Patterning Spherical Surfaces at the Two-Hundred-Nanometer Scale Using Soft Lithography**

By *Kateri E. Paul*, *Mara Prentiss*, and *George M. Whitesides**

Two soft lithographic techniques—topographically directed photolithography (TOP) and near-field contact-mode photolithography—have been used to pattern spherical surfaces with features as small as 175 nm. Each technique has the ability to pattern more than a 60° arc of a spherical surface, albeit with distortions at the edge. Use as an optical polarizer demonstrates an application of these types of patterned surface.

1. Introduction

This paper describes the patterning of spherical surfaces with feature sizes in the range of ~200 nm using soft lithography. Soft lithography[1,2]—a set of techniques characterized by the use of an elastomeric pattern-transfer element—has been used extensively to pattern surfaces that are flat[1] or cylindrical.[3–6] Replica molding[7] is able to pattern spherical surfaces at the micrometer scale; Nuzzo and co-workers used micromolding in capillaries (MIMIC) to fabricate thin-film transistors on a curved substrate.[8] The two approaches demonstrated here for patterning a *spherical* surface—topographically directed photolithography (TOP)[3,9] and near-field contact-mode photolithography[10,11]—have each previously been applied to pattern both flat and cylindrically curved surfaces, and are able to produce features smaller than 100 nm on these surfaces.

The ability to pattern spherical surfaces would be useful in a number of areas of optics and optoelectronics. Spherical surfaces patterned with features at the 100 nm scale could enable fabrication of optical and sensing devices with wide (> 60°) fields of view.[12] Curved surfaces are difficult to pattern using conventional photolithography, especially at sub-micrometer feature sizes, for several reasons. The depth of focus of most lithographic systems limits topography of the substrate to approximately $\pm\lambda/2$, where λ is the wavelength of light used for exposure. As the critical dimensions of patterns decrease, the wavelength of light used to pattern the features typically also decreases and therefore limits topography across the exposure area to a few hundred nanometers. In our case, we use 365–436 nm broadband UV light; this choice limits our topography to about ± 180 nm. The characteristics of the pattern-transfer element also limit the ability of projection photolithography to pattern curved surfaces. The masks used to define the pattern in conventional lithographic techniques are usually rigid. In contact-mode lithography, a rigid, planar mask will only come into contact with a spherically curved surface at a single point; in projection-mode photolithography, the features from the mask will only be in focus in a small area of the exposed region.

Several alternative approaches to patterning spherical surfaces have been described that address the shortcomings of traditional photolithographic techniques. Goodberlet and co-workers adapted conventional contact-mode lithography to pattern at the nanoscale. They fabricated a 150 μm thick, deep-ultraviolet-transparent fused silica mask, bearing embedded chromium features patterned by electron-beam (e-beam) writing and lift-off. This embedded amplitude mask forms conformal contact with substrates, including a substrate with a circular divot 1 μm deep and 3 mm in diameter.[13] This technique generated features of lines and corners with periodicities at the 200 nm level using 220 nm light for exposure, and is able to generate both large and small features simultaneously. Because of the high in-plane stiffness of the mask and the ability to align through the mask, pattern-placement errors were less than 60 nm using this technique.[13,14] Other innovations for patterning curved surfaces include combining step-and-flash imprint lithography[15–17] and ion beam proximity printing[18] on substrates having a diameter of 1 in. (1 inch = 2.54 cm) with features as small as 1.2 μm,[12] and the use of steerable micromirrors to pattern silicon spheres having a diameter of 1 mm with micrometer-scale features (www.ballsemi.com).[19–21]

In this paper we describe fabricating features on spherical surfaces using near-field contact-mode photolithography and TOP; we generate structures as small as 175 nm. In both techniques, we used a thin poly(dimethylsiloxane) (PDMS) membrane to generate test patterns of lines, dots, and loops by these techniques. TOP has the ability to pattern an 85° arc of the surface, while near-field contact-mode photolithography has the ability to pattern up to a 65° arc. Each method is simple, but because in the current embodiment both involve distortion of a flat, elastomeric membrane around a sphere, the techniques are currently limited to single-layer patterning where only local

