

Improved Pattern Transfer in Soft Lithography Using Composite Stamps

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Composite stamps composed of two layers—a stiff layer supported by a flexible layer—extend the capabilities of soft lithography to the generation of 50–100-nm features. The preparation of these stamps was adapted from a procedure originally developed by Schmid et al. (*Macromolecules* 2000, 33, 3042) for microcontact printing. This paper demonstrates how pattern transfer using other soft lithographic techniques—micromolding in capillaries, microtransfer molding, and phase-shifting lithography—can be improved using two-layer stamps relative to stamps made of Sylgard 184 poly(dimethylsiloxane).

Introduction

Soft lithographic techniques are currently most useful for patterning features and for fabricating structures on the size scale of 500 nm and larger.¹ The extension of these methods to produce structures in the sub-100-nm range is limited in part by the low elastic modulus of the form of poly(dimethylsiloxane) most commonly used in fabricating stamps (Sylgard 184 PDMS). The high compressibility (2.0 N/mm²) of 184 PDMS causes shallow relief features of a stamp to deform, buckle, or collapse;^{2,3} in addition, these relief structures tend to deform upon release from the master because of surface tension.⁴ The mechanical characteristics of the elastomeric pattern transfer element are critical to the replication of features and generation of patterns with high fidelity. This paper demonstrates how composite stamps composed of two layers—a stiff layer supported by a flexible layer—can generate free-standing features down to 50 nm.

Schmid et al.⁵ at IBM-Zurich examined alternative siloxane polymers having mechanical properties different from those of 184 PDMS to improve the performance of microcontact printing (μ CP) to improve the performance of microcontact printing (μ CP) on metallic surfaces; they achieved submicron accuracy over large areas (5 × 5 cm²). They formulated a polymeric composite based on vinyl and hydrosilane end-linked polymers—herein referred to as *h*-PDMS (“hard” PDMS)—that could replicate high-density patterns at the 100-nm scale. Although the high modulus (~9 N/mm²) of *h*-PDMS worked well for replication, handling of these stamps was difficult for three reasons: (i) cutting and releasing them from the master caused cracking across the face of the stamp and resulted in the formation of debris along the edges of the stamp; (ii) the stamp would spontaneously break off the master upon cooling in some circumstances

because of the high coefficient of thermal expansion (450 $\mu\text{m m}^{-1} \text{ }^\circ\text{C}^{-1}$ for *h*-PDMS vs 260 $\mu\text{m m}^{-1} \text{ }^\circ\text{C}^{-1}$ for 184 PDMS); and (iii) manual pressure on the stamp was required to achieve conformal contact with a substrate. This pressure created long-range, nonuniform distortions over the large areas of contact that were examined.

To improve the utility of *h*-PDMS for use in μ CP, Schmid et al.⁵ tested several composite designs that used a rigid support (glass or quartz) for a thin *h*-PDMS layer. These designs included multilayer stamps (a thin layer of *h*-PDMS on a slab of 184 PDMS attached to a quartz plate) and two-layer stamps (thin layers of *h*-PDMS or 184 PDMS molded to glass foils).^{5,6} The stamp that conformed best to uneven substrate topology with minimal distortion over large areas consisted of a thin (30 μm) layer of *h*-PDMS supported on a flexible glass foil (100 μm thick).

We have modified this strategy to fabricate a composite, two-layer stamp that uses a thick (~3 mm) slab of 184 PDMS to support a thin (30–40 μm), stiff layer of *h*-PDMS to extend other soft lithographic techniques—phase-shifting lithography, microtransfer molding, and micromolding in capillaries^{7–9}—to the sub-100-nm regime. These two-layer stamps are easy to handle,¹⁰ and they release without difficulty from the master during their preparation. The structures generated using these stamps are significantly improved relative to those generated with 184 PDMS: they are symmetrical and have narrow line widths (smallest features ~ 50 nm). This modification is most useful when fabricating nanostructures but will be useful for certain larger features as well.

