

Elastomeric Optics

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This paper describes optical components prepared using poly(dimethylsiloxane) elastomers and liquid metals as constituent materials. Most optical components are fabricated from rigid materials such as glass, rigid polymers, or metals. By contrast, the elastomeric optics described here are designed to be deformable. Because the structure of the optical surface can be deformed easily, a single elastomeric optical component can be adapted to several applications. This paper provides procedures for the fabrication of elastomeric diffraction gratings, mirrors, and lenses and characterizes some basic properties of these optical elements.

Introduction

Optical components—diffraction gratings, lenses, and mirrors—are typically fabricated from materials such as glass, quartz, silica, rigid polymers, or metals. These materials have the advantages of structural rigidity and strength. For certain applications, however, structural rigidity is a limitation. One such class of applications requires optical elements that can be modified structurally, in real time, to optimize their performance: this class of elements has been given the name “adaptive optics”.¹ Adaptive optics have commonly been constructed by assembling smaller, rigid elements that can be moved independently.¹ Our strategy for the fabrication of adaptive optics is to fabricate a single element from materials that are deformable—that is, materials that can be stretched, bent or compressed. These deformations, if controlled, can be used to modulate the properties (the periodicity of a diffraction grating, for example) of an optical component (Figure 1). These elements are not likely to give the highest optical performance, but they offer many useful characteristics: low cost, *large* changes in optical properties, durability, and, in some instances, new types of performance.

Poly(dimethylsiloxane) (PDMS) elastomers are well suited as materials for the fabrication of deformable optical elements: (i) they can be deformed reversibly and repeatedly without permanent distortion or relaxation of features; (ii) they can be molded at a scale suitable for optical applications (0.1–10 μm size features) with high fidelity; (iii) they can be transparent at optical and UV–vis wavelengths (300–800 nm); (iv) they are durable, chemically inert, and nonphotoreactive, and (v) they are nontoxic, commercially available and inexpensive (<\$25/lb for useable although not usually optimal materials).

In this paper, we describe the fabrication of three types of elastomeric optical elements: diffraction grat-

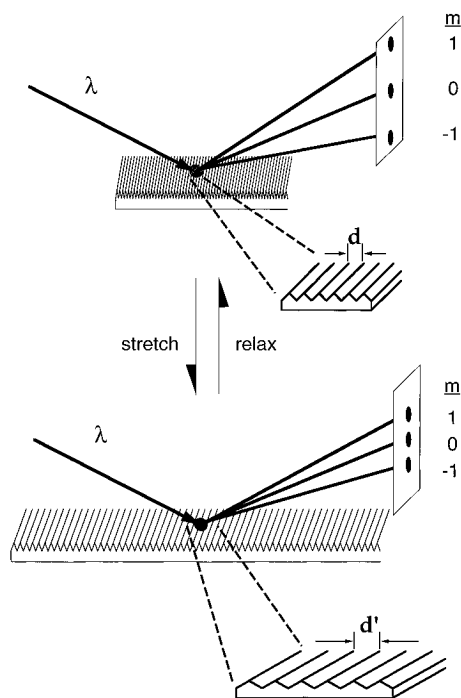


Figure 1. Stretching an elastomeric diffraction grating changes the periodicity of the grating and alters the spacing of the diffraction pattern. Features are not drawn to scale.

ings, lenses, and mirrors. Lenses and transmission gratings were prepared by molding PDMS elastomers into the desired shape. The fabrication of adaptive reflection gratings and mirrors required a reflective surface that could be significantly deformed. Gold films deposited directly on PDMS elastomers cracked severely (and irreversibly) when the elastomer was bent, stretched, or compressed.² As an alternative to solid metal films, we used liquid metals (mercury and gallium) to form reflective surfaces. Mercury and gallium

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(1) Hubin, N.; Noethe, L. *Science* **1993**, 262, 1390–1394.

(2) Gold films were deposited onto elastomeric gratings with an adhesion promoting layer (titanium) on top and bottom. This structure was encapsulated in a second layer of PDMS in an attempt to reduce cracking of the film. Even in this configuration, we observed cracking of the gold film and degradation of the diffracted beams.

