

Maskless photolithography: Embossed photoresist as its own optical element

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This letter demonstrates that features embossed on the surface of a layer of photoresist can direct UV light in the photoresist layer. These topographical features act as optical elements: they focus/disperse and phase shift incident light in the optical near field, inside the resist layer. A number of different surface topographies have been examined, which give 50–250 nm features after exposure and development. This method gives patterns of complex features over large areas, in a parallel process, that can then be transferred into silicon or metal. It provides a method for controlling the intensity of light inside a thin film of photoresist. © 1998 American Institute of Physics.

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This letter describes a procedure—combining embossing and photolithography—for the fabrication of features ranging in size from 50 to 250 nm. In this procedure, the topography of the surface of a layer of photoresist patterns UV light in the optical near field *inside* that layer. This method involves three steps: (i) embossing the surface of a layer of photoresist with features that act as lenses and phase shift elements; (ii) exposing this topographically patterned photoresist layer to flood illumination with incoherent, polychromatic, and uncollimated light ($\lambda=350\text{--}440\text{ nm}$); and (iii) developing the exposed photoresist following conventional procedures. In this form of photolithography, there is no mask in the conventional sense; rather, a mold having appropriate surface topography to emboss the photoresist is the source of the pattern, and the embossed surface of the photoresist acts as its own optical element. We refer to this technique as “topographically directed photolithography” and abbreviate the phrase as TOP. We have examined the features derived from flood illumination of several different patterns on the surface of the resist: *curved features* and *square pyramidal* structures act as lenses, ray directors, and reflectors; *steps* in the resist generate small features due to abrupt shifts in phase of the illuminating radiation. We have also combined the embossed structures with conventional amplitude masks during the exposure to generate other patterns.

The elastomeric molds used to transfer the pattern to the photoresist surface were cast in polydimethylsiloxane (PDMS) against a master as described previously.¹ We used solvent-assisted embossing^{2,3} to emboss the surface of the photoresist (1805, 1813; Shipley) that was spun on primed silicon wafers. We exposed the patterned photoresist to flood UV light ($\lambda=300\text{--}460\text{ nm}$) in a standard mask aligner (Karl Suss MJB3 UV400): the lamp output was 10 mW/cm^2 , with exposure times tuned to accommodate fluctuations in this output. A dilute solution of Microposit 351 Concentrate (1:5 in $18\text{ M}\Omega$ water) developed samples in 1 min. A scanning electron microscope (LEO 982 Digital scanning electron microscope) imaged the features. Reactive ion etching (Plasma

Sciences, RIE-200) with a combined plasma of SF_6 (23 sccm) and O_2 (3 sccm) at 30 W for 2 min transferred the photoresist patterns into the silicon. We also transferred patterns into gold by lift-off,⁴ using 5 nm of Cr as an adhesion promoter and 50 nm of Au.

Figure 1 summarizes the process by which solvent-assisted embossing formed the topography on the surface of the resist. We applied a small amount ($<1\text{ mL}$) of solvent to an elastomeric mold made of PDMS having an appropriate pattern in bas relief on its surface, and then placed the mold on the surface of a layer of photoresist.² The solvent swelled the photoresist and formed a gel that conformed to the to-