Results and Discussion

Figure 1 summarizes the procedure for preparing a composite stamp from *h*-PDMS and 184 PDMS (see Experimental Section). This composite stamp combines

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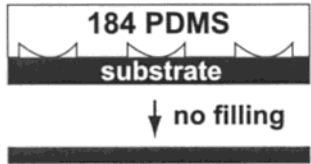
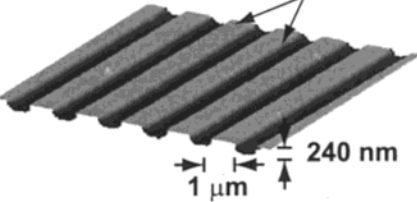


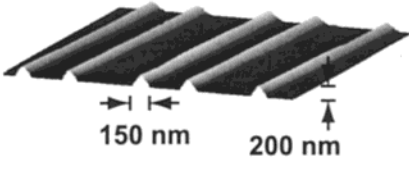
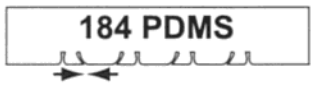

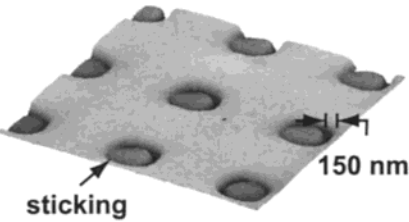
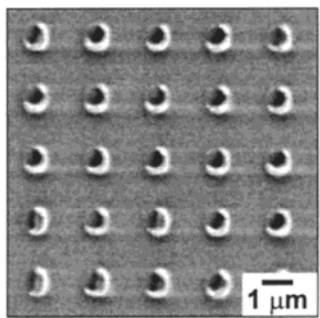
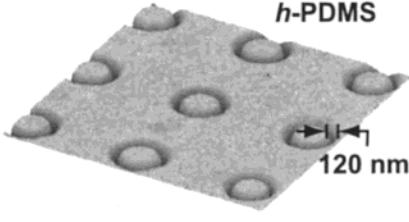
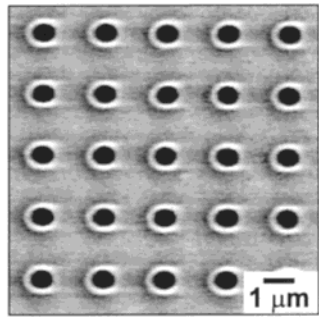


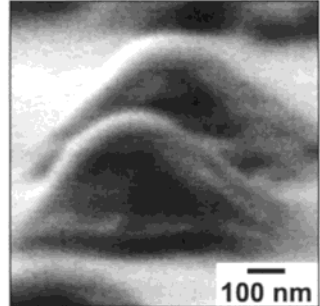
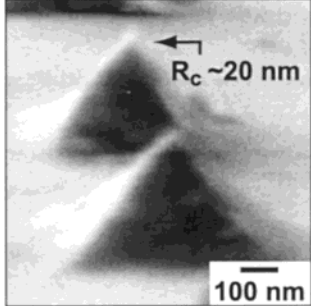
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(10) Stamps made of thin layers of *h*-PDMS supported by 184 PDMS exhibit cracking along the surface if they are bent at large angles (>60°).

Table 1. Typical Deformations that Occur in Elastomeric Stamps and a Comparison of Pattern Transfer in Different Soft Lithographic Techniques from Stamps of 184 PDMS with Stamps of *h*-184 PDMS

	<i>Example application</i>	Sylgard 184 PDMS	<i>h</i> -184 PDMS
Roof collapse	<p><i>Micromolding in capillaries</i></p> 	<p>no pattern transfer due to roof collapse</p>	<p>Lines of polyurethane</p> 
	<p><i>Replication of recessed features</i></p> 	<p>collapse</p> 	<p><i>h</i>-PDMS</p> 
Lateral collapse	<p><i>Replication of raised features</i></p>  <p><i>Molding of sub-micron features</i></p> 	<p>sticking</p>  	<p><i>h</i>-PDMS</p>  
	<p><i>Replication and molding of sharp features</i></p>  <p>photoresist (Shipley 1805)</p> 		

the advantages of both a more rigid layer (to achieve high-resolution pattern transfer) and a more flexible support (to enable conformal contact with a surface without external pressure).