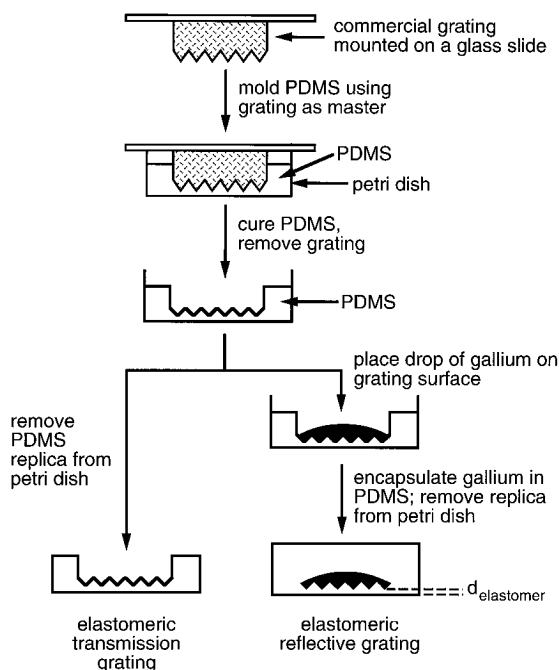


Figure 2. Schematic of the procedure for the fabrication of deformable gratings. Features are not drawn to scale. See text for details.

have been used as high-quality mirrors, and as liquids, can be deformed without permanent damage.^{3,4} This combination of molded elastomers—which constituted a structural backbone for an optical element—and liquid metals—which provided a flexible, moldable reflective surface—allowed the fabrication of deformable, reflective optical elements.

Fabrication

Elastomeric Gratings. Elastomeric replica diffraction gratings that operated in transmission were prepared by molding poly(dimethylsiloxane) (PDMS) elastomers using a rigid diffraction grating as a master (Figure 2). Siloxane elastomers used in these experiments were fabricated using a commercially available two-pack formulation that relies on a hydrosilylation reaction to form a cross-linked network.⁵

A commercial diffraction grating⁶ (“master”) was mounted on a glass slide and suspended over a petri dish containing degassed, uncured PDMS⁷ that covered the relevant features of the grating. The PDMS was degassed again under reduced pressure and cured by heating (2 h, 60 °C); after curing, the “master” grating was removed. The resulting elastomeric grating replicated in reverse the relief of the features on the master grating: raised regions of the replica corresponded to recessed regions of the master. For elastomeric transmission gratings, the elastomeric “replica” grating was removed from the petri dish and used without further processing.

Fabrication of reflective, elastomeric gratings required additional steps (Figure 2): (i) liquid gallium or mercury was placed on the surface of the grating produced as described

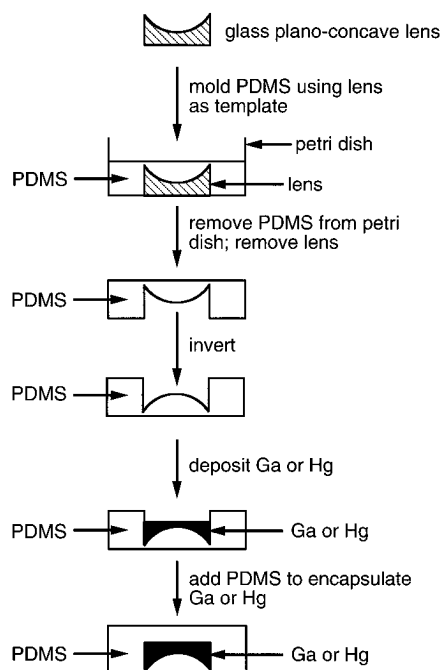


Figure 3. Schematic of the procedure for the fabrication of deformable mirrors. Features are not drawn to scale. See text for details.

above; (ii) degassed PDMS was added to encapsulate the liquid metal; (iii) the elastomeric/liquid metal grating was removed from the petri dish.

Elastomeric Mirrors. Figure 3 shows the procedure used to fabricate elastomeric mirrors. PDMS was cast against a polished, concave glass lens (“master”) in a petri dish. The PDMS was degassed and cured by heating; after curing, the PDMS was removed from the petri dish and the “master” lens was removed from the cured PDMS. Gallium or mercury was then placed on the surface of the PDMS where the lens had been removed. The metal was then encapsulated by a second layer of PDMS.

