Using an elastomeric phase mask for sub-100 nm photolithography in the optical near field

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(Received 30 January 1997; accepted for publication 21 March 1997)

Bringing an elastomeric phase mask into conformal contact with a layer of photoresist makes it possible to perform photolithography in the near field of the mask. This technique provides an especially simple method for forming features with sizes of 90–100 nm in photoresist: straight lines, curved lines, and posts, on both curved and planar surfaces. It combines experimental convenience, new optical characteristics, and applicability to nonplanar substrates into a new approach to fabrication. Nanowire polarizers for visible light illustrate one application for this technique. © *1997 American Institute of Physics.* [S0003-6951(97)03420-7]

This letter describes a remarkably convenient photolithographic method for forming features with sizes of 90–100 nm. Exposure of photoresist to light passing through an elastomeric phase mask in conformal contact with the resist allows photolithography to be carried out in the near optical field. Standard photolithographic methods employing rigid phase masks can produce features with similar sizes, but the fragile masks, complex imaging optics, and ultraviolet (248 nm) lasers that are required make this approach experimentally difficult.[1,2] With the method described here, patterns of photoresist with feature sizes as small as 90 nm can be formed rapidly ($\sim$1 s) over large areas with only an elastomeric phase mask and incoherent, polychromatic ultraviolet light.

Light passing through a transparent element with relief on its surface is diffracted in the far field; its intensity is modulated in the near field. If the depth of surface relief of a binary phase mask shifts the phase by an odd multiple of π, then the intensity in the near field of the mask is reduced to zero at every phase edge.[3,4] As the phase shift deviates from an odd multiple of π, the depth of modulation of the intensity decreases. The widths of the regions in which the intensity is reduced are on the order of one quarter of the wavelength of the light used for exposure, *evaluated in the medium into which the light propagates from the mask*;[5,6] the widths are insensitive to the magnitude of the phase shift.

The contrast generated by rigid phase masks has been used to expose photoresist by placing the resist either near the mask[7] or at the image plane of a system of imaging optics arranged with the mask at the object plane.[1,8] With an elastomeric phase mask, the photoresist can be brought directly into conformal contact with the mask. Using this configuration to expose photoresist circumvents limits in resolution determined by the numerical aperture of imaging optics, eliminates the need to control actively the distance between a rigid phase mask and the photoresist layer, and allows exposure over large areas.

Figure 1 summarizes a scheme for generating an elastomeric phase mask and using it for photolithography. A prepolymer of polydimethlysiloxane (PDMS) cast and cured against photolithographically patterned lines of photoresist on silicon forms an elastomeric phase mask that is transparent to visible and near-ultraviolet light.[9] The depth of the relief on the surface of this mask determines the modulation of the phase, and therefore the depth of modulation of the intensity in the near field. To maximize the modulation of the intensity, the depth of surface relief was adjusted to induce a phase shift of π for the average wavelength of light used for exposure.

The elastomeric binary phase mask fabricated using this procedure was allowed to come into conformal contact with the resist. Exposure of the resist through the mask produced