Typical Deformations in Elastomeric Stamps. Table 1 shows representative deformations that occur in elastomeric stamps molded against masters having critical dimensions as small as 100 nm. Typical deformations due

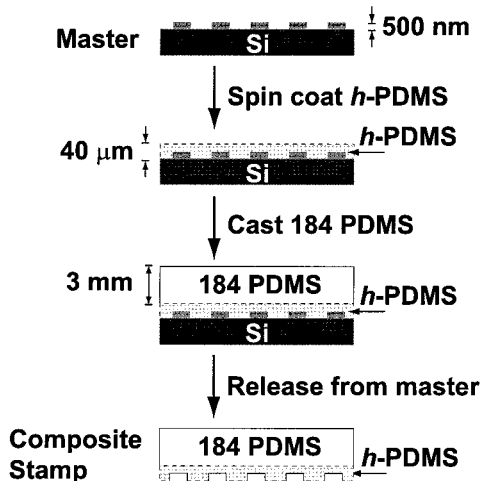


Figure 1. Procedure for fabricating a two-layer composite stamp. *h*-PDMS is spin-coated onto a master and cured at 60 °C for 30 min (after this process, the layer is still tacky). PDMS 184 prepolymer is poured on top of this *h*-PDMS layer and cured at 60 °C for at least 1 h. The composite stamp is released from the master by (i) cutting around the patterned areas with a razor blade and (ii) removing the stamp from the surface using tweezers.

to the low modulus of 184 PDMS include: (i) roof collapse, (ii) lateral collapse, and (iii) rounding by surface tension. We compared the fidelity of the patterns transferred by different soft lithographic techniques from stamps of 184 PDMS with stamps of *h*-184 PDMS.

Roof Collapse. Stamps having wide and shallow relief features in contact with surfaces tend to collapse at aspect ratios (width-to-height) of less than 0.3,² because of the low elastic modulus of the 184 PDMS elastomer. In periodic patterns (e.g., parallel lines), this deformation is evident to the eye by the loss of the diffraction pattern of a stamp when placed in conformal contact with a flat surface. Stamps made of 184 PDMS patterned with 1- μ m lines spaced by 1 μ m lose their diffraction pattern when the features in bas-relief are less than 300–350 nm tall. We found that the composite PDMS stamps patterned with 1- μ m lines spaced by 1 μ m are able to withstand collapse down to 120 nm. These channels can be filled by capillarity with a liquid pre-polymer and cured under UV light.⁸ An AFM image of the negative replica of the channels in polymer is shown in Table 1.

Lateral Collapse. We also explored how well *h*-184 PDMS can replicate and mold closely spaced, narrow structures compared to 184 PDMS. We observed two types of lateral collapse of features patterned in 184 PDMS that were not observed with *h*-184 PDMS. Replication of masters having 150-nm-wide and 250-nm-deep trenches spaced by 1 μ m in PDMS produced lines in surface relief. An AFM image of 184 PDMS showed that portions of adjacent lines collapsed together; these lines remained stable and well-separated in the composite PDMS (Table 1). The mechanical stability of the composite PDMS also enabled accurate replication of masters having in surface relief 900-nm diameter rings with 120-nm widths. The 184 PDMS, however, is unable to replicate these closely spaced, submicron structures, because their low moduli allow the inner and outer portions of the rings to stick together. The SEM images of rings that were molded in polyurethane from *h*-184 PDMS molds showed that the replica-molded structures reproduced the circular shape of the 120-nm-wide rings of the master, whereas the sticking of the sidewalls in the 184 PDMS mold inhibited accurate reproduction of the master (Table 1).

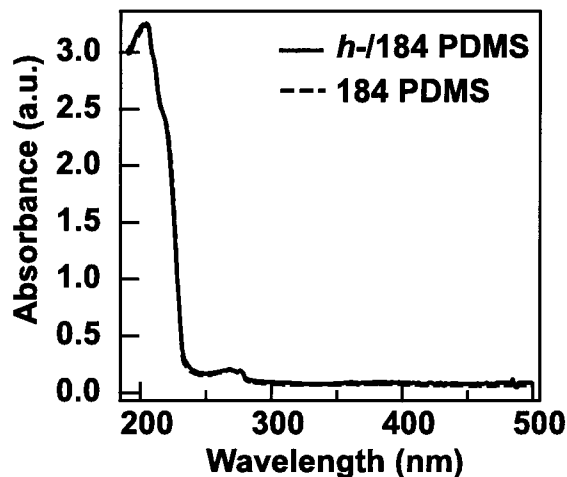


Figure 2. UV-vis absorbance of the composite *h*-184 stamp compared with that of a 184 stamp. The two are indistinguishable in this range of frequencies.