Elastomeric Lenses. Elastomeric lenses were fabricated using procedures described previously.^{8,9} Patterned self-assembled monolayers (SAMs)^{10–13} were used to control spatially the deposition of PDMS on a gold surface (Figure 4). Microcontact printing^{14–16} on a gold film,¹⁷ using a patterned elastomeric “stamp” and hexadecanethiol ($\text{HS}(\text{CH}_2)_{15}\text{CH}_3$) “ink”, formed SAMs terminated by CH_3 (hydrophobic) on certain regions of the surface of the gold. Immersing the gold surface into a 1.0 mM ethanolic solution of mercaptohexadecanoic acid ($\text{HS}(\text{CH}_2)_{15}\text{COOH}$) formed SAMs terminated by COOH (hydrophilic) in regions of the gold not derivatized by microcontact printing. The substrate was submerged in water,

(8) Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1994**, *10*, 2790–2793.

(9) Kim, E.; Whitesides, G. M. *Chem. Mater.* **1995**, *7*, 1257–1264.

(10) Nuzzo, R. G.; Fusco, F. A.; Allara, D. L. *J. Am. Chem. Soc.* **1987**, *114*, 1990–1995.

(11) Bain, C. D.; Evall, J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1989**, *111*, 7155–7164.

(12) Ulman, A. *An Introduction to Ultrathin Organic Films*; Academic Press: San Diego, CA, 1991.

(13) Whitesides, G. M.; Gorman, C. B., Self-Assembled Monolayers: Models for Organic Surface Chemistry. In *Handbook of Surface Imaging and Visualization*; Hubbard, A. T.; CRC Press: Boca Raton, FL, 1995; pp 713–733.

(14) Kumar, A.; Whitesides, G. M. *Appl. Phys. Lett.* **1993**, *63*, 2002–2004.

(15) Kumar, A.; Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1994**, *10*, 1498–1511.

(16) Wilbur, J. L.; Kumar, A.; Kim, E.; Whitesides, G. M. *Adv. Mater.* **1994**, *7*, 600–604.

(17) Gold films were formed by electron-beam evaporation of ~0.5–1.5 nm of titanium (adhesion promoter) and ~20–50 nm of gold (99.999%, Materials Research Corp., Orangeburg, NJ) onto a 4 in. silicon wafer (having a 2-nm-thick native oxide surface).

(3) Borra, E. F.; Content, R.; Girard, L.; Szapiel, S.; Tremblay, L. M.; Boily, E. *Astrophys. J.* **1992**, *393*, 829–847.

(4) Borra, E. F. *Sci. Am.* **1994**, *270*, 2, 76–81.

(5) Clarson, S. J.; Semlyen, A. J. *Siloxane Polymers*; Prentiss-Hall: Englewood Cliffs, NJ, 1993.

(6) In these experiments, we used commercial diffraction gratings (Edmund Scientific) for masters. We have also used masters prepared by standard fabrication techniques (micromachining or photolithography, for example).

(7) We chose specific elastomers (within the PDMS family) based on the desired properties (durometer, elasticity, and optical opacity) of the final product for each application: these elastomers are identified in later sections of the paper.

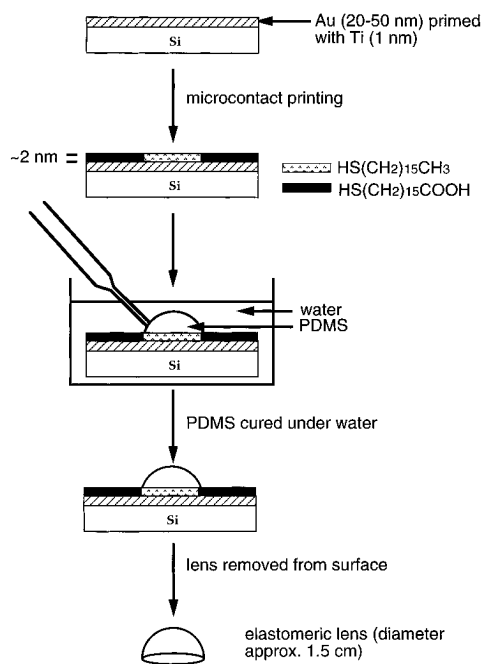


Figure 4. Schematic of the procedure for fabricating deformable elastomeric lenses. Microcontact printing formed a patterned SAM with hydrophobic and hydrophilic regions. A hydrophobic, liquid polymer (poly(dimethylsiloxane), PDMS) was delivered with a pipet to the surface of the patterned SAM, while the SAM was submerged in water. The PDMS spontaneously assembled on the hydrophobic regions in the shape of a lens. The PDMS was cured by heating and removed from the surface of the SAM. Features are not drawn to scale.

