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Generation of 30−50 nm Structures Using Easily Fabricated, Composite PDMS Masks

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This communication describes a method to generate simple nanostructures with critical dimensions down to 30 nm, over cm^2-sized regions, using masks made by soft lithography. Patterned structures having dimensions of tens of nanometers are useful in ultradense data storage, subwavelength optics, and devices for studying mesoscale physics.[1] The top-down technique most often used to generate sub-50 nm features is electron-beam writing, although X-ray photolithography and scanning probe methods find specialized uses.[2] These serial methods require access to sophisticated equipment and can pattern only small areas (0.01−1 mm^2).

We and others have developed a set of soft lithographic techniques that can routinely generate patterns with feature sizes down to 100 nm using procedures that do not require complex facilities.[3] These methods commonly use stamps made of poly(dimethylsiloxane) (Sylgard 184 PDMS) with μm-scale features to pattern surfaces and to generate structures in photoresist, polymers, and metal. Following the lead of the IBM Zurich laboratory,[4] and using composite PDMS masks composed of a thin, hard (*h*) PDMS layer supported by a soft, flexible Sylgard 184 PDMS layer, we have recently improved the resolution of these structures down to 50 nm.[5] Free-standing structures in photoresist (lines and dots) generated from this composite mask can have aspect ratios of ~1:6 and be patterned over cm^2-sized areas. We have molded composite PDMS against these structures to form stamps and masks patterned with feature sizes down to 100 nm.

Here we demonstrate that the use of composite masks in phase-shifting lithography can generate arrays of rings in positive-tone photoresist with line widths as small as 30 nm. These structures show the dimensions that can be supported in commercial *g*-line (436 nm) UV resists. The use of composite masks combined with controlled undercutting by wet etching can transfer these rings in photoresist into arrays of slots in metal films with features down to 40 nm. In addition, the masks can generate wells in negative-tone photoresist with diameters as small as 100 nm. These nanowells provide a simple template to prepare arrays of uniformly sized, nanocrystalline salts having lateral dimensions down to 30 nm.

Figure 1A shows the scheme we used to prepare masters. Masters in photoresist with arrays of circular posts were generated by (i) exposing the resist through a composite mask of 2 μm lines spaced by 2 μm, (ii) rotating the mask 90°, and (iii) exposing the resist again. Posts of different sizes can be achieved using different types of positive-tone resist.[6] These masters were replicated in composite PDMS to prepare phase-shifting masks having features down to 100 nm over areas of 2.5 cm × 2.5 cm. Figure 1B schematically depicts the types of structures produced in positive and negative resists using these masks; the patterns have the same periodicity as the master.

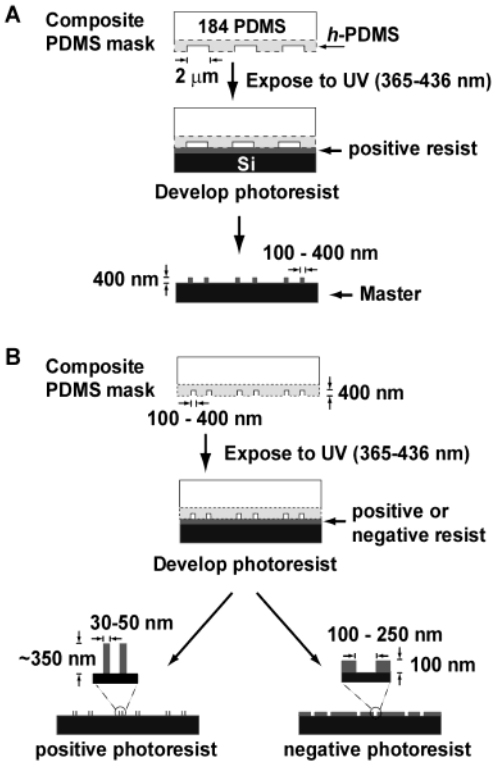

Figure 1. (A) Scheme representing the preparation of masters with features down to 100 nm using phase-shifting photolithography. (B) Illustration depicting the types of nanostructures generated in positive- and negative-tone resist through phase-shifting masks molded against masters from (A).