Surface Tension. Another type of deformation that can occur in elastomeric stamps is the rounding of sharp corners due to surface tension after the stamp is released from the master. Calculations suggest that the lower limit for the radius of curvature (R_c) of corners in an elastomer such as 184 PDMS is on the order of 50 nm.⁴ We prepared masters of square pyramids by anisotropic etching of Si substrates¹¹ patterned by photolithography and obtained the inverted pattern by electroplating of gold and nickel and subsequent removal of the Si substrate. Using solvent-assisted embossing,¹² we wet an elastomeric mold patterned with recessed square pyramids with acetone, placed it on a \sim 400-nm layer of photoresist (Shipley 1805), and allowed the solvent to dissipate by diffusion into the resist and the stamp. After we removed the mold, the surface of the resist was patterned with a topography complementary to that of the mold. SEM images of embossed surfaces showed that the square pyramids that were transferred from the composite PDMS mold exhibited sharp edges and a well-defined apex (with $R_c \approx 20$ nm), whereas the pyramids from the 184 PDMS mold showed smooth edges and a rounded apex.

Phase-Shifting Photolithography Using Composite Masks. The mechanical stability of composite stamps enabled replication and molding of structures down to 100 nm. We explored whether this increased stiffness would facilitate generation of narrow line widths and smooth edges in near-field photolithography.^{9,13} We measured the absorption spectrum of the composite stamp to verify that it remains transparent to short-wavelength ultraviolet light, as required for some soft lithographic techniques such as phase-shifting lithography (Figure 2). The spectra of a composite *h*-184 PDMS stamp and a 184-only PDMS stamp (same path length, 3 mm) are indistinguishable.

We exposed thin (\sim 400 nm) layers of photoresist on Si wafers to UV light (365–450 nm) through composite elastomeric phase-shifting masks with features in bas-relief in conformal contact with the resist. After development, lines of photoresist were produced at the edges of the relief features of the mask (Figure 3A). A phase-shifting mask made of only 184 PDMS generated lines that were

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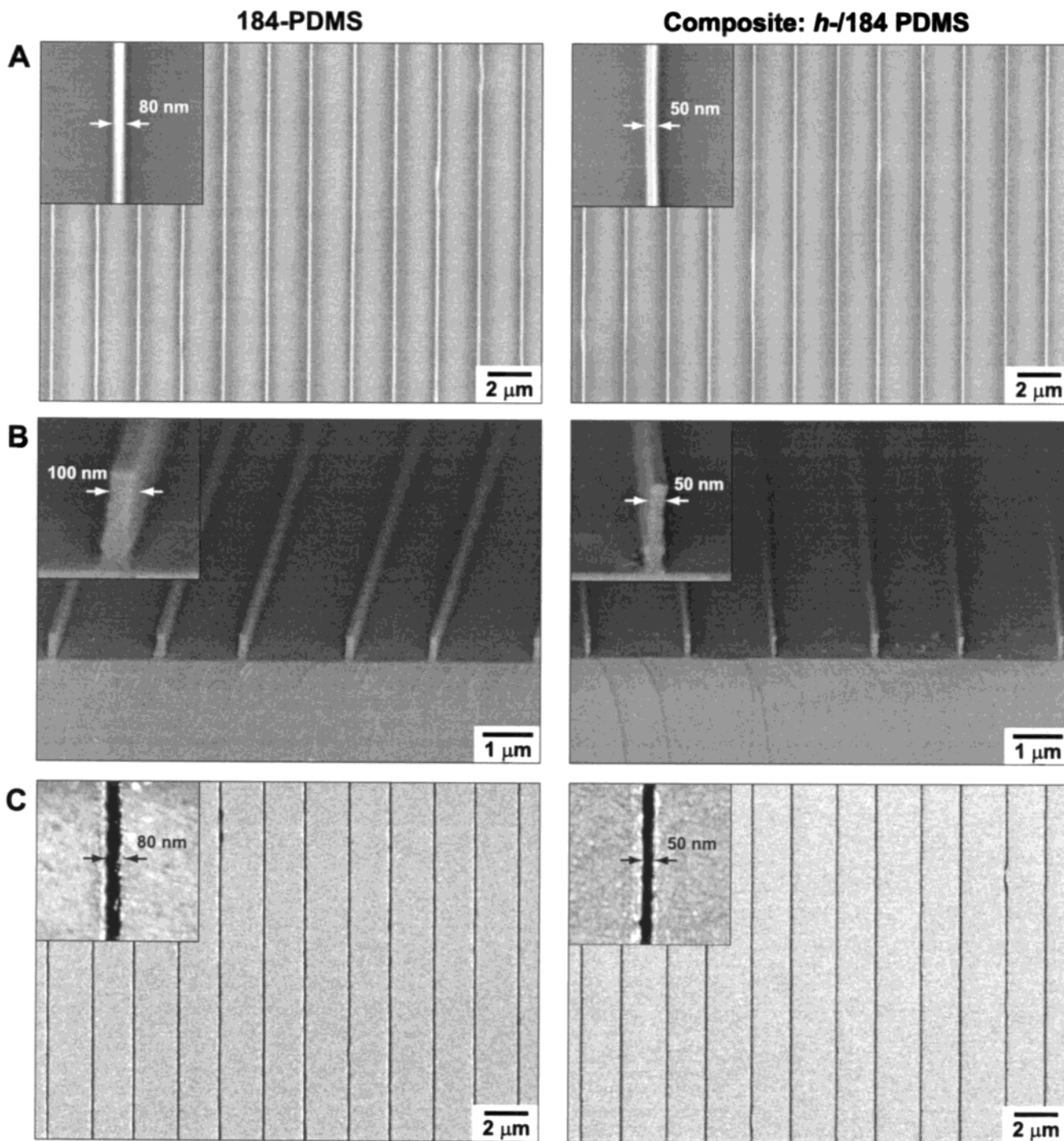