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dimensional tolerance is important: examples of structures that meet these criteria are patterned optical elements, sensors, microanalytical systems, and microelectromechanical systems (MEMS).[2]

2. Results and Discussion

The methods we used to pattern the spherical surfaces are given in the Experimental section. Figures 1 and 2 illustrate the process of TOP and near-field contact-mode photolithography, respectively. Figure 3 shows the features obtained by TOP on a hemispherical surface. The membranes used to mold the photoresist were fabricated using a holographic diffraction grating having sinusoidal topography at a wavelength of 417 nm. The embossed features in photoresist were also approximately sinusoidal. The smallest features generated using the gratings with a period of 417 nm are ~175 nm lines of photoresist separated by ~242 nm spaces. These features were imaged near the apex of the hemisphere and are shown in Figures 3a,b. Figures 3c,d were obtained with a 30° tilt of the sample; the largest variation between features at the apex and at an angle of 30° was 25 nm.

The features obtained by near-field contact-mode photolithography on hemispherical substrates are shown in Figures 4 and 5. Figure 4 shows features of lines and posts generated using an elastomeric phase mask having 1 µm lines and 1 µm spaces. To generate posts, the photoresist was exposed twice; for the second exposure the mask was rotated 90° with respect to its alignment in the first exposure. The smallest width of the lines generated are ~200 nm, while the posts have diameters of ~225 nm. Figure 5 shows features of rings on the left, generated by 1.5 µm diameter posts on the PDMS phase membrane and on the right, by 1 µm diameter wells in the PDMS phase membrane. In both cases, the narrowest line widths are ~200 nm. The photoresist features are uniform over the apex of the hemisphere where the light for exposure is incident normal to the PDMS phase mask membrane. As the angle of exposure increases to 15° in (b), and to 30° in (c), the features become distorted due to the oblique angle of illumination. The distortion is most evident in images taken at 30°, where the width of the line furthest from the apex has roughly double the width of the line closer to the apex. There are several possible methods for improving the uniformity of the exposure over the surface; one would be simply to use less collimated light (the light in our mask aligner is about 95 % collimated), a second would be to pass the light through a lens that would provide illumination at normal incidence across the surface of the hemisphere, and a third would be to rotate the sphere under a colli-

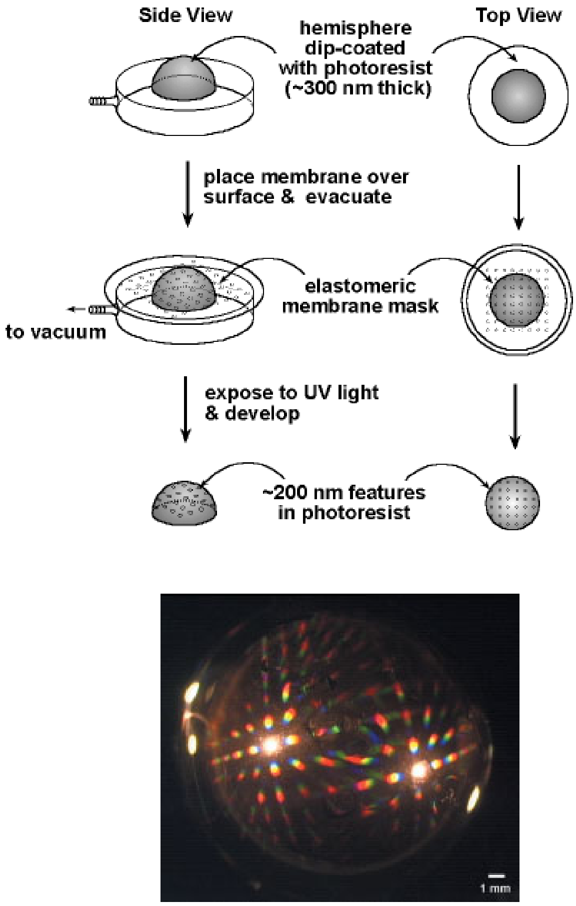

Fig. 2. Schematic representation of an epoxy hemisphere patterned by near-field contact-mode photolithography. A thin, PDMS membrane (200–500 µm) is used as a phase mask and brought into contact with the photoresist-coated hemisphere under a vacuum. The assembly is then exposed to UV light and developed. The color image shows diffraction from a half inch (~1.3 cm) sphere patterned with square loops of 1 µm over a >60° arc.