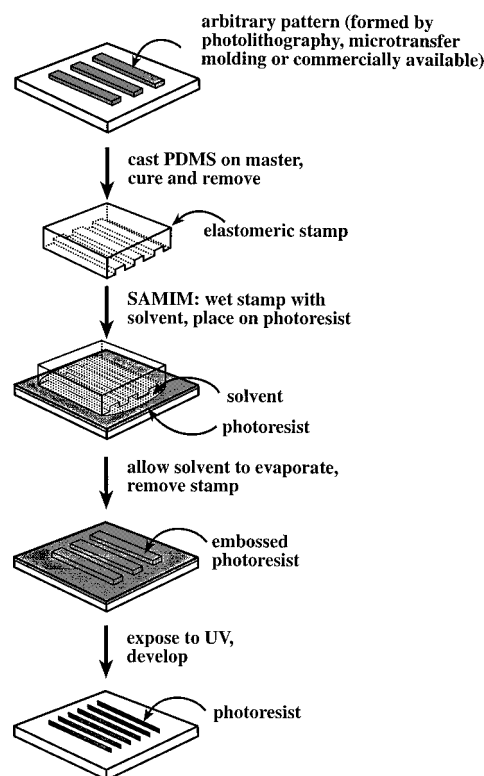


FIG. 1. Scheme illustrating the fabrication of embossed and exposed features in photoresist using a PDMS (polydimethylsiloxane) mold.

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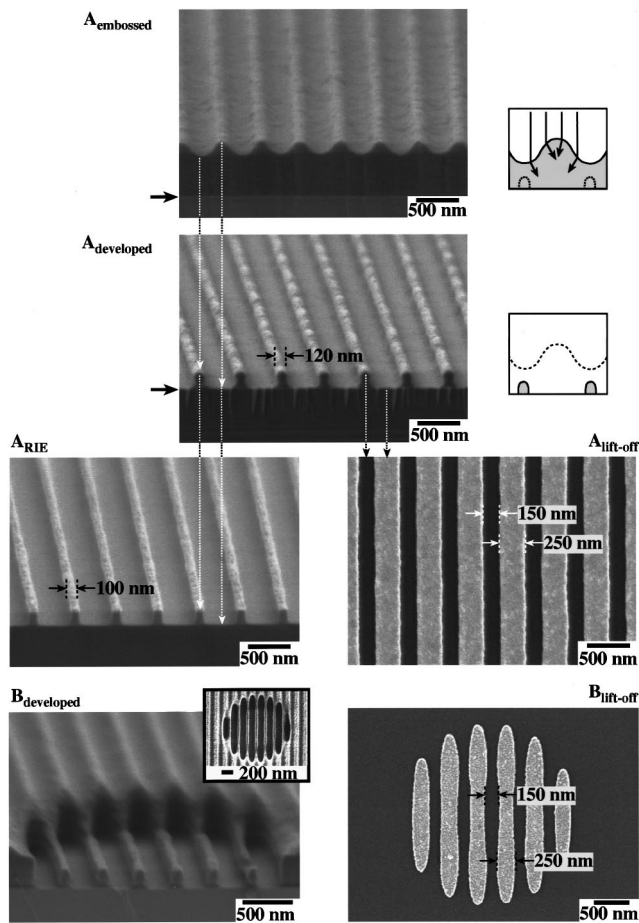


FIG. 2. Features produced by flood exposure ($\lambda=350\text{--}440\text{ nm}$) of an embossed 2400 lines/mm holographic grating. Dashed arrows show where the features originate. (A_{embossed}): grating embossed on a $0.48\text{-}\mu\text{m}$ thick layer of photoresist; ($A_{\text{developed}}$): exposed for 2.75 s and developed for 1 min. The black arrow at the left of the image indicates the photoresist/substrate interface and the drawings at the right show the exposure process schematically. The photoresist pattern was then transferred into silicon (A_{RIE}): by RIE and gold ($A_{\text{lift-off}}$): by lift-off. ($B_{\text{developed}}$): an embossed 2400 lines/mm holographic grating was covered with an amplitude mask of $3\text{-}\mu\text{m}$ circles separated by $11\text{ }\mu\text{m}$ and exposed for 1.85 s. ($B_{\text{lift-off}}$): the resulting pattern was transferred into gold by lift-off.