Figure 3. Scanning electron micrographs (SEMs) of structures produced using phase-shifting photolithography with elastomeric masks patterned with $2\text{-}\mu\text{m}$ lines spaced by $2\text{-}\mu\text{m}$ and having bas-relief features $\sim 400\text{ nm}$ high. The insets show magnified images. (A) Parallel lines of photoresist produced at the edges of a mask. Left frame: Lines produced from a 184 PDMS mask are $80\text{--}100\text{ nm}$ in width, and rough along the edges. Right frame: Lines produced from the composite mask are uniform and 50 nm in width. Light regions are photoresist (Shipley 1805), and dark regions are Si/SiO₂. (B) Cross-sectional images of the lines in part A. (C) Pattern in photoresist transferred into Au using lift-off. Left frame: from left frame in A. Right frame: from right frame in A. Light regions are Au, and dark regions are Si/SiO₂.

$80\text{--}100\text{ nm}$ in width and $\sim 350\text{ nm}$ in height. The minimum dimension of lines produced from the composite mask is 50 nm , and they have a similar height (Figure 3B). We transferred these patterns into gold by lift-off, using electron-beam evaporation to deposit 2 nm of Ti as an adhesion promoter, followed by 25 nm of gold (Figure 3C).

One application for patterned lines in metal is the construction of arrays of palladium nanowires as wire-grid polarizers. We fabricated these wires by exposing thin ($\sim 350\text{ nm}$) layers of photoresist on glass substrates

coated with palladium (30 nm) through a composite mask to UV light. After etching the palladium¹⁴ that was not protected by the patterned photoresist, we generated nanowires of $\sim 90\text{ nm}$ in width (Figure 4A). Because these line widths are smaller than the wavelength of the incident IR light (800 nm), they attenuate light polarized parallel to the wires more strongly than light polarized perpen-

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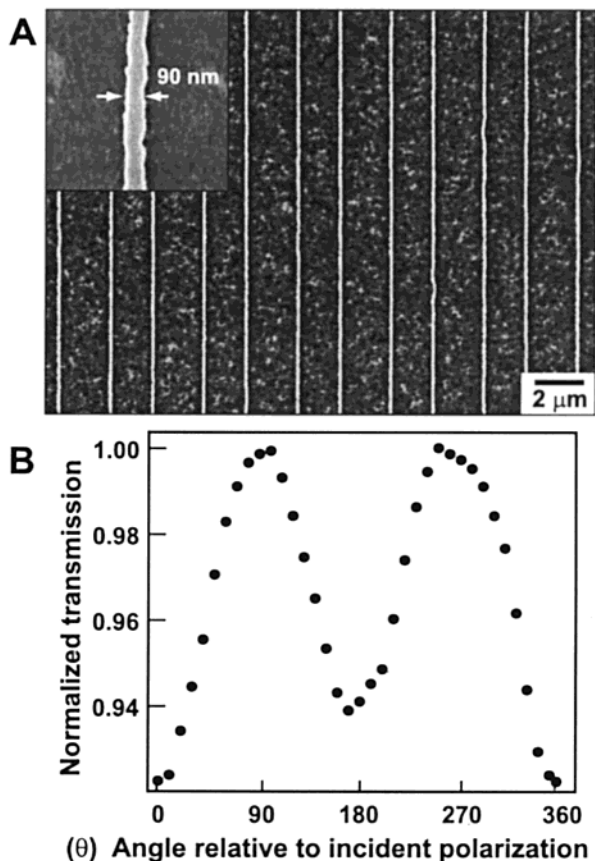


