist. We used these arrays of microspheres to fabricate two types of elastomeric membranes: (i) membranes that have microspheres embedded in their surface and (ii) membranes that have hemispherical wells in their surface. Both types of membranes act as amplitude masks that pattern the intensity of illumination in the near field incident on the photoresist. Microspheres in the first type of membrane act as convergent lenses that generate recessed microstructures in positive photoresist. Hemispherical wells in the second type of membrane act as divergent lenses that produce protrusive microstructures in positive photoresist. This method can generate dense, regular arrays of microstructures with a variety of profiles—circular or hexagonal holes, circular posts, hollow posts, and cones—depending on the sizes and refractive indices of the spherical lenses and the distance between the lenses and the photoresist. This technique provides a simple route to large areas (>4 cm^2) of repetitive, simple microstructures.

1. Introduction

High-precision microspheres (size variation <5%) of different sizes and materials are commercially available at low cost. Different techniques have been developed to generate crystals of microspheres or to pattern microspheres [1–3]. These techniques make possible the formation of repetitive microstructures comprising spherical elements; these structures cannot be easily produced using conventional lithography. Microstructures based on assembled or patterned microspheres have been used for several applications—e.g., chemical sensors [4], photonic crystals [5], diffraction gratings [6], optical elements for unconventional lithography [7–9], and imaging optics [10,11]—and we have described their use for projection photolithography to generate hexagonal arrays of 2D micropatterns [12,13]. Microsphere projection lithography requires the use of transparent spheres with diameters (d_{sphere}) larger than the minimum focal spot produced by the spheres. Spheres with small diameters (e.g., $d_{\text{sphere}} \leqslant 3$ μm) are not particularly useful in projection lithography since the small image fields of these spheres does not allow the formation of complicated patterns. In addition, the high curvatures of small spheres increase spherical aberration, reduce resolution, and yield distorted patterns. Projection photolithography also requires the use of convergent lenses to project real images into photoresist; divergent lenses ($n_{\text{lens}} < n_{\text{medium}}$; n_{lens} = refractive index of lenses; n_{medium} = refractive index of surrounding medium) such as microspherical air lenses cannot be used for projection lithography. Although small microspheres ($d_{\text{sphere}} \leqslant 3$ μm) and divergent spherical lenses are not suitable for projection lithography, they can produce well-defined micrometer-scale images in the near field under flood illumination [14]. Figure 1 illustrates the use of transparent microspheres and spherical wells for patterning flood illumination in the near field. This paper demonstrates the use of microlenses with $d_{\text{sphere}} \leqslant 3$ μm for the fabrication of repetitive, topographically patterned microstructures with simple profiles.

Figure 1a sketches the concentration of incident illumination by spherical microlenses under collimated illumination. Based on Rayleigh's criteria [15,16], the resolution δ and

* Corresponding author.
E-mail address: gwhitesides@gmwgroup.harvard.edu (G.M. Whitesides).

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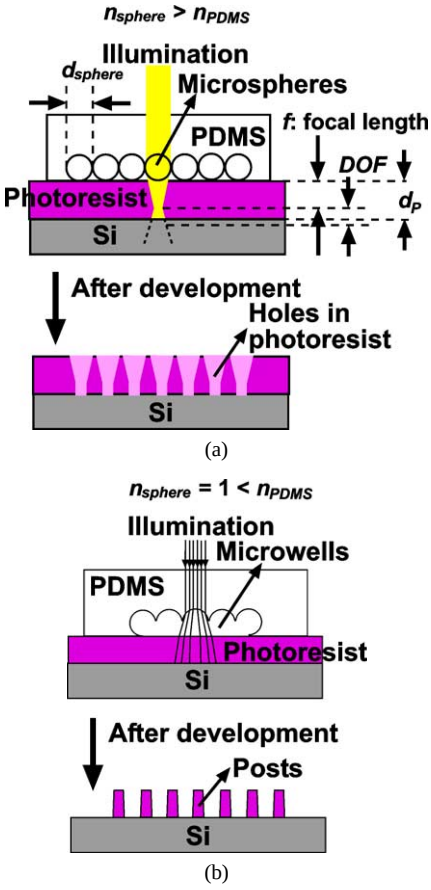