pography of the mold. After the solvent diffused into the resist and/or the PDMS ($\sim 3\text{ min}$), the mold was removed: the surface of the resist had topography complimentary to that of the mold. Solvent-assisted embossing is convenient to use in the laboratory for several reasons: (i) Since the elastomeric mold conforms to the surface of the resist, it can be used with nonplanar substrates. (ii) The solvent causes the polymeric resist to swell into the mold—essentially no applied pressure or liquid movement over long distances is needed and the technique, therefore, can be applied to large areas ($>50\text{ cm}^2$) of the substrate. (iii) Unlike conventional embossing, heat and pressure are not required. (iv) The elastomeric mold is easily removed from the surface without damage to the resist or the mold. Although conventional embossing⁵ can be used to emboss the surface at the softening point of the photoresist, this method only works over small areas and the mold may be damaged on removal. Another serious drawback of conventional embossing in the application described here is that the temperature required to soften Novolac-based photoresists results in decomposition of the photosensitive component (the diazonaphtho-

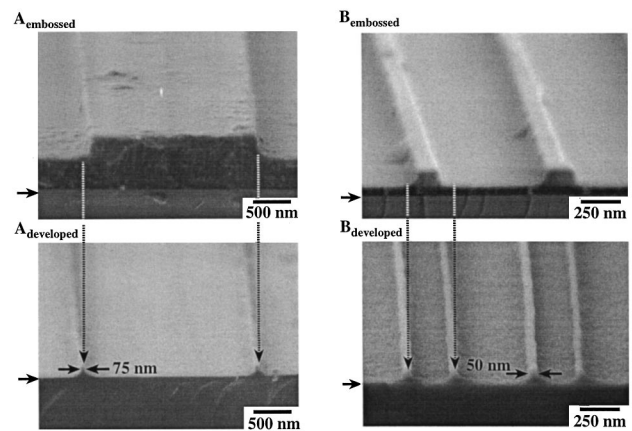


FIG. 3. Features generated using rectangular topographies. All samples were developed for 1 min. The black arrow at the left of the images indicates the photoresist/substrate interface. (A_{embossed}): lines with $2\text{-}\mu\text{m}$ width and $4\text{-}\mu\text{m}$ periodicity embossed on a $0.50\text{ }\mu\text{m}$ layer of photoresist. ($A_{\text{developed}}$): exposed (A_{embossed}) (3 s); width of features is $\sim 75\text{ nm}$. (B_{embossed}): lines (150-nm wide, with periodicity 800 nm) embossed on a $\sim 200\text{ nm}$ layer of photoresist. ($B_{\text{developed}}$): exposed (B_{embossed}) (0.85 s); features are $\sim 50\text{-nm}$ wide.

quinone).⁶ Exposure to UV light and development of these embossed patterns does not yield features.

Flood illumination of holographic gratings embossed on the photoresist surface [Fig. 2 (A_{embossed})], followed by development, gave arrays of lines [Fig. 2 ($A_{\text{developed}}$)]. We believe that the curved features of the embossed grating act as cylindrical lenses and direct the light into the resist layer (Fig. 2). To establish the correspondence between the embossed features and those generated by exposure and development, we exposed an embossed sample through a conventional chrome amplitude mask [Fig. 2 ($B_{\text{developed}}$)]: the structure remaining after development corresponds to the concave regions of the embossed surface. Transfer of photoresist patterns into silicon and metal layers was accomplished with reactive ion etching (RIE) and lift-off. RIE generated 100-nm features [Fig. 2 (A_{RIE}) in silicon. Lift-off generated 250-nm gold lines, separated by 150 nm [Fig. 2 ($A_{\text{lift-off}}$); Fig. 2 ($B_{\text{lift-off}}$)].