Figure 4. (A) SEM image of arrays of palladium nanowires (~ 90 nm) on glass formed using phase-shifting photolithography with a composite mask. (B) Measured intensity of infrared light (800 nm) transmitted by the polarizer as a function of angle between the nanowires and the polarization of the incident light. Light regions are Au, and dark regions are glass.

dicular to the wires.¹⁵ These 90-nm-wide palladium wires supported on a glass substrate produced $\sim 10\%$ polarization contrast between orthogonal directions (Figure 4B). This contrast could be improved by decreasing the spacing between the wires.

We investigated the symmetry and edge roughness of structures produced in photoresist using composite and 184-only elastomeric phase-shifting masks. In experiments similar to those with lines, we generated "dots" in photoresist by two perpendicular exposures through masks using UV (365–436 nm) light (Figure 5A). The dots formed by a 184 PDMS mask are larger (175 nm, smallest dimension) than the ones produced by a composite mask. These orthogonal exposures reveal how the properties (e.g., stiffness) of the elastomeric mask affect the generated features. The dots produced from the composite mask are circular, whereas the dots produced from the 184-only mask are unsymmetrical.

In addition, we generated rings in photoresist by exposing photoresist through 184 PDMS and composite PDMS phase masks having $1\text{-}\mu\text{m}$ -diameter circular posts on their faces (Figure 5B). The rings produced from the 184 PDMS mask are slightly oblong, whereas the rings generated from the composite mask are circular and symmetrical. We replicated these rings into slabs of *h*-/184 PDMS to observe the roughness of the edges of the rings in photoresist (Figure 5C). The contrast between

the smooth edges of the pattern produced using the composite mask and the jagged edges observed using the 184 phase mask suggest that the light does not undergo a sharp π -phase shift at the PDMS/air interface in the 184 PDMS mask. Because of the buckling of the 184 PDMS bas-relief features in contact with the surface, the photoresist at the edges of the features in the mask is not fully exposed and hence exhibits a residual tail. This tail can also be seen in the inset of the left panel of Figure 5A.

These examples suggest that the use of a stiffer material (*h*-PDMS) in contact with the photoresist layer reduces sidewall buckling and unwanted sagging from the relief features.^{2,3,13} This increased mechanical stability improves the edge resolution, symmetry, and line width of the features generated by phase-shifting photolithography.

Conclusions

Composite polymeric stamps that use a thick, flexible 184 PDMS slab to support a thin, stiff *h*-PDMS underlayer extend the capabilities of soft lithography to sub-100-nm features. This technique, originally developed by Schmid et al.⁵ for microcontact printing, provides a useful increase in capabilities throughout soft lithography. We are able to generate ~ 50 -nm features (in photoresist and gold) by phase-shifting photolithography, to replicate submicron structures having features spaced by 100 nm in *h*-/184 PDMS and to mold ~ 100 -nm features in polyurethane by micro-transfer molding. Addition of a stiff layer to the elastomeric transfer element makes it possible to extend soft lithography to structures with <100 -nm resolution in practical processes.

Key advantages to using this composite stamp in soft lithography include (i) more accurate replication of the original master by molding and printing, (ii) 100-nm or better resolution because of minimal sagging of bas-relief structures, (iii) better masks and molds for phase-shifting photolithography, and (iv) achievement of smaller features (50 nm) with better edge resolution. Disadvantages of using this two-layer stamp include (i) preparation of the *h*-PDMS layer, which requires three steps rather than one for 184 PDMS, (ii) difficulty in cleaning the surface of the stamp because the *h*-PDMS layer cracks easily, (iii) a higher thermal instability because of higher thermal expansion coefficient of *h*-PDMS, and (iv) occasional delamination of the structures made in photoresist from the surface of the master when the molded stamp is removed from it. Separating the stamp and a master made from photoresist can be difficult with the hard PDMS.