Fig. 1. Nearfield contact photolithography using different spherical lenses. (a) By transparent microspheres. (b) By spherical air lenses.

the depth of focus (DOF) of a lens are described by Eqs. (1) and (2), where λ is the incident wavelength and f the focal length of the lens:

$$\delta = 1.22\lambda \frac{f}{d_{\text{sphere}}}, \tag{1}$$

$$\text{DOF} = 1.22\lambda \left(\frac{f}{d_{\text{sphere}}}\right)^2. \tag{2}$$

Spherical lenses have high numerical apertures (NA) and small f-number (f-number $= f/d$; $d =$ diameter of the lens) due to the high curvatures of their surfaces. For spherical lenses with f-number $\sim$1 (i.e., $f \sim d_{\text{sphere}}$) under illumination with light having $\lambda \sim 0.4$ μm, the resolution δ (i.e., the minimum focal spot) is $\sim$0.5 μm and the DOF is $\sim$0.5 μm. The DOF allows the formation of high-definition patterns on an image plane P with the distance d_P between the lens and the plane P less than ($f +$ DOF), i.e., $d_P \leqslant (f + 0.5)$. Thus, spherical lenses with $d_{\text{sphere}} = 1$ μm can generate high-definition microstructures in photoresist with a maximum height $\sim$1.5 μm. Microstructures produced at d_P larger than 1.5 μm may have reduced resolution, due to diffraction. The relations allow an estimation of the minimum size of features in the focal plane, the approximate upper limits on the height of the microstructures, and the corresponding aspect ratios of these structures. For a spherical lens with $d_{\text{sphere}} = 1$ μm, $d_P \leqslant 1.5$ μm. The aspect ratio is less than (maximum d_P)/(minimum feature size δ) $\sim 1.5/0.5 = 3$. Thus, a spherical lens with $d_{\text{sphere}} = 1$ μm can produce a microstructure with an aspect ratio $\sim$3. This estimation shows that this simple technique can generate submicrometer features with high aspect ratios.

2. Materials and methods

2.1. Preparation of elastomeric membranes with microspheres embedded in the surface

We followed the procedure described previously to fabricate the membranes [12]. Monolayers of microspheres were prepared by slow evaporation of a diluted aqueous suspension ($\sim$0.1% by volume) of polystyrene (PS) microspheres (Polysciences Inc., Warrington, PA) on thermally oxidized silicon substrates (Silicon Sense, Nashua, NH). We deposited a layer of fluorosilane (tridecafluoro-1,1,2,2-tetrahydrooctyl-trichlorosilane, United Chemical Technologies Inc., Bristol, PA) on the sphere-covered substrate from the vapor phase. Elastomeric membranes were prepared by casting PDMS (poly(dimethylsiloxane), Sylgard 184, Dow Corning, Midland, MI) onto the microsphere-covered substrates. To minimize the adhesion of the cured PDMS to the silicon substrate, we peeled the membranes from the substrates under ethanol. Provided we followed this procedure, all the microspheres detached from the substrates and remained embedded in the surface of the membranes. Figure 2a illustrates the process schematically.

2.2. Preparation of PDMS membranes with arrays of hemispherical microwells on the surface

We prepared a monolayer of microspheres using the same procedure as described above. We deposited an aqueous solution of polyacrylic acid (PAA, Aldrich Chemical Company Inc., 1% in deionized water) with a thickness $\sim$0.5 mm on the monolayer of microspheres and allowed this resulting solution to evaporate. The dried film of PAA (thickness $\sim$100 nm) formed a release layer on the microspheres, but adhered to the silicon substrate. We silanized the surface of the PAA film using the same fluorosilane as described above and used the PAA-covered substrate as a master for replica molding. We cast a 2-mm-thick PDMS membrane onto the PAA-covered substrate and removed the membrane from the substrate in air. The surface of the PDMS membrane showed an array of hemispherical wells (Fig. 2b).