and degassed, uncured PDMS (hydrophobic) was delivered using a pipet to the surface of the patterned SAM. The PDMS assembled spontaneously on the hydrophobic regions forming sections of hemispheres that acted as lenses. The shape of the hemispheres could be modified prior to curing by adjusting the specific gravity of the solution in which the lenses were formed.^{8,9} The lenses were cured by heating and then removed from the substrate.

Performance

Gratings. To characterize the performance of the elastomeric gratings, we mechanically stretched (and relaxed) the gratings and measured the angular displacement, the ellipticity,¹⁸ and the intensity of the first-order diffraction (FOD) spot. The gratings were stretched and relaxed in a home-built jig (Figure 5a) that prevented twisting and bending of the grating during stretching. The light from a helium–neon laser ($\lambda = 632.8$ nm, 3 mW) was directed into the center of the grating at the blaze angle of the grating. The resulting diffraction pattern was visualized on a screen in the far field (15–50 cm from the front face of the grating); linear displacement of the FOD spot was measured using a ruler. The ellipticity and intensity of the first-order beam were obtained from the image of the spot recorded using a CCD camera.

Figure 5b shows the performance of a typical elastomeric diffraction grating, operating in transmission, for one “stretch/relax” (S/R) cycle. The angular displacement of the FOD spot increased with increased stretching. The spot was circular at all points (ellipticity ~ 1) and its intensity varied by less than 20% (the error in

(18) We define the ellipticity = [(width of the spot at center)/(height of the spot at center)].