In summary, this paper demonstrates that using composite PDMS stamps comprising a stiff layer embossed with the pattern and a softer backing layer can extend the resolution of soft lithography to the sub-100-nm regime. These composite stamps are useful for generating submicron features for functions in optics and microelectronics that do not require multilayer registration, such as filters, sensors, and electrode arrays.

Experimental Section

Fabrication of the Two-Layer Stamp. To prepare *h*-PDMS, we mixed and degassed for 1–2 min 3.4 g of a vinyl PDMS prepolymer (VDT-731, Gelest Corp., www.gelest.com), 18 μL of a Pt catalyst (platinum divinyltetramethyldisiloxane, SIP6831.1, Gelest Corp.), and one drop of a modulator (2,4,6,8-tetramethyl-

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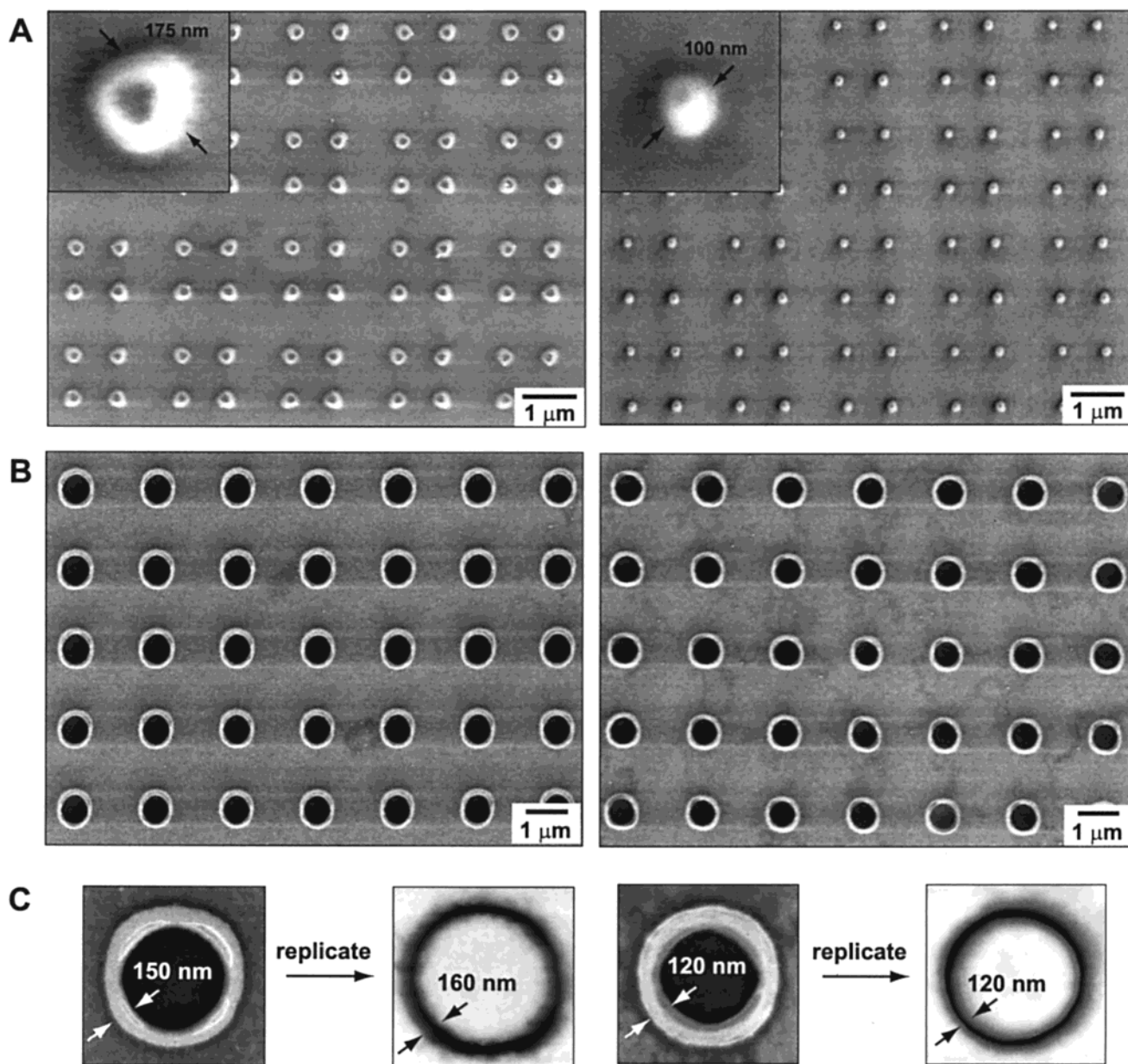