2.3. Preparation of PDMS membranes with arrays of microwells formed using a double layer of microspheres

We prepared a monolayer of microspheres using the same procedure as described above. To form a double layer of

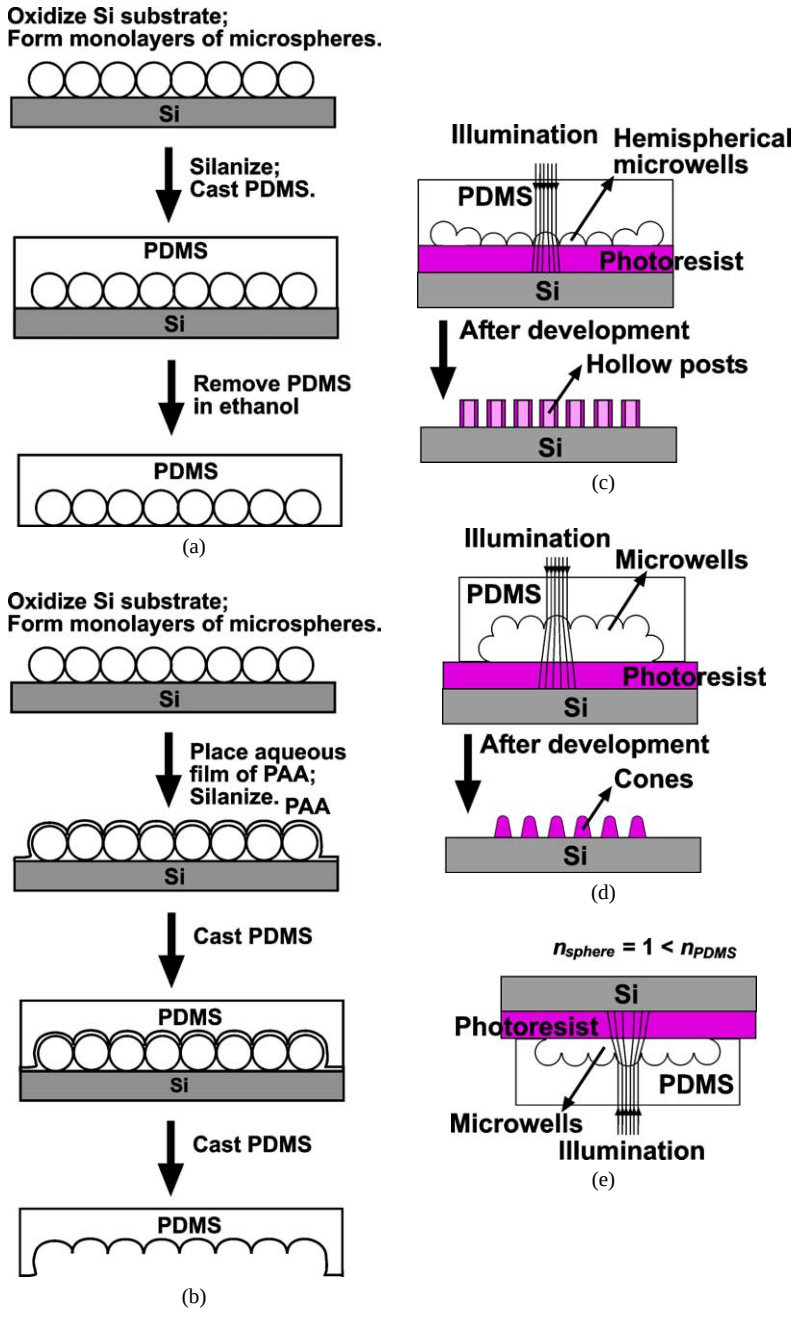

Fig. 2. (a) Fabrication of PDMS membranes with arrays of microspheres embedded in the surface. (b) Fabrication of PDMS membranes with arrays of microspherical wells in the surface. (c, d) Near field photolithography using hemispherical 1-μm air lenses. (c) The hemispherical wells on the membrane sag onto the photoresist and form hemispherical voids between the membrane and the photoresist. (d) The hemispherical air lenses in the PDMS membrane are produced using a double layer of microspheres. The crystal of the microspheres has a lateral dimension <100 μm. The small area of the air lenses minimizes the sagging of the membrane. (e) Inverted PDMS membrane and substrate with bottom illumination to avoid the sagging of the membrane.

microspheres, we crystallized a second monolayer of microspheres onto this first monolayer, using the same procedure. To improve the adhesion of the microspheres to the substrate, we wetted the spheres with an aqueous solution of PAA. After the film of PAA had dried, we oxidized and silanized the film using tridecafluoro-1,1,2,2-tetrahydrooctyltrichlorosilane. We cast PDMS onto the surface of the sphere-covered substrate. On removal of the PDMS membrane from the substrate, the double layer of the microspheres adhered to the substrate, and an array of hemispherical microwells formed in the surface of the membrane.