The steps at the edges of the embossed rectangular gratings [Fig. 3 (A_{embossed}); Fig. 3 (B_{embossed})] generated patterns that are similar to those generated by near-field phase-shift lithography.^{7,8} Lines fabricated using rectangular gratings with an embossed periodicity of $4\text{ }\mu\text{m}$ are $\sim 100\text{-nm}$ wide [Fig. 3 ($A_{\text{developed}}$)], and with an embossed periodicity of $\sim 800\text{ nm}$, the features are $\sim 50\text{-nm}$ wide [Fig. 3 ($B_{\text{developed}}$)].⁹ In both cases, the embossed gratings have sloping rather than vertical photoresist sidewalls, and the lines that result from exposure, for reasons we have not clarified in detail, are spaced farther apart than is expected from the edge periodicity. A similar effect occurs with other line patterns: embossed patterns of diamonds [Fig. 4 (A_{embossed})] and posts $1.5\text{ }\mu\text{m}$ in diameter [Fig. 4 (B_{embossed})] also give $\sim 100\text{-nm}$ lines that appear outside the perimeter of the embossed features [Fig. 4 ($A_{\text{developed}}$); Fig. 4 ($B_{\text{developed}}$)]. Both patterns were transferred into silicon by RIE [Fig. 4 (A_{RIE}); Fig. 4 (B_{RIE})] and gold by lift-off [Fig. 4 ($A_{\text{lift-off}}$); Fig. 4 ($B_{\text{lift-off}}$)]. We are currently defining the interactions between the light and resist topography and composition that give rise

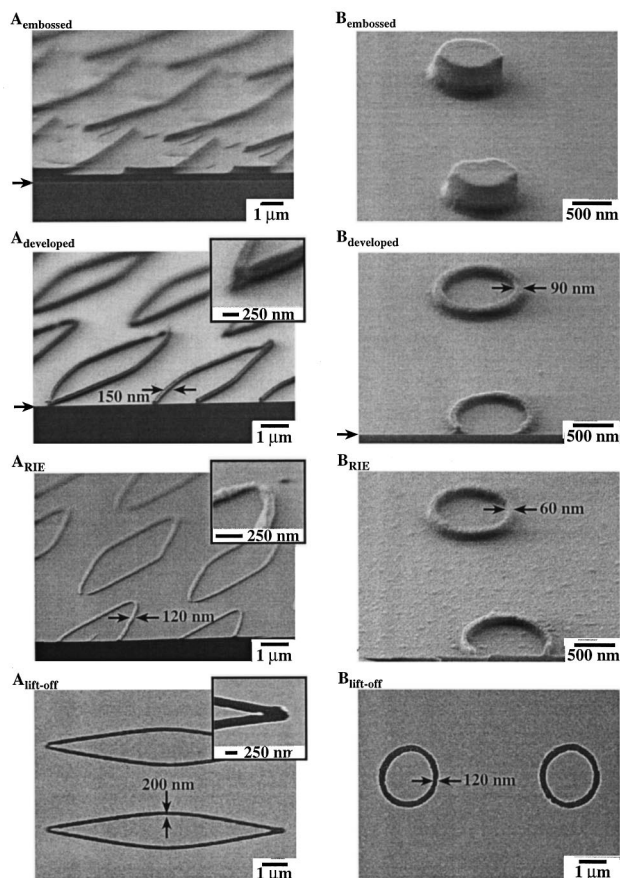


FIG. 4. Curved features generated using rectangular topographies. All samples were developed for 1 min. The black arrow at the left of the images indicates the photoresist/substrate interface. (A_{embossed}): diamond pattern, 300-nm deep, embossed on ~ 500 -nm thick layer of photoresist. ($A_{\text{developed}}$): exposed (A_{embossed}) (2.0 s); features are ~ 150 -nm wide. ($A_{\text{developed}}$) was then transferred into silicon (A_{RIE}) by RIE and gold ($A_{\text{lift-off}}$) by lift-off. (B_{embossed}): circles with a diameter of $1.5 \mu\text{m}$ and a depth of 300 nm embossed on ~ 500 -nm layer of photoresist. ($B_{\text{developed}}$): exposed (B_{embossed}) (1.75 s); features are ~ 80 nm wide. ($B_{\text{developed}}$) was then transferred into silicon (B_{RIE}) by RIE and gold ($B_{\text{lift-off}}$) by lift-off.

to this displacement of features after exposure and development.