Figure 5. SEM images of structures produced using phase-shifting photolithography with elastomeric masks. (A) Dots of photoresist (ShIPLEY 1805) formed by exposing through masks patterned with parallel lines ($1\text{-}\mu\text{m}$ spaced by $1\text{-}\mu\text{m}$), rotating the mask 90° , and exposing again. Left panel: Dots produced from a 184 PDMS mask are round and $\sim 100\text{ nm}$ in diameter. Right panel: Dots produced from the composite mask are asymmetric and $\sim 175\text{ nm}$ in diameter. (B) Rings of photoresist (ShIPLEY 1805) formed by exposing through a mask having relief structures of $1\text{-}\mu\text{m}$ round posts. Left panel: Rings produced from a 184 PDMS mask are oblong with line widths of $\sim 150\text{ nm}$. Right panel: Rings produced from the composite mask are round and have line widths of $\sim 120\text{ nm}$. (C) SEM images of a magnified view of the rings of photoresist in B, and AFM images of the rings replicated in slabs of *h*-/184 PDMS. Left panel: Ring in photoresist generated from a 184 PDMS phase mask. The replicated structure exhibits jagged and uneven edges. Right panel: Ring in photoresist generated from a composite phase mask. The replicated structure exhibits smooth edges.

tetravinylcyclotetrasiloxane, 87927, Sigma-Aldrich, www.sigmaaldrich.com). We then gently stirred 1 g of a hydrosilane prepolymer (HMS-301, Gelest Corp.) into this mixture. Immediately (within 3 min), we spin-coated a thin layer ($30\text{--}40\text{ }\mu\text{m}$) of *h*-PDMS onto a Si master (1000 rpm, 40 s) and cured it for 30 min at 60°C (the *h*-PDMS is still slightly tacky). We then poured a liquid pre-polymer layer ($\sim 3\text{ mm}$) of Sylgard 184 PDMS (Dow Corning, www.dowcorning.com) onto the *h*-PDMS layer and cured it at least an hour at 60°C . We released the composite stamp from the surface by cutting and carefully peeling the stamp from the surface while still warm.

Soft Lithographic Techniques. (i) *Molding Experiments.* Polyurethane (NOA 61, Norland Optical Adhesives, www.norlandprod.com) molded to PDMS stamps was cured by exposure to a broadband UV source (100 W) for 10–20 min. For molding in capillaries, a drop of polymer was placed at one of the edges

of the stamp, and capillarity pulled the polymer into the channels. This assembly was cured in UV light for 20 min, and then the stamp was removed.

(ii) *Solvent-Assisted Embossing.* Elastomeric molds with recessed features were wet with acetone ($<1\text{ mL}$) and placed in conformal contact with a layer of photoresist (ShIPLEY 1805, ShIPLEY Corp., www.microchem.com) spun at 4000 rpm for 40 s. The mold was removed after $\sim 2\text{ min}$.

(iii) *Phase-Shifting Lithography.* Elastomeric masks with patterned bas-relief features ($400\text{--}450\text{ nm}$) were placed in conformal contact with a layer of positive photoresist (ShIPLEY 1805) at 5500 for 40 s. This assembly was exposed to broadband UV light ($365\text{--}436\text{ nm}$, Karl Suss MJB3 UV400) for 4–6 s. A dilute solution of Microposit 351 (1:5 in $18\text{ }\Omega\text{M}$ water) developed samples in 1 min.

Etching of Palladium Films. Palladium areas not protected by the patterned photoresist were removed using an FeCl_3 -based etchant (TFP, Transene, Inc., Danvers, MA) that had been diluted to a ratio of H_2O /etchant of 5:1. The etching time was between 40 and 60 s.

Image Characterization. SEM images were recorded using a LEO 982 Digital scanning electron microscope. AFM images were recorded in tapping mode using a Dimension 3100 AFM (Digital Instruments) with a Nanoscope IV controller.

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