

Fabrication of photonic crystal lasers by nanomolding of solgel glasses

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We demonstrate the formation, in a single process step, of periodic arrays of features of surface relief with submicrometer lateral dimensions in hybrid organic and inorganic solgel glasses by using elastomeric molding techniques. Lasers formed with molded photonic crystal resonators that consist of triangular, square, and honeycomb lattices of cylindrical posts and holes show emission spectra and lasing thresholds that are similar to devices formed by conventional high-resolution photolithographic patterning of thick layers of thermally grown oxide. © 1999 Optical Society of America

OCIS codes: 140.3490, 160.6060, 220.4610.

1. Introduction

Periodic arrays of submicrometer features of surface relief are extremely useful in integrated optics. They form the basis, for example, for output and input couplers, beam splitters, lenses, reflectors, spectral filters, laser resonators that use distributed feedback, and other elements. Although several techniques—holographic lithography, high-resolution photolithography, and direct-write electron-beam lithography—currently exist for fabricating these structures, they all have the disadvantages that they are expensive and generally require multiple processing steps. There is considerable interest, therefore, in the development of simple methods that can form nanometer patterns of relief in materials that are useful for integrated optics.

Approaches that rely on nanomolding or embossing of solgel glasses are attractive for this type of fabrication because they are low in cost and potentially require only a single step. Although rigid stampers have been used with various degrees of success in the past,¹⁻⁴ newer embossing methods that use elastomeric or flexible molds have the advantages that they

allow uniform patterning over large areas at low pressures and can be removed easily and nondestructively from the embossed solid.⁵ We recently demonstrated use of elastomeric molding to fabricate polymeric laser resonators based on distributed feedback, distributed Bragg reflectors, and a variety of two-dimensional photonic crystals.⁶⁻⁸ Lasers formed by use of these structures showed characteristics (emission threshold, emission linewidth, and spatial uniformity) similar to devices formed with photolithography. In this paper we describe the successful application of similar techniques to materials that are more useful for conventional integrated optics than organic polymers: organic and inorganic hybrid glasses [organically modified silicates (ORMOSIL's) or organically modified ceramics (ORMOCER's)] formed at low temperatures with solgel techniques.^{4,9-13} The results demonstrate (i) that nanomolding with an elastomeric master can produce, in a single step, high-quality ORMOSIL laser resonators based on two-dimensional photonic crystals that have feature sizes as small as ~150 nm, and (ii) that these resonators can be used with organic gain materials to form working lasers with good characteristics. These lasers represent, to our knowledge, the first active devices to be fabricated by molding or embossing solgel materials.

The solgel process provides a convenient, solution-based synthetic route to many types of inorganic solid.^{14,15} A well-known and significant disadvantage, however, is that shrinkage induced by drying of the solid often leads to cracking of thick structures. As a result, multiple coatings of conventional solgel glasses are typically required to form waveguides that can support multiple modes. Hybrid matrices

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Received 29 March 1999; revised manuscript received 28 June 1999.

0003-6935/99/275799-04\$15.00/0

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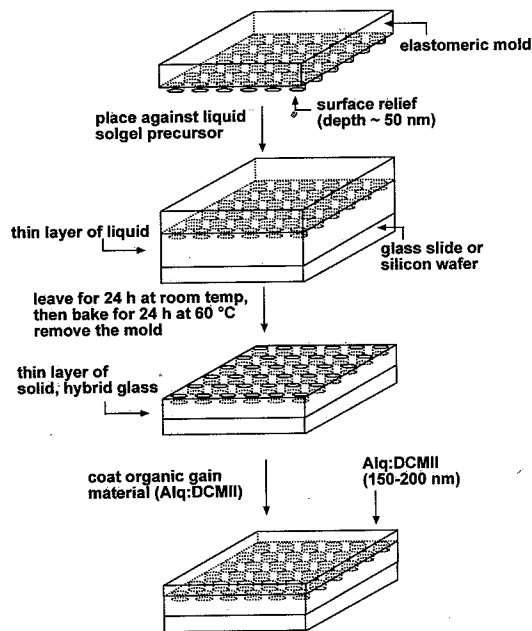


Fig. 1. Fabrication of lasers by elastomeric molding of a sol-gel precursor. Polydimethylsiloxane (PDMS) was cast and cured against a photolithographically generated master. A drop of sol-gel precursor on a substrate is compressed between the PDMS mold and the surface. Gelation at room temperature for 24 h was followed by drying at 60 °C for 24 h. Removal of the PDMS mold yielded a thin embossed solid film. Deposition of an organic gain material [~ 200 nm of tris(8-hydroxyquinoline) aluminum (Alq) doped with 0.5–5.0 wt of the laser dye 4-dicyanomethylene-2-methyl-6-(*p*-dimethylaminostyryl)-4*H*-pyram II (DCMII)] onto this film yielded a working photopumped laser.