2.4. Procedure for photolithography

To perform contact-mode photolithography, we placed a PDMS membrane containing an array of microlenses on a photoresist-coated substrate. The membrane made confor-

mal contact with the resist layer without additional pressure. We used photoresist (Microposit S1818, Shipley Inc.) with thickness ∼2 μm when forming 3D structures. We used a UV light source (Karl Suss Mask Aligner, Model MJB3 UV400) to expose the resist through the microlens array. The light source was equipped with a mercury lamp with emission peaks at 365, 405, and 436 nm. After exposure, we removed the membrane from the resist and developed the resist in a basic solution of sodium hydroxide (Microposit 351 developer, Shipley Inc.). The microstructures in photoresist were examined with a scanning electron microscope (LEO 982 Digital scanning electron microscope) operating at 1 keV.

3. Results and discussion

3.1. Microstructures generated using elastomeric membranes with microspheres embedded in the surface

Figure 1a illustrates the formation of micrometer-scale holes in positive photoresist using a monolayer of microspheres for contact photolithography. Figures 3a–3d show some representative microstructures generated by PS microspheres embedded in the surface of PDMS. Individual microspheres generate volcano-shaped, circular microstructures in photoresist. Figures 3a and 3b show two examples: the structure shown in Fig. 3a was produced using an indi-