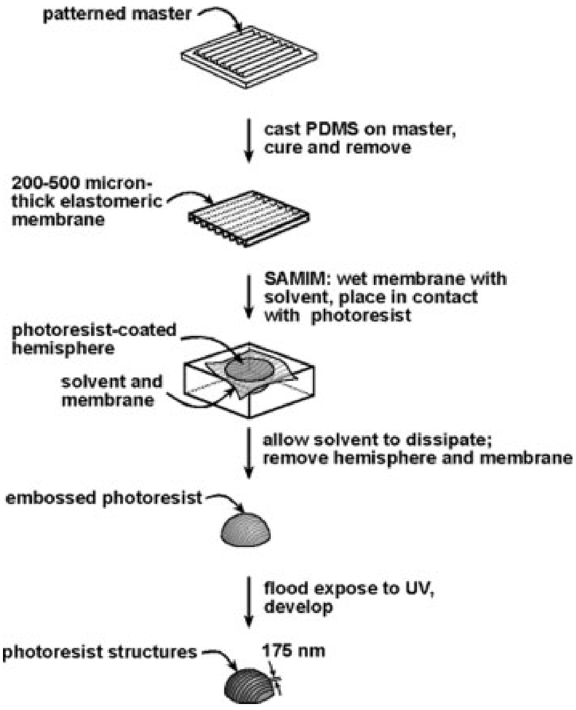

Fig. 1. Schematic representation of a polymer hemisphere patterned using TOP. A photoresist-coated substrate is placed in a spherical mold with a PDMS membrane wetted with solvent. When the solvent dissipates, the substrate is removed and the membrane is peeled away to reveal the embossed surface. The resist is then flood exposed to UV light and developed.

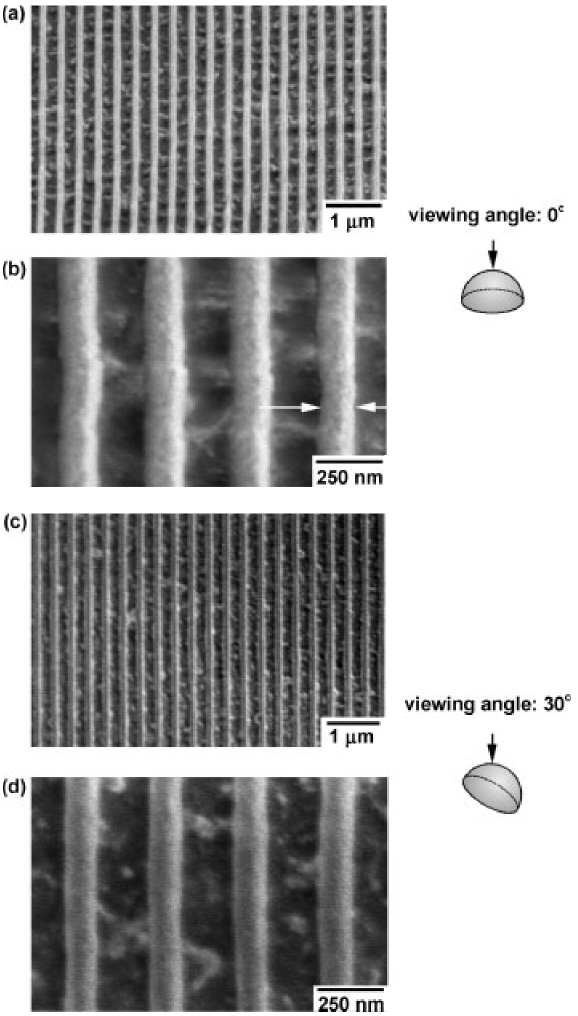

Fig. 3. Scanning electron microscope (SEM) images of representative results generated by TOP using a PDMS membrane patterned with a sinusoidal grating having a periodicity of 417 nm. a,b) Features near the apex of the patterned hemisphere. c,d) Features at about 30° from the apex. The smallest features generated by this method are of ~175 nm. The roughness of the surface is due to damage during the plasma oxidation.

mated beam that illuminated the sphere through an aperture. This type of process would expose the surface in such a way that the direction of exposure was always approximately normal to the surface.