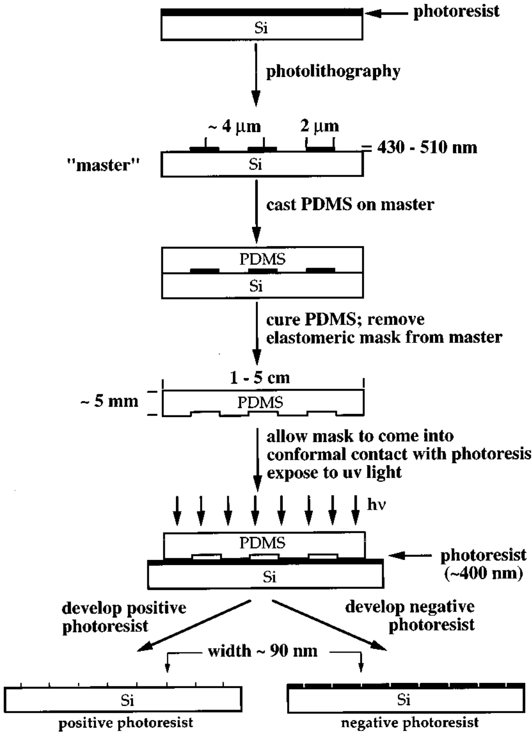

FIG. 1. Schematic illustration of the process used to conduct photolithography in the near field with a conformal elastomeric phase mask. The phase mask is formed by casting and curing a prepolymer of polydimethylsiloxane (PDMS) on a master relief structure, generated by photolithography in photoresist. The mask is placed in contact with a layer of photoresist ($\sim$400 nm thick) cast onto a support such as silicon or quartz; because the mask is elastomeric, the surfaces come into conformal contact. Exposure of the photoresist to ultraviolet light through the mask and subsequent development of the photoresist produces structures having features with widths 90–100 nm. Both negative and positive photoresists can be used.

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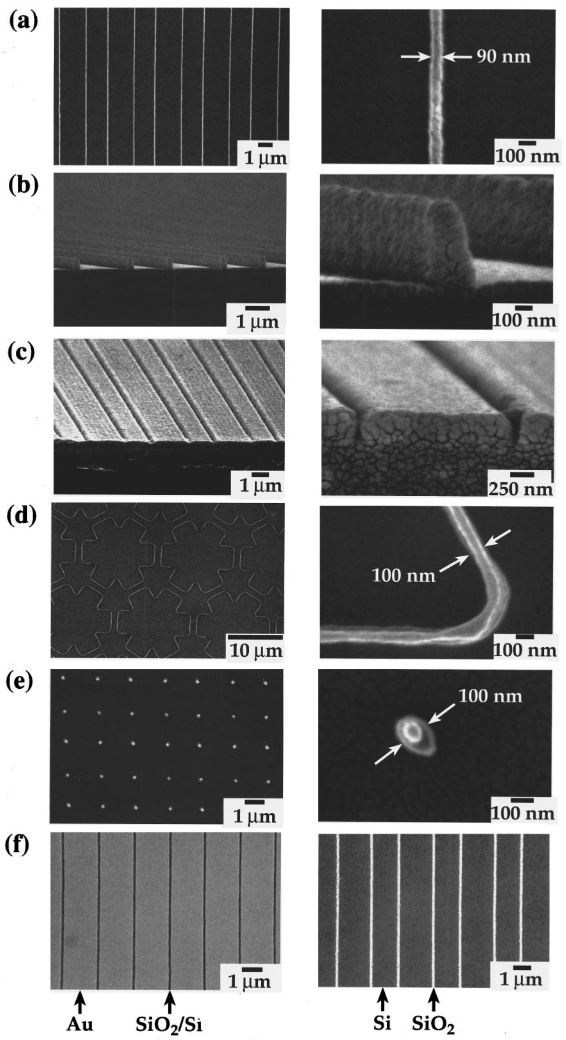

FIG. 2. Scanning electron micrographs (SEMs) of structures produced using near field photolithography with an elastomeric phase mask. Light regions correspond to photoresist and dark regions correspond to SiO_2/Si. In (a)–(e), the right frame is a magnified view of the left frame. (a) Parallel lines of positive photoresist produced by exposure through an elastomeric phase mask with surface relief consisting of parallel lines (2 μm spaced by 2 μm). (b) Cross-sectional images of the lines shown in part (a). (c) Cross-sectional images of trenches formed in negative photoresist by exposure through an elastomeric phase mask like the one used to generate the structures shown in parts (a) and (b). (d) Patterns of photoresist formed by exposure through an elastomeric phase mask with relief structure consisting of an array of connected triangles (5 μm diameter). (e) Posts in photoresist formed using an elastomeric phase mask with a relief structure consisting of parallel lines (2 μm) spaced by 2 μm. The posts were formed by exposing the photoresist through this mask, rotating the mask by 90°, and then exposing the resist again. (f) Left frame: Pattern in photoresist transferred to gold using lift-off. Right frame: Pattern in photoresist transferred to silicon dioxide using reactive ion etching.

lines in positive photoresist, and trenches in negative resist (Fig. 2). Arrays of straight and curved lines and posts with minimum dimensions of 90–100 nm with better than 10% reproducibility are possible. Figure 2(f) shows patterns that were transferred from photoresist into silicon dioxide by reactive ion etching,[10] and into gold using lift-off.[11]