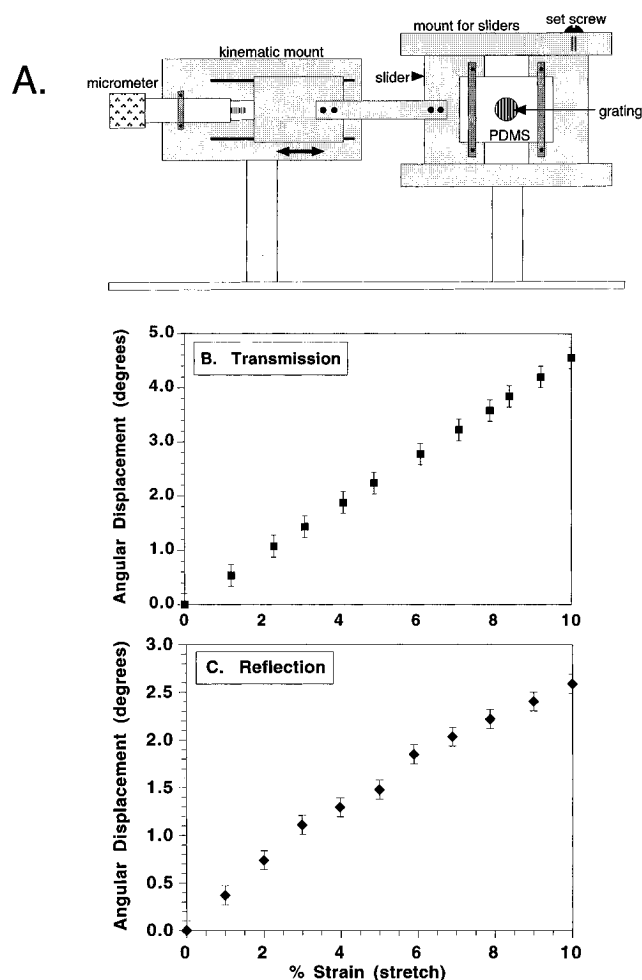


Figure 5. (a) Schematic of the homebuilt jig used to test the performance of elastomeric gratings and mirrors. The grating or mirror was mounted on two aluminum sliders held in an aluminum mount. One slider was fixed in place with a set screw. The other slider was attached to a kinematic mount. This mount was equipped with a micrometer; turning the micrometer screw ($<1\text{--}2$ mm/s) in the appropriate direction either stretched or relaxed the grating or mirror. (b) Plot of the angular displacement of the first order diffraction (FOD) spot of an elastomeric grating operating in transmission as a function of mechanical stretching. The grating was fabricated from Hüls PELD 15 silicone elastomer cast on a commercial-grade, ruled, blazed ($17^\circ 27'$) diffraction grating with 600 grooves/mm ($1.6\ \mu\text{m}$) spacing. (c) Plots of the angular displacement of the FOD spot of a reflective, elastomeric grating as a function of mechanical stretching. The grating was fabricated from Dow Corning Sylgard 184 silicone elastomer cast on a commercial-grade holographic grating with 1200 grooves/mm ($0.8\ \mu\text{m}$) spacing. The liquid metal used to create the reflective surface was gallium. Error bars (b, c) represent our best estimate of the uncertainty in the measurements.

our measurement) over the range of stretching measured. The zeroth-order diffraction spot moved less than 1° during stretching. The data were reproducible over 500 repetitions of the S/R cycle.¹⁹

To test the gratings at higher frequencies of stretching, we mounted a grating²⁰ on a piezoelectric translator. For S/R cycles ($<0.5\%$ strain) at frequencies below

(19) During the 500 repetitions, the first-order diffracted spot reproducibly returned to its initial position when released: there was no evidence of incomplete mechanical recovery. We cannot, however, rule out the possibility that under more extreme circumstances (at larger strain or over longer time scales, for example) imperfections in the elastomer could lead to incomplete mechanical recovery due to creep.

2 kHz, the angular displacement changed reproducibly and the ellipticity and intensity of the FOD spot remained constant over $\sim 10^6$ cycles. At frequencies larger than 2 kHz, the performance of the grating degraded: the angular displacement of the FOD spot was not reproducible, and the change in the angular displacement of the FOD spot was not in phase with the motion of the piezoelectric. We did not explore alternative elastomers or changes in the design of the gratings to achieve improved performance at higher rates. These experiments established that, for small S/R cycles, the performance of the grating was reproducible over more than 10^6 repetitions.

We characterized the reflective, elastomeric diffraction gratings by procedures similar to those used for the transmission gratings. Figure 5c plots the angular displacement of the FOD spot as a function of strain. In the regime measured in Figure 5c, the position of the zeroth-order spot and the ellipticity and intensity of the first-order diffraction spot changed less than 30% during a given S/R cycle. The performance of the grating depended on the amount of pressure used to clamp the grating to the sliders (Figure 5a). Excessive pressure distorted the grating and changed the shape of the spots in the diffraction pattern; insufficient pressure allowed the grating to slip during S/R cycles.

The performance of reflective, elastomeric gratings fabricated with both gallium and mercury depended on the thickness ($d_{\text{elastomer}}$, Figure 2) of the elastomer that covered the liquid metal grating (see Figure 2). For values of $d_{\text{elastomer}} < \sim 500 \mu\text{m}$, the surface (both the PDMS polymer and the liquid metal beneath it) of the grating behaved like the surface of a liquid: slight vibrations or air currents distorted or moved the surface. For values of $d_{\text{elastomer}}$ between $\sim 500 \mu\text{m}$ and $\sim 2 \text{ mm}$ the surface of the grating was more stable. Values of $d_{\text{elastomer}} > \sim 2 \text{ mm}$ increased scattering of light (see below) but did not noticeably increase the stability of the surface of the grating.

The performance of the reflective gratings also varied with the choice of liquid metal. The weight of mercury caused distortions in the surface of the grating. Gallium caused less distortion of the grating because it is less dense ($\rho = 5.907 \text{ g mL}^{-1}$) than mercury ($\rho = 13.546 \text{ g mL}^{-1}$) and because gallium wets PDMS (mercury does not) and therefore required less metal to cover the surface of polymer.

Elastomeric Mirrors. To measure the performance of the elastomeric mirrors, we mounted them in a jig similar to that shown in Figure 5a.²¹ The light from a He-Ne laser was directed into the front face of the mirror at an angle ($20\text{--}40^\circ$ from normal to the face of mirror) to create an elliptical output spot. The resulting output spot was visualized on a screen in the far field ($6\text{--}20 \text{ cm}$). Stretching (and relaxing) the mirror altered the curvature of the mirror: this alteration changed the ellipticity of the output spot (Figure 6a). We measured the ellipticity at two different far-field distances (6 and

19 cm) from the front of the mirror. The ellipticity of the output spot at these two distances differed by less than our experimental error in the measurement ($<5\%$) indicating that there was little astigmatism.