Figure 6 shows features generated by lift-off with gold. We used photoresist patterns generated by TOP using as a master a sinusoidal grating with a wavelength of 417 nm. Gold features are uniform over the patterned area (> 60° arc of the surface). Figure 6a shows a representative area near the apex of the hemisphere; the inset image shows the features with line widths of ~275 nm. Images taken from a 15° tilt (b), and a 30° tilt (c), show a 10–15 % difference in line width. The difference in feature size can be attributed to the difference in the incident angle of the illumination of the sinusoidal grating at various regions of the substrate.

In order to demonstrate the utility of patterning on a curved surface, we tested samples prepared by TOP, followed by lift-off, and similar to those shown in Figure 6, for their ability to polarize transmitted light. We measured the intensity of a polarized laser beam ($\lambda = 633$ nm) transmitted through the patterned sample incident on a photoelectric detector connected to a multimeter (Fluke 73III). A schematic representation of the experimental set-up is shown in Figure 7. In order to test a specific angle of the surface we held the sample stationary and rotated an analyzing polarizer, testing at several polarizations of the laser beam incident on the sample. A plot of sample experimental results is shown (Fig. 7b). The polarization ratio for the patterned surface is ~5, consistent with a Jones matrix analysis of the experimental setup.[22,23]

3. Conclusions

Patterning spherical surfaces presents challenges to conventional lithography and becomes especially difficult for features in the size range below one micrometer. New techniques are necessary to transfer two-dimensional patterns with small feature sizes to a curved surface. Here, we show that a flexible, elastomeric membrane can generate features as small as 175 nm in positive photoresist, using two soft lithographic techniques: TOP and near-field contact-mode photolithography. The advantages of these techniques are that they are simple and flexible. Both techniques require only broadband UV light to generate features with sizes in the 200 nm range across greater than a 60° arc of the surface. The disadvantages of the techniques are the limitations of resolution, alignment, and registration imposed by the use of a flat, two-dimensional elas-

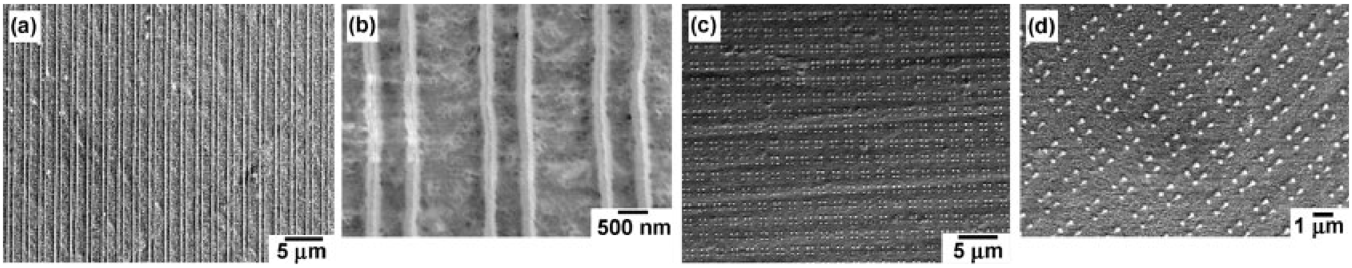

Fig. 4. Scanning electron microscope (SEM) images of features generated using near-field contact-mode photolithography. a,b) An array of lines patterned using a phase mask having features of 1 µm lines spaced by 1 µm on the surface. The smallest linewidth is ~200 nm. c,d) An array of photoresist dots generated with the same phase mask using two perpendicular exposures. The roughness of the surface is due to etching of the epoxy surface by the oxygen plasma. Images were taken 15–30° away from the apex.