Composite masks patterned with 250 nm posts in bas-relief generated arrays of rings having 40 nm line widths, and masks with 350 nm posts produced rings having 30 nm line widths in positive-tone photoresist (Figure 2A and B). These narrow line widths, nearly a factor of 10 smaller than the wavelength of the UV light (365−436 nm) used for exposure, result directly from the use of phase-shifting masks with feature sizes less than 500 nm.[7] The smallest features in photoresist often have some defects: they are slightly nonuniform, and their sidewalls are not completely vertical.

Because of the residual resist at the edges and the center of the rings, we were unable to achieve the small line widths (30−40 nm) in metal films by depositing metal and performing lift-off. We therefore combined phase-shifting lithography with another edge lithography, controlled undercutting,[8] to fabricate annular slots in thin films of palladium (Pd), which have small grain sizes (15−20 nm). These slots were generated by (i) patterning rings of photoresist on thin (30−50 nm) films of Pd, (ii) overetching the Pd that was

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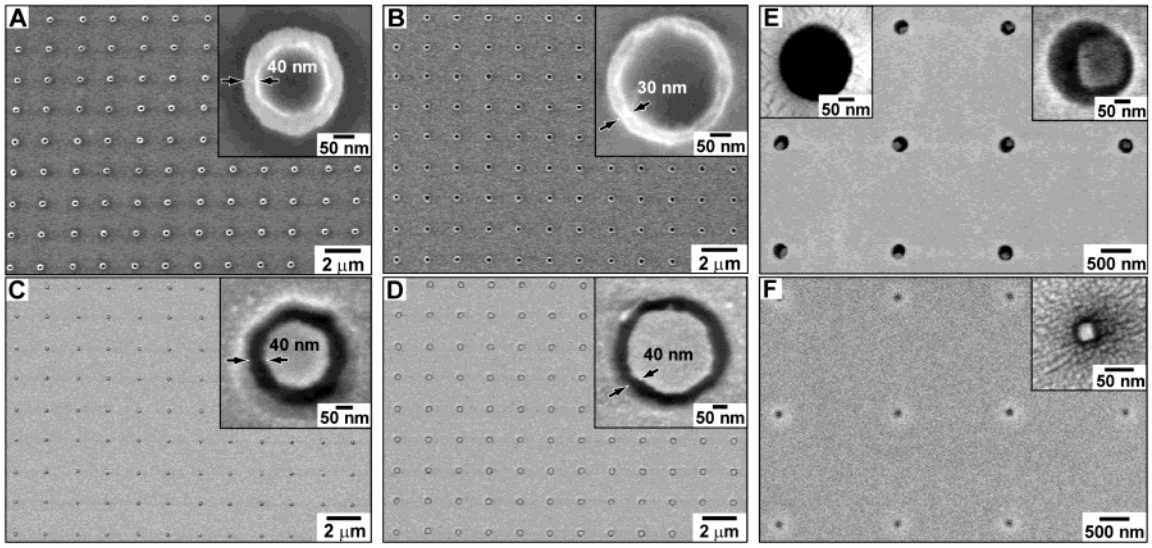

Figure 2. (A and B) Scanning electron micrographs (SEM) of rings of photoresist produced at the edges of a phase-shifting mask patterned with 250 nm circular posts and 350 nm circular posts spaced by 2 μm. Light regions are photoresist, and dark regions are Si/SiO_2. (C and D) Arrays of rings etched in palladium films (bright) supported on Si substrates (dark) generated from masters having 250 nm diameter and 350 nm diameter posts. (E) Array of individual NaCl crystals crystallized in 250 nm diameter wells. (left inset) Magnified area of an unfilled 250 nm diameter well; (right inset) magnified area of a 100 nm NaCl crystal. (F) Array of 30 nm NaCl nanocrystals in 100 nm diameter wells. The roughness in (E) and (F) is due to thin (3−5 nm) layers of gold.

not protected by the patterned resist, (iii) depositing the same thickness of Pd as the film in (i), and (iv) performing lift-off. The circular structures were produced uniformly over large areas (> cm^2) and had critical dimensions as small as 35−40 nm (Figure 2C and D).[9]

We also produced structures in negative-tone resist (SU-8-2002) by exposing substrates through masks with 250 and 100 nm diameter posts in bas-relief. Instead of generating recessed rings in epoxy, the composite PDMS masks generated recessed wells (Figure 2E, left inset) with the same lateral dimensions as the features on the mask. The requisite postexposure baking of negative resists causes a broadening of the features formed in the exposed resist because of lateral diffusion of the cross-linked molecules in the resist; hence the line widths of the rings increase and overlap during the baking step to form a well after development.