consisting of interpenetrating organic and inorganic networks prepared by use of a metal alkoxide with a reactive organic moiety avoid the cracking problem because the organic groups in the developing inorganic matrix enable structural relaxation.^{4,9–13} These materials (e.g., ORMOCER's or ORMOSIL's) can yield thick, mechanically hard coatings with good optical properties; they also can be formed at relatively low temperatures. These characteristics make them ideal choices for use with low-cost fabrication procedures based on molding.^{4,12}

Figure 1 illustrates the steps for fabrication. Casting and curing an elastomeric prepolymer [polydimethylsiloxane (PDMS)] against patterns of surface relief defined by photolithography yields elastomeric molds. A ~ 30 -min exposure to 1–2 drops of tridecafluoro-1,1,2,2-tetrahydrooctyl-1-trichlorosilane under reduced pressure (~ 10 mm Hg) passivates the surfaces of the molds and facilitates their release from the gelified solid.

We prepared the precursor solution (sol) by mixing 4.7 g of glycidoxypropyltrimethyloxysilane with 1.2 g of tetramethoxysilane and 1 g of 0.1 N oxalic acid in water; we stirred this mixture at room temperature for ~ 2 h. One drop of aqueous ammonia was added to 1 ml of the sol and the resulting mixture was vigorously shaken (~ 1 min) until it was homogeneous; decanting (~ 1 – 2 min) allowed degassing of

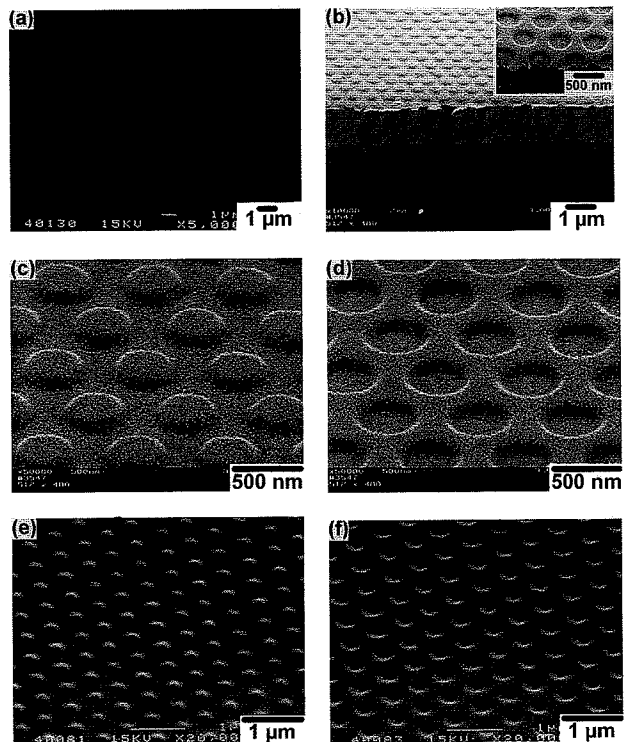


Fig. 2. Scanning electron micrographs of photonic crystal structures (50 nm deep) embossed on a thin (2- μ m) film of ORMOSIL. These micrographs show that both raised and depressed submicrometer features of surface relief can be prepared by embossing by use of an elastomeric mold. (a) Structures of submicrometer features patterned over large areas with high fidelity. (b) A 2- μ m-thick film coated on a silicon wafer with a 2- μ m-thick thermal oxide layer embossed with raised features. The inset shows a similar film embossed with depressed features. (c)–(f) Triangular arrays of raised and depressed features of surface relief with various periods.

trapped air bubbles. A PDMS mold was placed in contact with several drops of this mixture on a clean substrate (silicon wafers or glass slides). Removal of the mold after this system was kept at room temperature for 24 h and baked in an oven at 60 °C for 24 h, which yielded a solid, embossed film of ORMOSIL (~ 2 μ m thick). The relief on the PDMS mold determines both the lateral dimensions and the depth of relief on the molded film (in this case a depth of ~ 50 nm).

Figure 2 shows scanning electron micrographs of a variety of photonic bandgap structures in molded ORMOSIL films several micrometers thick. The patterns consist of periodic arrays of cylindrical posts or holes with submicrometer diameters, arrayed in triangular, square, and honeycomb lattices. The images suggest that the structures are replicated with a spatial resolution that comfortably exceeds both the smallest dimensions of the features (~ 150 nm) in these photonic crystals and in structures (~ 250 nm) that are useful for applications in telecommunications. We believe that it is likely that suitable molds will allow formation of features considerably smaller than those demonstrated here. Cross-sectional views show the depths of the surface relief and con-