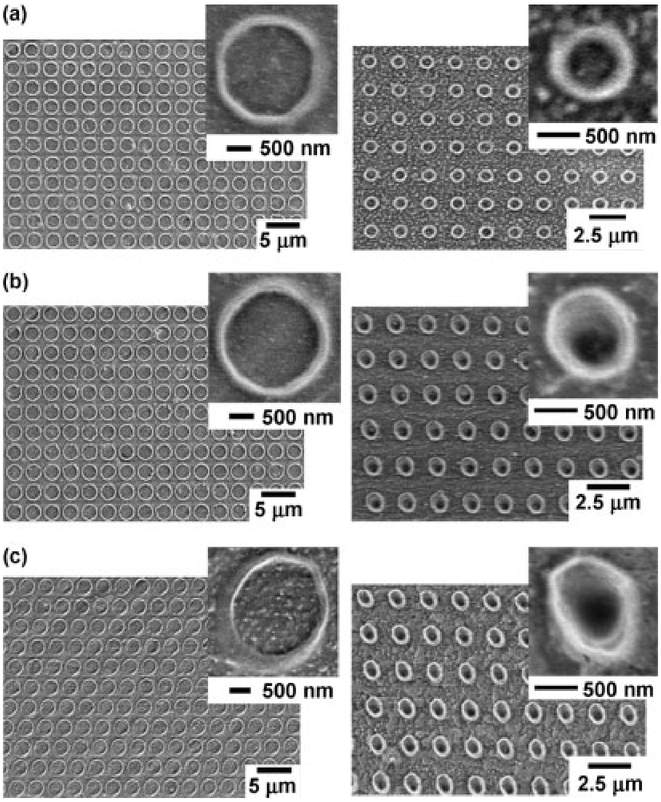

Fig. 5. Scanning electron microscope (SEM) images of features generated on an epoxy hemisphere in photoresist using near-field contact-mode photolithography. Images on the left show features patterned with 2.5 µm loops while images on the right show features patterned with 1 µm loops. Images in (a) were taken at the apex (0°), while images in (b) and (c) at 15° and 30° from the apex, respectively. Distortion increases the linewidth of the loops as the angle of illumination increases.

tomeric mask stretched around a spherical surface. The fabrication of an optical polarizer demonstrates that these techniques, with further engineering, could be used to fabricate applied optical systems for imaging technologies. Whether they can be engineered to provide the registration required for fabrication of multi-layer devices with useful feature sizes remains to be seen.

There are several other techniques for generating nanometer-scale features using soft lithography; both controlled over-etching[24] and topographically directed etching[3,25] require patterns generated by photolithography—conventional photolithography as well as the techniques used here—to serve as a photoresist mask for further steps. The photoresist patterns generated by the techniques demonstrated here could further be used to pattern metal layers for the soft lithographic etching techniques.

Although the size of the features varies over the surface with the angle of the incident light, further engineering could provide an optical lens system to bend the incoming light so that it is incident normal to the molded photoresist or phase mask surface over this exposed area. Engineering the master to account for the curvature of the spherical surface would remove the distortion caused by applying a flat membrane to a spherical surface. While the techniques as described here are sufficient for

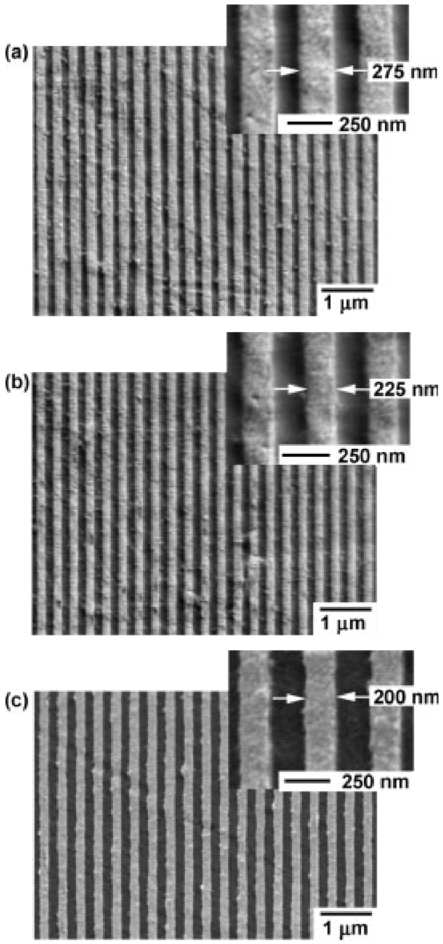

Fig. 6. Patterns in gold generated on hemispheres using TOP. a) Features near the apex of the hemisphere; the width of the gold line is ~275 nm as shown in the inset. b) Lines at a tilt of 15° from the apex with a linewidth of ~225 nm, and c) images at a tilt of 30° from the apex with a linewidth of ~200 nm.