Elastomeric Lenses. To evaluate the performance of the elastomeric lenses, we placed them between two parallel plates mounted on translation stages: the lenses were held in place by the pressure exerted on their edges by the two plates (Figure 6b). Reducing the distance between the plates compressed the lens along one axis (A_1 , Figure 6b). Figure 6c shows a plot of the focal length (in both axes) of a 1-cm-diameter lens as the lens was compressed along the axis A_1 . The light from a helium-neon laser ($\lambda = 632.8 \text{ nm}$, 3 mW) was directed into the center of the back side of the lens. The output from the lens was visualized on a screen in the far field ($5\text{--}30 \text{ cm}$) from the front side of the lens. The focal length of the lens along the axis A_1 changed; the focal length along the axis perpendicular to A_1 (and in the plane of the lens) did not change within the error of our measurements ($\sim 20\%$). The insets in Figure 6c show images of the output of the lens at selected focal lengths visualized at a fixed distance ($\sim 5 \text{ cm}$) from the front of the lens.

Discussion

Our work to date has focused on developing techniques for the fabrication of simple elastomeric optical elements such as diffraction gratings, lenses, and mirrors. We have demonstrated that, in principle, elastomeric optical elements can be used to control the position and shape of light. Several issues remain that need to be addressed if these optical elements are to be used for practical applications:

Optical and Mechanical Properties. The commercial PDMS used in these experiments (Sylgard 184, Dow Corning) contains fillers that improve the materials properties (elasticity and hardness, for example) of the elastomer. These fillers scatter light. The extent of scattering depended on the thickness of the PDMS used. For transmission and reflection gratings, where the thickness of the PDMS was less than $\sim 2 \text{ mm}$, scattering did not affect the performance. For lenses, which can be as thick as several cm, scattering was a serious problem. Attempts to remove the fillers from commercial prepolymers of PDMS by centrifugation failed since the MW of the fillers is comparable to the molecular weight of the poly(dimethylsiloxane) chains in the preelastomer. The commercial PDMS elastomers are also imperfect elastomeric networks: over long time scales or under large applied stresses, the hysteretic behavior of these materials may result in incomplete mechanical recovery. For practical applications, the optical elements require good optical quality, and the ability to recover completely from applied stresses. Some of these problems should be solved by preparing these components from PDMS elastomers that are ideal networks and that contain no filler particles.⁵ We have not yet explored this possibility.

Structural Stability. The elastomeric optical elements may be distorted unintentionally by environmental influences. Gravity, for example, can cause the optical element to bend under the force of its own weight. One solution is to place the optical element in a mount that provides sufficient support to prevent

(20) The grating was fabricated from Sylgard 184 silicone elastomer (Dow Corning Corp., Detroit, MI) cast on a commercial-grade, ruled, blazed ($17^\circ 27'$) diffraction grating with 1200 grooves/mm ($0.83 \mu\text{m}$ spacing). Other elastomers may respond at different rates.

(21) The jig used for experiments with the elastomeric mirrors had both sliders attached to kinematic mounts so that the mirror was stretched by pulling from both sides. The mirror was glued to the sliders (not clamped) with RTV silicone adhesive.

