

Communications

Fabrication of Glass Microstructures by Micro-Molding of Sol-Gel Precursors**

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This paper demonstrates that the molding of a sol-gel precursor against an elastomeric replica of the desired features (a form of soft lithography)^[1] is a convenient method to generate submicrometer patterns of glasses on a substrate. We were able to fabricate glass (silicon dioxide doped with boron oxide, titanium oxide, or aluminum oxide) structures with micrometer-scale features supported on a flat Si/SiO₂ substrate, as well as free-standing membranes.

In molding, an initially fluid material is allowed to acquire its final geometry by solidifying in a mold. This technique allows the reproduction of the fine details of the mold: replica molding of structures in polymers has generated structures with 10 nm sized features.^[2] The molding of sol-gel precursor solutions has produced monolithic silica pieces^[3] as well as Fresnel lenses or gratings with sub-micrometer periods.^[4] Replica molding is a method that has several potentially useful features. It does not require photolithography and can be used without access to a clean room. Once the mold is fabricated, many replicas can be produced.^[2] It has a theoretical limit to resolution that is much below that that can be achieved by photolithography. It can be used to make patterns on curved substrates. The throughput of a process based on molding can be high and its cost low. Unlike electron-beam or scanning tunneling microscopy (STM) writing, molding allows parallel fabrication. We believe that micro-molding is a type of process that will be widely useful in microfabrication.

The sol-gel process is a versatile method for synthesizing many inorganic oxides.^[5] This method generates materials with controlled chemical composition and low levels of impurities. Most common glasses, with the exception of some halide glasses, have been successfully synthesized; these compositions range from high purity silica to an eight-com-

ponent glass ceramic.^[6] Other materials that have been prepared by sol-gel process include PZT ceramics (i.e., Pb(Zr,Ti)O₃),^[7,8] electro-optic films,^[9] high efficiency phosphors,^[10] and electrochromic glasses.^[11]

The use of sol-gel chemistry to prepare materials has one unattractive characteristic: the shrinkage induced in the drying stage gives rise to high stresses in the structures. These stresses can cause the deformation and breaking of the structures. In order to reduce these stresses, drying additives can be used.^[12] The incorporation of non-hydrolyzing organic groups in the material (methyl or phenyl) gives structures with higher compliance and allows structural relaxation during the drying stage.^[13] Controlled slow drying can also decrease the risk of cracking of the glass; it will, however, result in long process times. Good adhesion of the glass to the substrate is necessary to prevent the delamination of the structure.

We wished to fabricate glass structures with dimensions in the range of 0.1 μm to several micrometers by non-lithographic methods, and have examined the molding of sol-gels in an elastomeric mold. This paper first summarizes this method and then shows and characterizes different geometries of structures that we were able to fabricate.

General Procedure: The reaction involved in the gelation of the precursor solution (sol) is a two-step hydrolysis and polycondensation^[5] of tetramethylorthosilicate (TMOS), the main constituent of all glasses studied. Other alkoxides react similarly. In the case of molding between a substrate and a patterned elastomer, a drop of precursor was put on the freshly cleaned substrate and the mold was then placed face down on the surface (Fig. 1). A pressure of roughly 10 psi (ca. 69 kN m⁻², i.e., ca. 0.7 atm) was applied and the area of the patterned surface was typically 1–5 cm² with feature sizes in the micrometer range. It is important that the liquid dewets the surface and allows contact of the elastomer and the substrate in regions where no sol-gel-derived material is desired. The dewetting is driven by both the applied pressure and the difference of the interfacial tensions of the precursor and the stamp. More precisely, the dewetting speed is proportional to S , where $S = \gamma_{LS} + \gamma_{LE} - \gamma_{SE}$; γ_{LS} is the liquid–substrate interfacial tension, γ_{LE} is the liquid–elastomer interfacial tension, and γ_{SE} is the substrate–elastomer interfacial tension.^[14] Since γ_{SE} is fixed, we had to increase the interfacial tensions of the precursor solution in order to accelerate the dewetting. Although pressure improves the definition of the features, it cannot be increased too much because of the deformations induced in the mold. Diluting the precursor in acetonitrile, a polar solvent with low viscosity and high surface tension ($\gamma = 29.3 \text{ mJ m}^{-2}$) that does not swell the mold, allowed us to obtain satisfactory dewetting for all the patterns that we

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[**] This work was funded by ONR/ARPA and by Saint-Gobain Recherche, France. This work made use of MRSEC Shared Facilities supported by the NSF under award number DMR-9400396. The authors thank Yuan Lu and Steve Shepard for their help during the use of these facilities.