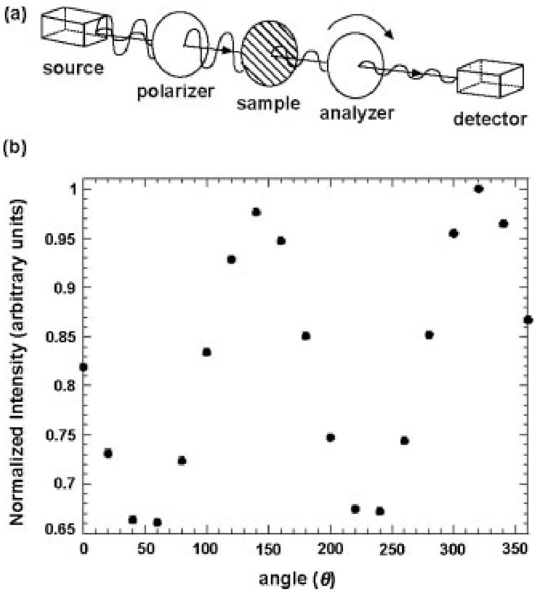

Fig. 7. a) Schematic diagram of the experimental setup used to measure the polarization of a patterned spherical substrate. b) Graph of representative experimental data showing the normalized intensity plotted versus the angle of polarization.

single-level fabrication without alignment, the ability to align masks or molds designed for spherical surfaces with a combination of the aligner designed at Motorola[26] and the system designed by Willson and co-workers[12] may provide a useful route to multilevel fabrication in the future.

4. Experimental

Fabricating Substrates: We obtained chrome steel balls with diameters of 3/8, 1/2, 5/8, and 3/4 in., having a diameter tolerance of 0.000025 in. (635 nm) from Small Parts (www.smallparts.com). We molded the balls in PDMS to a depth of half their diameter to generate hemispherical molds, removed the ball, and used UV-curable epoxy (Norland Optical Adhesive 73 or Epotek UVO-114, Epoxy Technologies, Billerica, MA) to fabricate hemispherical replicas in the PDMS mold. Polymer substrates were oxidized for 1 min in a plasma of oxygen at 75 W and 125 sccm O_2. All substrates were held with tweezers and dipped by hand in hexamethyldisilazane (HMDS, ShinEtsuMicroSi, Phoenix, AZ) for 10 s to improve adhesion of the subsequent layer of photoresist and allowed to dry for 10 min. Substrates for near-field contact-mode photolithography were dipped by hand in Shipley 1805 photoresist (MicroChem Co., Newton, MA) thinned 1:4 by weight in propylene glycol methyl ether acetate (PGMEA, Aldrich), while substrates for TOP were dipped in 1805 resist diluted 1:2 in PGMEA. The photoresist-coated sphere was placed for 5 min on a cleanroom-compatible cloth that absorbed excess photoresist. The samples were baked in an oven at 90 °C for 10 min. In order to determine the thickness of the photoresist films, we spun a thin layer of epoxy on a silicon wafer, dip-coated the wafer in the diluted photoresist, allowed the film to dry at an angle of 45°, and then baked the wafers as described above. We then patterned the photoresist layer by contact-mode photolithography using an amplitude mask of 10 µm features. Atomic force microscopy (Digital Nanoscope 3, www.di.com) conducted in tapping mode on the photoresist surface determined the thickness of the resist to be 250 ± 30 nm for the dilution of 1:4 and 600 ± 30 nm for the dilution of 1:2.