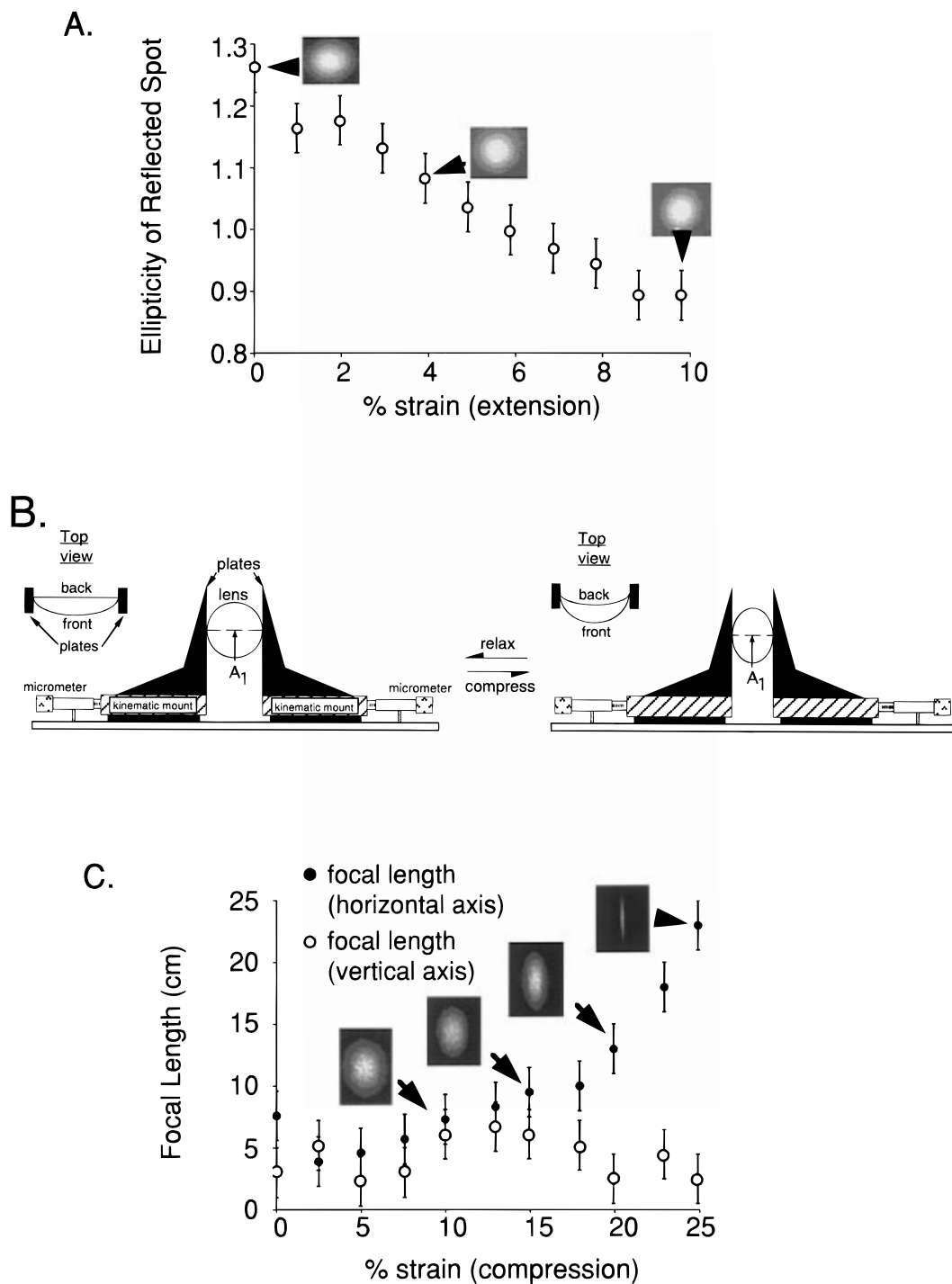


Figure 6. (a) Ellipticity of a laser beam that was reflected from the surface of an elastomeric mirror could be controlled by stretching the mirror. The insets show images of the output spot from the mirror where the ellipticity of the spot is >1 (elliptical spot, major axis in horizontal plane), ~ 1 (circular spot), and <1 (elliptical spot, major axis in vertical plane). These images were taken at a distance of ~ 6 cm from the front of the mirror. (b) Schematic of the jig used to test the performance of elastomeric lenses. The lens was held (by pressure) between aluminum plates attached to kinematic mounts. The mounts were equipped with micrometer screws; turning the micrometer screws in the appropriate direction either compressed the lens or allowed the lens to relax. Compressing the lens changed the curvature of the lens along the axis (A_1) in which it was compressed ("top view"). Typically the lenses were ~ 1 – 2 cm in diameter (uncompressed). Drawing is not to scale. (c) Compressing an elastomeric lens along one axis (A_1 , Figure 6b) increased the focal length of the lens along that axis. The lens was not compressed in the axis perpendicular to A_1 , and the focal length in that direction did not change (within the error of our measurement).

distortion. Another is to affix a cover slip or glass flat to the surface of the grating using a mobile liquid layer (water or silicone oil, for example) and use the surface tension of the liquid to pull the surface of the optical element flat against the cover slip. A third solution involves incorporating rigid (but not connected) objects around the perimeter of the active region of the optical

element. A fourth solution would be to mount the optical element in a geometry in which gravitational distortions are acceptable or correctable.