This method can also generate ~100 nm features on curved substrates by placing a thin elastomeric phase mask in conformal contact with the surface of a *curved* object that is coated with photoresist, and exposing it to light that is

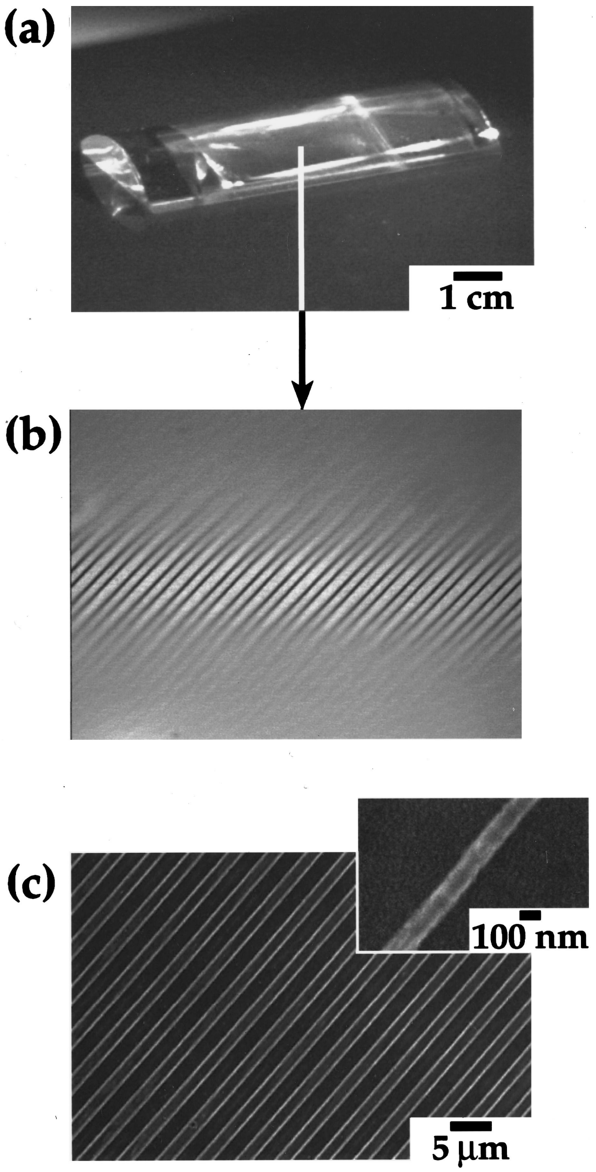

FIG. 3. (a) Photograph of a cylindrical lens with patterned photoresist on its surface. The resist was exposed in the near optical field of a thin elastomeric phase mask in conformal contact with its surface. (b) Optical micrograph generated by focusing a microscope on the part of the sloping surface of the lens that lies in the center of the field-of-view. This image highlights the limited depth of field associated with conventional photolithographic methods. (c) Scanning electron micrograph (SEM) of the same part of the lens illustrated in the optical micrograph in (b). The SEM shows uniform lines of photoresist with widths ~100 nm; this width is comparable to that achieved on planar substrates. In the scanning electron micrograph, dark regions correspond to glass and light regions correspond to photoresist. In the optical micrograph, the dark regions correspond to photoresist and the light regions correspond to glass.

close to normally incident. Figure 3 shows lines of photoresist formed on a cylindrical lens with a 15 cm radius of curvature.

An application that illustrates the usefulness of this photolithographic method is in the construction of arrays of gold nanowires for polarizers (Fig. 4). To form an array of nanowires, photoresist cast onto pieces of glass coated with gold was patterned using the procedure outlined in Fig. 1. Using KI to remove gold not protected by the patterned resist produced gold nanowires. Because the widths of these lines are