Fabricating Membranes: Thin, planar, poly(dimethylsiloxane) (PDMS, Sylgard 184, Dow Corning, Midland, MI) membranes served as our phase masks and our molds. We used commercially available substrates, such as holographic gratings (Edmund Scientific, Barrington, NJ) and samples produced by conventional photolithography or soft lithography as our masters. Membranes cast on holographic gratings were fabricated by pouring a layer of pre-polymer over the patterned surface of the 2.5 cm × 2.5 cm master and curing under the weight of a polystyrene Petri dish. The membrane was removed from the master under ethanol to prevent tearing. To generate a membrane from a photoresist master on a 3 in. diameter silicon wafer, we passivated the surface with a fluorinated silane ((tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-trichlorosilane, United Chemical Technology, Bristol, PA) by vapor deposition. We then applied liquid PDMS pre-polymer to the silicon masters by spin coating at 1500 rpm for 10 s. The PDMS cured in an oven at 70 °C for 2 h or longer. Before removing the membrane, a second layer of PDMS (~500 µm thick) was applied to its edge using an applicator and cured; this layer provided a rim that improved the structural integrity of the membrane and prevented damage during handling.

Generating Nanoscale Features: To generate features by TOP, we transferred a pattern from an elastomeric mask to a layer of photoresist using solvent-assisted embossing [27]. The function of this topography was to pattern the intensity of light inside the photoresist film during a flood exposure. To bring the elastomeric membrane into conformal contact with the spherical surface, and to secure it during the molding process, we supported the substrate and membrane in a PDMS mold of half of the sphere. We placed the elastomeric membrane over the cavity, applied a small amount of 2-propanol to the membrane, and pressed the photoresist-coated hemisphere into the cavity with the membrane. The 2-propanol dissolved in the photoresist and formed a film of photoresist gel; the patterned membrane molded this gel. Finger pressure was required in order to keep the hemisphere in the cavity and in contact with the membrane until the solvent dissipated by a combination of evaporation and migration into the PDMS. When the photoresist was dry (after about 10 min), the hemisphere and the membrane were removed from the cavity by hand. We peeled away the dry membrane to expose the pattern from the membrane in bas-relief on the surface of the photoresist. Because of the low surface free energy of PDMS membrane, it released easily and did not damage the resist; the membrane was used repeatedly. The sample was then exposed to flood, partially incoherent UV light (365–436 nm, Karl Süss MJB300). To develop the photoresist, we held the hemisphere in developer (Microposit 351, 1:5 dilution in 18 MΩ water by volume) using tweezers for 60 s.

To generate features by near-field contact-mode photolithography, an elastomeric phase mask was placed in conformal contact with a substrate coated with a thin layer of photoresist [10,11]. In order to achieve uniform contact across at least a 60° arc of the surface of a hemisphere, we brought the PDMS membrane serving as our phase mask into contact with the photoresist-coated hemisphere by evacuating the area between the mask and the sample and held it under vacuum during exposure. We designed a vacuum chuck (2 in. diameter and 3/4 in. in height) to fit in the sample holder of our exposure tool (shown schematically in Fig. 2) and used the vacuum line that holds a chrome mask in place in the mask aligner as our vacuum source. The strength of the vacuum was tuned using a third line to the atmosphere that could be opened to decrease the pressure, or closed to increase the pressure. Pressures of 200–350 torr were satisfactory. We placed the coated hemisphere in the chuck and draped the membrane over the surface. A rigid plastic ring was placed on top of the membrane to form a seal between the membrane and the chuck and the system was evacuated. The substrate was exposed to UV light for 3–6 s through the membrane phase mask, removed from the vacuum, and developed as described above. Metal layers for lift-off were deposited using an electron-beam evaporator. We evaporated 2 nm of titanium as an adhesion layer, and 50 nm of gold (99.99 % pure, Materials Research Corp., Orangeburg, NY). The photoresist layer and the metal covering it were lifted off in acetone with sonication.

We characterized the patterns generated on hemispherical substrates by scanning electron microscopy (SEM, Leo 983, Leo Electron Microscopy, Thornwood, NY). In order to characterize the features at different points on the surface, we varied the tilt angle of the sample in the chamber and imaged the surface normal to the source of electrons, aligning the sample using a charge-coupled device (CCD) camera mounted in the chamber.