The ordered arrays of nanowells are useful for preparing arrays of uniform nanocrystals of inorganic salts. We filled the wells (each of volume ~z L) by discontinuous dewetting,[10] and salts of KBr and NaCl were formed by crystallization in the wells (Figure 2E and F).[11] In each experiment, only one crystal was produced per well, and over 99.9% of the nanowells contained nanocrystals; the crystals had uniform dimensions. We could grow crystals having different sizes simply by changing the concentration (1−5 M) of the salt solution. Crystals of NaCl grown in 100 nm wells have edge lengths as small as 30 nm (Figure 2F, inset).

The nanostructures we have generated suggest that simple, top-down patterning techniques can achieve 30−40 nm features; at this size scale, the integrity of the resist and the grain size of the metal limit the minimum feature sizes that can be generated. Our approach enables control over the density of nanostructures on surfaces because their pitch is determined by the original chrome mask. The *ease* of preparation of the master allows features having variable pitch (500 nm to 25 μm) to be formed over large areas (> cm^2) in a single (at most two) exposure(s). Drawbacks of these masters include their susceptibility to damages and possible structural imperfections (e.g., nonvertical sidewalls). The molding of composite PDMS against these high aspect ratio structures (>1:4 width: height) can cause the photoresist to delaminate from the substrate and result in the loss of the master. Another limitation is that only simple geometries (dots and lines) can be generated; such structures are useful, however, as templates for preparing other types of nanostructures (for example, the arrays of 30 nm crystals).

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References

(1) Mirkin, C. A.; Rogers, J. A. *MRS Bull.* **2001**, *26*, 506 and other articles in this issue.
(2) Smith, H. I.; Spears, D. L.; Bernacki, S. E. *J. Vac. Sci. Technol.* **1973**, 913−917. Crommie, M. F.; Lutz, C. P.; Eigler, D. M. *Science* **1993**, *262*, 218−219. Snow, E. S.; Campbell, P. M. *Science* **1995**, 1639−1641.
(3) Xia, Y. N.; Rogers, J. A.; Paul, K. E.; Whitesides, G. M. *Chem. Rev.* **1999**, *99*, 1823−1848. Michel, B.; Bernard, A.; Bietsch, A.; Delamarche, E.; Geissler, M.; Juncker, D.; Kind, H.; Renault, J. P.; Rothuizen, H.; Schmid, H.; Schmidt-Winkel, P.; Stutz, R.; Wolf, H. *IBM J. Res. Dev.* **2001**, *45*, 697−719.
(4) Schmid, H.; Michel, B. *Macromolecules* **2000**, *33*, 3042−3049.
(5) Odom, T. W.; Love, J. C.; Wolfe, D. B.; Paul, K. E.; Whitesides, G. M. *Langmuir* **2002**, *18*, 5314−5320.
(6) Shipley 1805 photoresist produced circular posts (100−250 nm in diameter) with dimensions smaller than AZ 5206 photoresist (350−400 nm in diameter).
(7) Rogers, J. A.; Paul, K. E.; Jackman, R. J.; Whitesides, G. M. *J. Vac. Sci. Technol., B* **1998**, *16*, 59−68.
(8) Love, J. C.; Paul, K. E.; Whitesides, G. M. *Adv. Mater.* **2001**, *13*, 604−607.
(9) Structures of this size (250−350 nm) in metal should act as band-pass filters in the near-IR (1.8−3 μm). We observe, however, little or no increase in the transmission of light through these slots: Spector, S. J.; Astolfi, D. K.; Doran, S. P.; Lyszczarz, T. M.; Raynolds, J. E. *J. Vac. Sci. Technol.* **2001**, *19*, 2757−2760.
(10) Jackman, R. J.; Duffy, D. C.; Ostuni, E.; Willmore, N. D.; Whitesides, G. M. *Anal. Chem.* **1998**, *70*, 2280−2287.
(11) Thalladi, V. R.; Whitesides, G. M. *J. Am. Chem. Soc.* **2002**, *124*, 3520−3521.

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