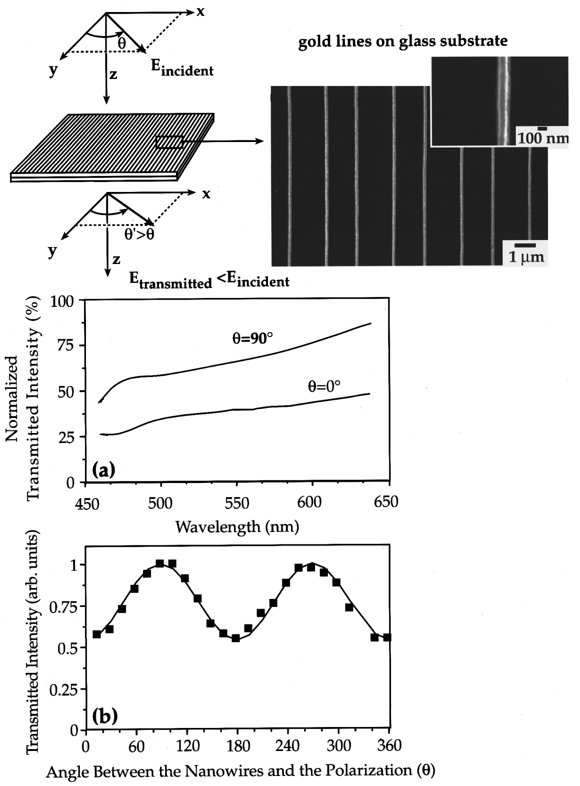

FIG. 4. Illustration of a polarizer that incorporates arrays of gold nanowires (~100 nm) formed using near field photolithography with an elastomeric phase mask. (a) Measured transmittance of the polarizer as a function of wavelength for light polarized perpendicular and parallel to the nanowires. The transmittance was measured relative to bare glass substrates. (b) Measured (symbols) and calculated (lines) intensity of red light (633 nm) transmitted by the polarizer as a function of angle between the nanowires and the polarization vector.

significantly smaller than the wavelength of visible radiation, they attenuate light polarized along the wires more strongly than light polarized perpendicular to them.[12,13] Figure 4 shows that a stack of two polarizers consisting of ~100 nm gold wires separated by 2 μm can produce a 2:1 contrast ratio for visible light. Addition of more polarizers to this stack increases the contrast; the contrast can also be improved by decreasing the separation between the wires.

Performing photolithography with an elastomeric phase mask in conformal contact with the resist represents a new method for generating complex patterns with feature sizes as small as 90 nm. This method has several desirable characteristics: it allows features with nanometer sizes to be produced from masks with features having sizes on the order of microns; the mechanical flexibility of the mask allows the mask to come into perfect contact with the photoresist, and enables patterning of nonplanar surfaces; mechanical compression and extension of the mask allows for adjustment of the features on its surface. The technique also has limitations, including the difficulty of achieving accurate registration with a flexible mask, and uncertainties in the distances between features. Also, production of nanometer features separated by nanometers requires features with similar sizes on the mask. For these reasons, we believe that this method complements other photolithographic methods and is well suited for generating single-level structures, where local linewidths are important but accurate distances between widely separated features in the pattern are not. Nanowire polarizers, optical notch filters,[14] optical memories,[15] and diffraction gratings with subwavelengths features represent applications in optics. The method will also be useful in fabricating nanoelectrode arrays for electrochemical studies, high frequency surface acoustic wave devices, and nanomechanical systems.[16]

This work was supported in part by ONR, ARPA, and NSF (PHY 9312572). This work made use of MRSEC Shared Facilities supported by the National Science Foundation (DMR-9400396). J.A.R. gratefully acknowledges the support from the Harvard University Society of Fellows. R.J.J. gratefully acknowledges a scholarship from NSERC of Canada. The authors would like to thank Yuan Lu and Stephen Shepard for their assistance in using SEM and photolithographic instruments.

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[10] Patterns in silicon dioxide were produced by performing reactive ion etching with a plasma of CF_4 on a piece of silicon with a native oxide layer and a patterned layer of photoresist. Oxide protected by the photoresist was not removed by the plasma. After etching, removing the photoresist with acetone left a pattern of silicon dioxide with the geometry of the resist.

[11] Patterns in gold were produced by evaporating gold onto a silicon wafer with patterned photoresist on its surface. Removal of the photoresist ''lifts-off'' gold deposited on its surface, and leaves a patterned layer of gold with the geometry of the resist.

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