Distortion. For reflective diffraction gratings and mirrors, the reflective surface was a liquid metal (Hg or Ga) covered with a thin (<500 μm) layer of PDMS. Using our jig, which stretched the gratings or mirrors

by pulling on their edges, the front surface of the PDMS was deformed more than the surface of the grating itself. The distortion of the PDMS caused it to act as a diverging lens, distorting the shape of the output spot. One possible solution to this problem would be to design an apparatus that stretched the grating more evenly (i.e., an apparatus that did not stretch the optical element by pulling on its ends); another solution would be to incorporate components (such as piezoelectric ceramics) into the elastomeric portions of the optical element; a third would be to develop reflective elastomeric gratings in which the metal surface is not covered by PDMS. This final solution would require a substantial departure from our current designs.

Conclusions

The central result of this paper is the development of a strategy for the fabrication of optical elements whose structure can be modified, in real time, to optimize their performance. This strategy produces components that are simple and inexpensive. It can be used to fabricate optical elements with scales ranging from one micron to several centimeters. We have fabricated optical elements that transmit light (transmission gratings, lenses) by casting PDMS elastomers using commercial optical elements as masters. Optics that operate in reflection (reflective diffraction gratings, mirrors) were prepared using PDMS to form the structural backbone of the optical element and liquid gallium or mercury to form a moldable, deformable reflective surface. We have characterized the basic performance of prototypical diffraction gratings, mirrors, and lenses.

Elastomeric optical elements are at an early stage of development. At present, they may be useful for simple applications where flexible control of the position and shape of light is needed. One possible application for elastomeric optics involves using elastomeric gratings to tune the frequency of grating-stabilized diode lasers. At present, changing the frequency of this type of laser requires changing the angle (which changes the effective period of the grating) between a rigid grating and the laser.²² The output of the laser is the specular reflection from the grating, so changing the angle of the grating to tune the frequency of the laser causes the direction of the output to change. This change in direction may induce frequency-dependent problems with the alignment of other optical elements that receive the output of the laser. If an elastomeric grating were used instead of a rigid grating, the period of the grating (and hence

the frequency of the laser) could be changed by stretching the grating. Since stretching the grating does not change the angle of the optically active surface, the direction of the output of the laser remains unchanged over a range of frequencies. Our attempts to demonstrate this application with our current design of reflective elastomeric gratings failed because we were not able to obtain stable feedback using the elastomeric grating in the external cavity of the laser. The poor feedback resulted from distortion and instability of the optical surface of the grating (see above), which caused the beam that was reflected back into the diode laser to diverge (that is, the reflected beam was not sufficiently collimated to obtain stable feedback). Further work on the design and development of elastomeric gratings will be needed for their implementation in this application.

As a second example, elastomeric mirrors might be used to reflect beams of light at various angles while conserving cylindrical symmetry. For rigid mirrors, changes in the angle at which a beam is reflected from a mirror result in changes in the ellipticity of the reflected beam. Since an elastomeric mirror can control the ellipticity of the output spot (by varying the radius of curvature), it can be used to maintain a cylindrically symmetric spot regardless of the angle of reflection. We have demonstrated this application in principle (Figure 6a); we have not attempted a "practical" application.

As a final example, the output of diode lasers is both astigmatic (different focal lengths along different axis of the beam) and noncylindrically symmetric; the modes of an optical fiber are nonastigmatic and cylindrically symmetric. An elastomeric lens—which has variable focal lengths (to correct astigmatisms) and can control the cylindrical symmetry of a beam—could be used to couple efficiently the output of a diode laser with the end of an optical fiber. We have fabricated optical elements that may be suitable for this application; strategies for manipulating individual micrometer-scale lenses and positioning them on optical fibers remain an important challenge.

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(22) Wieman, C. E.; Hollberg, L. *Rev. Sci. Instrum.* **1991**, 62, 1–20.