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[1] Y. Xia, G. M. Whitesides, *Angew. Chem. Int. Ed.* **1998**, *37*, 550.
[2] Y. Xia, J. A. Rogers, K. E. Paul, G. M. Whitesides, *Chem. Rev.* **1999**, *99*, 1823.
[3] A. J. Black, K. E. Paul, J. Aizenberg, G. M. Whitesides, *J. Am. Chem. Soc.* **1999**, *121*, 8356.
[4] R. Jackman, J. Wilbur, G. M. Whitesides, *Science* **1995**, *269*, 664.
[5] R. J. Jackman, S. T. Brittain, G. M. Whitesides, *J. Microelectromech. Syst.* **1998**, *7*, 261.
[6] J. A. Rogers, R. J. Jackman, G. M. Whitesides, *Adv. Mater.* **1997**, *9*, 475.
[7] Y. Xia, E. Kim, X.-M. Zhao, J. A. Rogers, M. Prentiss, G. M. Whitesides, *Science* **1996**, *273*, 347.
[8] M. K. Erhardt, H.-C. Jin, J. R. Abelson, R. G. Nuzzo, *Chem. Mater.* **2000**, *12*, 3306.
[9] K. E. Paul, T. L. Breen, J. Aizenberg, G. M. Whitesides, *Appl. Phys. Lett.* **1998**, *73*, 2893.
[10] J. A. Rogers, K. E. Paul, R. J. Jackman, G. M. Whitesides, *Appl. Phys. Lett.* **1997**, *70*, 2658.
[11] J. A. Rogers, K. E. Paul, R. J. Jackman, G. M. Whitesides, *J. Vac. Sci. Technol. B* **1998**, *26*, 59.
[12] P. Ruchhoeft, M. Colburn, B. Choi, H. Nounu, S. Johnson, T. Bailey, S. Damle, M. Stewart, J. Ekerdt, S. V. Sreenivasan, J. C. Wolfe, C. G. Willson, *J. Vac. Sci. Technol. B* **1999**, *17*, 2965.
[13] J. G. Goodberlet, *Appl. Phys. Lett.* **2000**, *76*, 667.
[14] J. G. Goodberlet, B. L. Dunn, *Microelectronic Engineering* **2000**, *53*, 95.
[15] M. Colburn, A. Grot, M. N. Amistoso, B. J. Choi, T. C. Bailey, J. G. Ekerdt, S. V. Sreenivasan, J. Hollenhorst, C. G. Willson, *Proc. SPIE—Int. Soc. Opt. Eng., Emerging Lithographic Technologies IV* (Ed: E. A. Dobisz), **2000**, *3997*, 453.
[16] M. Colburn, S. Johnson, M. Stewart, S. Damle, T. Bailey, B. J. Choi, M. Wedlake, T. Michaelson, S. V. Sreenivasan, J. Ekerdt, C. G. Willson, *Proc. SPIE—Int. Soc. Opt. Eng., Emerging Lithographic Technologies III* (Ed: Y. Vladimirsky), **1999**, *3676*, 379.
[17] T. Bailey, B. J. Choi, M. Colburn, M. Meissl, S. Shaya, J. G. Ekerdt, S. V. Sreenivasan, C. G. Willson, *J. Vac. Sci. Technol. B* **2000**, *18*, 3572.
[18] D. P. Stumbo, G. A. Damm, S. Sen, D. W. Engler, F.-O. Fong, J. C. Wolfe, J. A. Oro, *J. Vac. Sci. Technol. B* **1991**, *9*, 3597.
[19] N. Takeda, *US Patent 6 061 118*, **2000.**
[20] K. Powell, *US Patent 5 949 557*, **1999.**
[21] T. Kanatake, *US Patent 6 130 742*, **2000.**
[22] E. Hecht, A. Zajac, *Optics*, Addison-Wesley, Reading, MA **1979**.
[23] G. R. Fowles, *Introduction to Modern Optics*, 2nd ed., Dover Publications, New York **1989**.
[24] J. C. Love, K. E. Paul, G. M. Whitesides, *Adv. Mater.* **2001**, *13*, 604.
[25] J. Aizenberg, A. J. Black, G. M. Whitesides, *Nature* **1998**, *394*, 868.
[26] T. Burgin, V.-E. Choong, G. Maracas, *Langmuir* **2000**, *16*, 5371.
[27] E. Kim, Y. Xia, X.-M. Zhao, G. M. Whitesides, *Adv. Mater.* **1997**, *9*, 651.