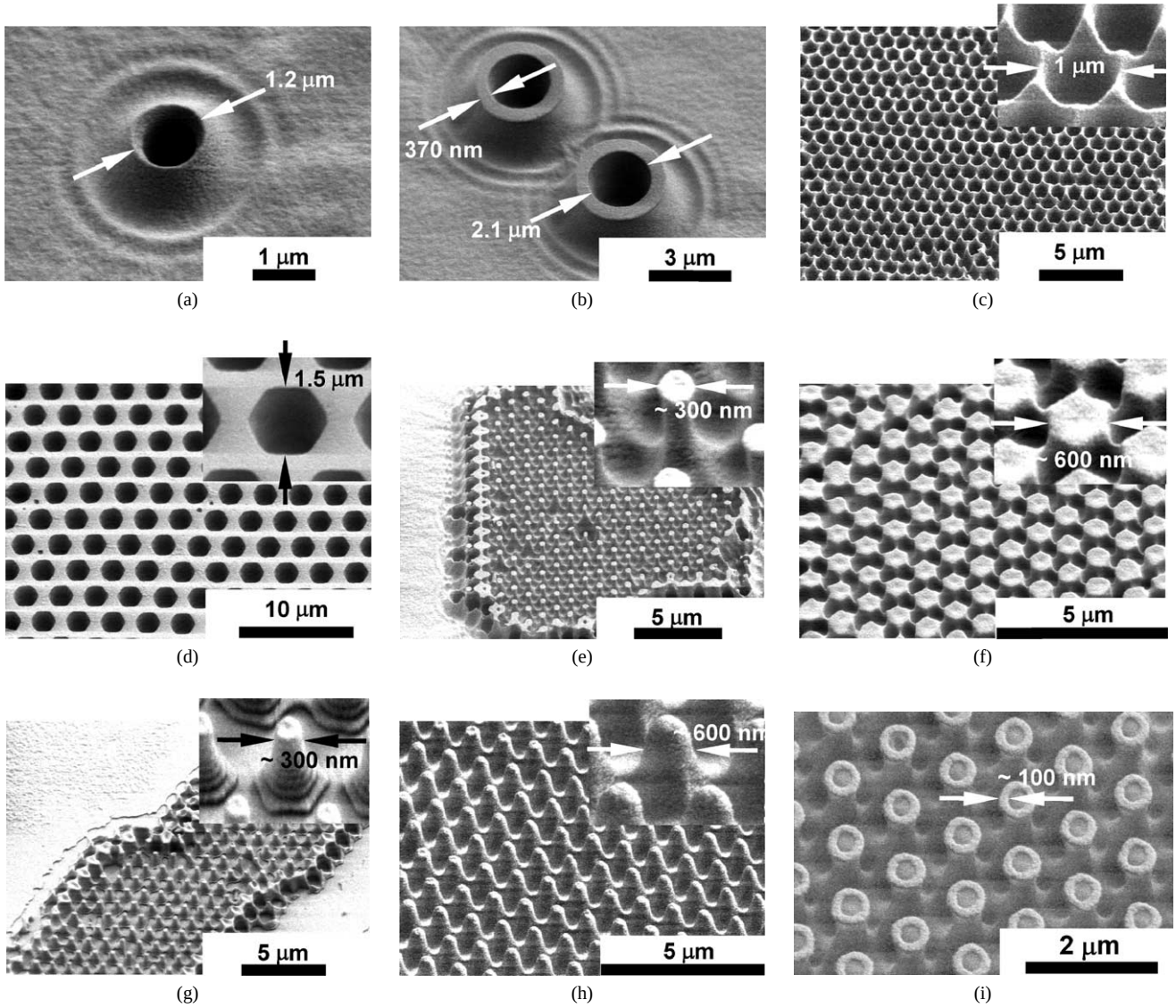

Fig. 3. Scanning electron micrographs (SEM) of microstructures in photoresist using different spherical microlenses embedded in PDMS membranes. (a) By an individual 1-μm PS sphere. (b) By two 3-μm PS spheres. (c) By a 2D array of 1-μm PS spheres. (d) By a 2D array of 3-μm PS spheres. (e)–(i) Hexagonal arrays of microstructures produced by a 2D array of 1-μm spherical air lenses. Arrays of posts shown in Figs. 3e–3g were produced by a PDMS membrane with a cross section shown in Fig. 1b. (e) Exposure time = 4 s, on a silicon substrate. (f) Exposure time = 2 s, on a silicon substrate. (g) Exposure time = 4 s, on a gold-coated substrate. (h) An array of cones with rounded tops produced by a membrane with a cross section shown in Fig. 2d. (i) An array of hollow posts produced by a membrane with a cross section shown in Fig. 2c.

vidual 1-μm PS sphere; it has a sharp rim on the top. Microstructures generated by 3-μm spheres also have volcano-shaped profiles but flat top surfaces. Figure 3b shows two such microstructures produced by two 3-μm spheres. The sharp edge resolution of these microstructures may be useful for the fabrication of field-emission arrays.

Figures 3c and 3d show hexagonal arrays of holes generated using 2D crystals of 1- and 3-μm spheres, respectively. Multiple scattering between neighboring microspheres resulted in the noncircular profiles of the holes. Comparison between Figs. 3c and 3d show that the profiles and the periods of microstructures produced by this technique can be controlled by the sizes of the spheres; submicrometer-scale modification of the profiles or periods of the microstructures can be achieved by using crystals of microspheres with different sizes or by using different exposure doses.