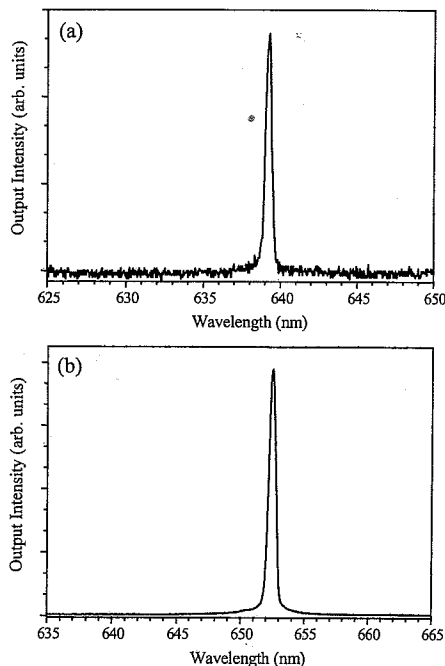


Fig. 3. Emission spectra from lasers that use resonators formed by molding arrays of cylindrical holes in layers of ORMOSIL on silicon. (a) Spectrum for a laser that uses a resonator that consists of cylindrical depressions ~ 50 nm deep, with 400-nm diameters and center-to-center separations of 600 nm in a triangular lattice. (b) Spectrum for a similar laser that uses depressions with diameters of 260 nm, depths of ~ 50 nm, and separated by 640 nm.

firm the near net shaping of the structures. We observed good uniformity over the entire ~ 1 cm \times 1 cm patterned area.

We produced lasers by depositing thin films of organic gain materials onto these resonators using procedures described previously.¹⁶ The layer of gain material itself forms a planar waveguide with ORMOSIL and air as the cladding layers. Photopumping these devices with the output of a pulsed nitrogen laser (~ 2 ns, 337 nm) caused lasing because of Bragg reflections induced by the photonic lattice molded in the ORMOSIL. Some of the laser emission scatters out of the plane of the waveguide at an angle allowed by phase-matching conditions. The grating thus also functions as an output coupler and offers a convenient way to characterize the laser emission. Figure 3 illustrates typical emission spectra for resonators with two different geometries; lasers that used resonators with other designs had similar spectra. The widths of the lines shown in Fig. 3 are limited by the resolution of our spectrometer. Figure 4 shows the dependence of the intensity of the emission on the intensity of the pump light and illustrates the expected linear relationship between these two quantities when the devices are operated above threshold. The threshold determined from Fig. 4 (~ 50 kW/cm²) and the emission spectra shown in Fig. 3 are, to within experimental errors, identical both to those that use photolithographically defined

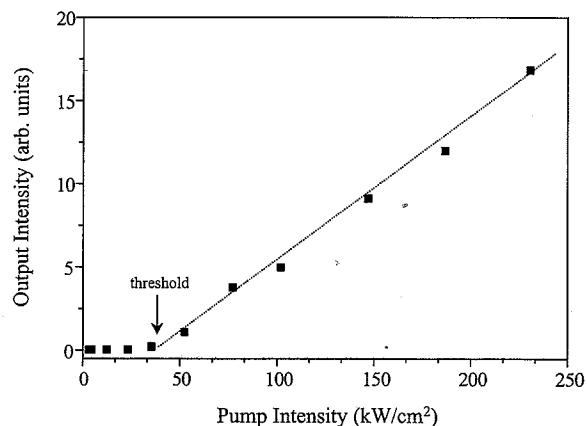


Fig. 4. Emission intensity (arbitrary units) as a function of the intensity of the pump light for the laser whose emission spectrum is illustrated in Fig. 3(b). As expected, these intensities are linearly related when the device is lasing. The threshold measured from these data is consistent with similar measurements on lasers that use resonators formed with conventional photolithographic procedures in thermally grown oxide.

resonators in oxide¹⁶ and to those built with resonators of molded polymer.⁸

We note that one disadvantage of these ORMOSIL devices is that irreversible shrinkage of the hybrid organic-inorganic matrix that can occur above 60 °C may limit their maximum operating temperature. By increasing the temperature or time of the baking step, it should be possible for one to reduce this sensitivity to high operating temperatures. For example, structures that we formed at 120 °C had optical characteristics as good as those baked at 60 °C, but should have a reduced sensitivity to high temperatures. In addition, although the organic portion of the matrix induces some degree of sensitivity to elevated temperatures, it also raises the overall hydrophobicity of the structures, thereby making them relatively insensitive to humidity. Also, the ability to select the organic component to yield glasses with the desired optical and physical characteristics¹⁴ often makes the design of ORMOSIL materials easier than that of purely inorganic systems.

In summary, this research demonstrates the possibility of producing high-quality laser resonators by elastomeric molding of organically modified solgel glasses. The techniques represent simple, single-step routes to patterning of hard glasses for applications in certain areas of integrated optics. Although in this paper we focused on photonic crystal lasers, the same techniques will certainly be suitable for more conventional resonators based on distributed feedback or distributed Bragg reflectors. It is important also to note that these methods can form relatively large structures, such as ridge waveguides.⁵ Furthermore, because the molds can have more than a single level of relief, it should be possible to mold directly complex structures such as ridge waveguides with integrated surface relief Bragg gratings. Ex-

ploration of these and other applications are the subjects of current research.

This research was partially supported by Defense Advanced Research Projects Agency, National Science Foundation ECS 9729405, and National Science Foundation DMR 9400396 (Materials Research Science and Engineering Center). We thank Yuan Lu for his help.

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