Embossed pyramids in photoresist [Fig. 5 (A_{embossed})] can be generated by using a mold that bears the pattern of anisotropically etched square pits in $\langle 100 \rangle$ silicon. When exposed using flood illumination, the pattern of light in the resist is most intense at the edges and the apex of each pyramid due to a combination of effects: the reflectivity of the sloped surface adds to the near-field and ray-directing effects. Development yields a pattern of cross-shaped trenches in the photoresist [Fig. 5 ($A_{\text{developed}}$)]. Evaporation of gold followed by lift-off gave gold crosses on the silicon [Fig. 5 ($A_{\text{lift-off}}$)].

This letter describes a form of photolithography in which features embossed on the surface of the photoresist act as optical elements: they focus/disperse and phase shift incident light. We believe that this technique provides a route, in a parallel process, to certain planar microstructures that cannot be easily produced using conventional photolithographic techniques, such as an infrared dipole array.¹⁰ Because this procedure does not require the use of an expensive light source or a cleanroom, and because it can be applied to large

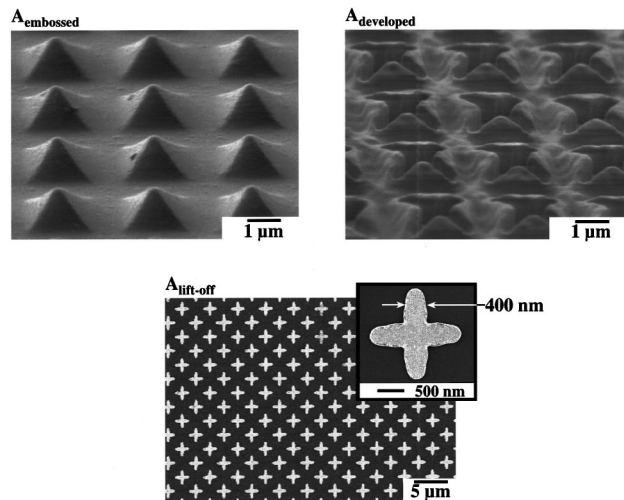


FIG. 5. Features generated using a mold bearing a square pyramidal pattern: (A_{embossed}): embossed on a $1.3\text{-}\mu\text{m}$ layer of photoresist. ($A_{\text{developed}}$): oblique view of pattern exposed 3.0 s and developed 1 min. ($A_{\text{lift-off}}$): features produced by lift-off.

areas, it also offers the advantage of low cost. It is a near-field optical method, and we expect the sizes of the features to become smaller as the index of the photoresist increases and the wavelength of the light used for exposure decreases. The pitch of the features produced will be limited by interference. The importance of the potential limitations—distortion of the patterns on transfer, feature sizes, generation of complex patterns with small spacings—remain to be defined.

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¹J. A. Rogers, K. E. Paul, R. J. Jackman, and G. M. Whitesides, *Appl. Phys. Lett.* **70**, 2658 (1997).

²E. Kim, Y. Xia, X.-M. Zhao, and G. M. Whitesides, *Adv. Mater.* **9**, 615 (1997).

³Y. Xia and G. M. Whitesides, *Angew. Chem. Int. Ed. Engl.* **37**, 550 (1998).

⁴W. M. Moreau, *Semiconductor Lithography* (Plenum, New York, 1998), pp. 607–617.

⁵S. Y. Chou, P. R. Krauss, and P. J. Renstrom, *Science* **272**, 85 (1996).

⁶M. Hanabata, *Adv. Mater. Opt. Electron.* **4**, 75 (1994).

⁷J. A. Rogers, K. E. Paul, R. J. Jackman, and G. M. Whitesides, *J. Vac. Sci. Technol. B* **16**, 59 (1998).

⁸J. Aizenberg, J. A. Rogers, K. E. Paul, and G. M. Whitesides, *Appl. Phys. Lett.* **71**, 3773 (1997).

⁹The mold for the latter sample was prepared by casting PDMS against a master prepared by embossing a 1200 lines/mm holographic grating on a layer of photoresist, exposing it to UV light and reactive ion etching.

¹⁰D. 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).