3.2. Microstructures generated using elastomeric membranes with arrays of hemispherical microwells in the surface

Figure 1b illustrates the formation of microstructures in photoresist using arrays of spherical microwells on the surface of PDMS. Figures 3e–3i show the microstructures produced by arrays of spherical microwells under different conditions. The arrays of micrometer-scale posts shown in Figs. 3e–3g were generated by the same membrane with an array of 1-μm spherical air lenses. Figure 1b sketches the cross-sectional view of the membrane. Since the air lenses inside the array do not have the rigid support required to maintain their distance from the photoresist, they sag. The sagging of the PDMS membrane can result in variation in the image distances and nonuniformity in the microstructures that are produced. To avoid this problem, we focused our attention on microstructures produced by small arrays of air lenses. We used small-area (lateral dimension <100 μm) 2D crystals of 1-μm microspheres to generate small arrays of air lenses.

The array of posts shown in Fig. 3e was produced with an exposure time of $\sim$4 s, whereas the interconnected microstructures shown in Fig. 3f were generated with an exposure time of $\sim$2 s. The increased exposure dose generated an array of separate, circular posts. Comparison of the two structures demonstrates that the profiles of the microstructures can be controlled by the exposure dose.

The microstructures shown in Fig. 3g were generated using the same array of 1-μm air lenses on a reflective substrate (a silicon substrate coated with a 50-nm layer of gold). The increased reflectivity of the substrate resulted in intense standing waves and generated layers of concentric rings on the posts [16]. The distance between neighboring concentric rings is $\sim$130 nm. Standing waves generated linear, 100-nm-scale features on the lateral surfaces of the microstructures; they thus provide a simple route for lateral patterning of microstructures of photoresist.

The array of cones shown in Fig. 3h was generated using the PDMS membrane shown in Fig. 2d. The relatively large distance between the hemispherical wells and the photoresist generated cone-shaped features rather than posts with flat tops. The array of hollow posts shown in Fig. 3i was produced using the PDMS membrane as shown in Fig. 2c. The sagging of the membrane formed arrays of hemispherical voids between the membrane and the photoresist. Exposure of photoresist through these voids produced circular, hollow posts with a thickness of the cylindrical shells $\sim$100 nm.

4. Conclusions

This paper demonstrates that self-assembled crystals of microspheres can be used for near field photolithography to generate repetitive, uniform microstructures with simple profiles. This technique does not require the use of chrome masks or expensive optical facilities. Since it produces microstructures by illumination of photoresist in the near field, the short optical path minimizes diffraction and enhances the resolution of these microstructures. The high-definition profiles, and the high density of the microstructures produced by this method, cannot be easily generated by conventional lithography.

Although this technique generates dense arrays of microstructures at low cost, it has several disadvantages: (i) It produces only hexagonal arrays of microstructures with simple profiles. It is difficult to generate microstructures in nonhexagonal arrays or with complicated profiles using this method. (ii) The use of elastomeric membranes as the support of the lens arrays allows variation in the microstructures. The elasticity of the membranes allows sagging of air lenses and reduces the uniformity of the microstructures [17]. This problem can be minimized if the system is inverted, and the membrane supported on a rigid backing, during exposure (Fig. 2e). (iii) The intrinsic defects in self-assembled crystals of microspheres form voids in the corresponding array of lenses and generate defects in the repetitive microstructures in photoresist that they generate on illumination. Thus, this technique is limited to defect-tolerant microfabrication.

This technique provides a cost-effective route for the fabrication of certain types of dense, repetitive microstructures with simple profiles. Microstructures generated by this technique may be useful for the fabrication of optical elements such as gratings, filters, and photonic crystals. They also have potential applications in the fabrication of surfaces for studying wetting, adhesion, and friction, of field-emission arrays, and of optical structures.

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