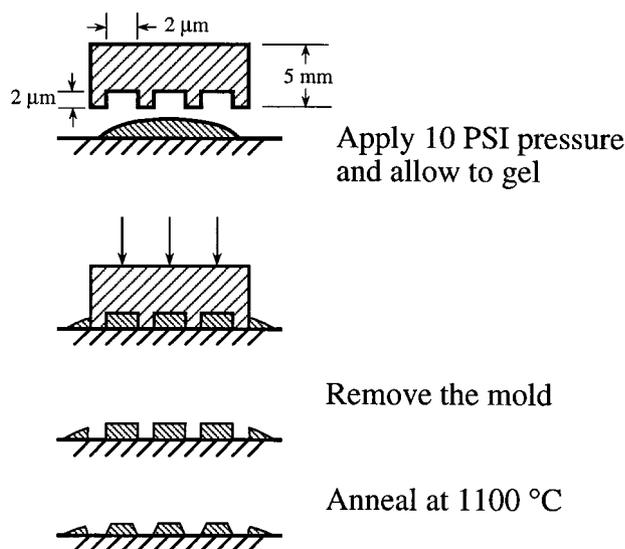


Fig. 1. Schematic outline of the molding method used to fabricate structures supported on a flat substrate. A droplet of precursor was compressed between the silicone mold and the surface by applying a pressure of roughly 10 psi (ca. 0.7 atm). The high interfacial free energy of the solution caused the precursor to dewet the substrate completely where the mold and the substrate were in contact.

used. For instance, the precursor defined below as sol A had a contact angle with the elastomeric mold of 30° after 1 h of aging, whereas the same precursor after diluting in acetonitrile had a contact angle of 55°, corresponding to a higher interfacial tension.

Although gelation occurred within an hour, the mold and the structure were allowed to remain undisturbed for 12 h, to allow reasonable consolidation. The gelling time can, however, be further decreased by raising the pH of the precursor to 4–5 before casting, and we produced some structures in less than 30 min. The density of defects was slightly higher when gelation occurred rapidly, and all the structures shown in the figures in this paper were produced at pH values between 3 and 4. After removing the mold, the structure was annealed at high temperature (400 °C to 1100 °C) to eliminate trapped solvent and to consolidate the glass.

Patterned Solids: In order to establish the sharpness of the details that molding can reproduce, we first molded a silica sol-gel precursor against a silicon wafer that had been patterned by anisotropic etching with square pyramidal pits. Figure 2 shows the array of silica pyramids prepared by this method. The radius of curvature at the tip is less than 50 nm and the angle θ of the side of the pyramid to the surface is 54–58°. This value is compatible with that obtained with this type of silicon etching (54.7°).^[15] This geometry shows that the shrinkage that takes place during the annealing step is essentially isotropic. The high surface energy of the end of the tip is not sufficient to cause substantial deformation and rounding during the sintering at this temperature. This important result makes it very likely that it will be possible to fabricate even smaller struc-

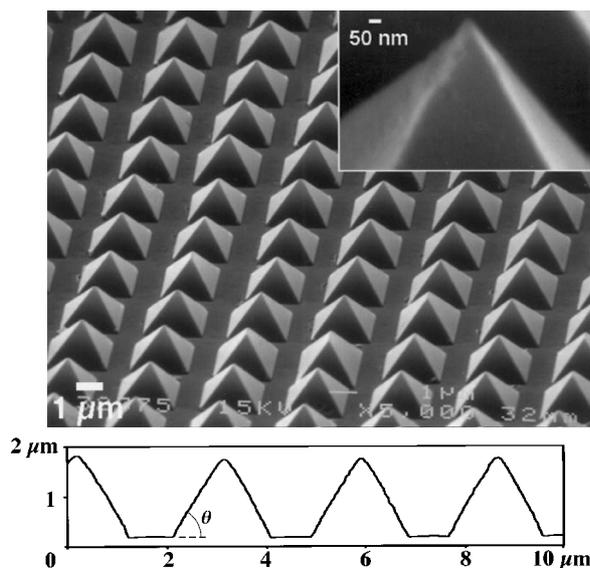


Fig. 2. a) Scanning electron micrograph of the surface of an unsupported patterned piece of silica. The sol-gel precursor was molded against a Si/SiO₂ wafer whose surface had been passivated by silanization. The structure was annealed at 1100 °C. It measured 5 × 5 × 0.3 mm³. b) A cross-section along the axis of the pyramids imaged by non-contact atomic force microscopy on the same silica sample after covering it with gold by sputtering.

tures by this method, provided that suitable molds are available.

Membrane: We have fabricated free-standing patterned films by molding a titanosilicate sol against a wafer coated with aluminum. The size of the holes in the membrane can easily be controlled by changing the features of the original mold. The membrane was released by dissolving the aluminum. Such inorganic membranes may have applications in separation techniques and as catalyst supports.

Once the membrane was separated from the substrate, it was floated on the surface of water and could be easily transferred to another substrate. This method allowed us to generate membranes of large area (larger than 5 cm²) and submicrometer thickness with no observable defects. Figure 3 shows a 200 nm thick membrane made of titanosilicate glass. This membrane presents 1.5 μm diameter holes. This film was resistant enough to withstand the large capillary forces applied during drying. It was also flexible and we observed regions of the film with small radii of curvature (~10 μm, not shown). It did not break when one drop of a suspension of silica beads in water was passed through it (Fig. 3b). The final composition of the film, as given by X-ray photoelectron spectroscopy (XPS), was 7 % TiO₂ and 93 % SiO₂.

Optical Waveguides: Molding techniques are also very convenient for fabricating silica-on-silicon structures. We have generated optical waveguides of doped silica on Si/SiO₂. The silica was doped with aluminum oxide in order to increase its refractive index. A large (1–2 μm) and weakly confining ($\Delta n = 0.01$) core is used in general to produce single-mode, low-loss waveguides.^[16] Low scattering by the edges of the core can be achieved by an annealing

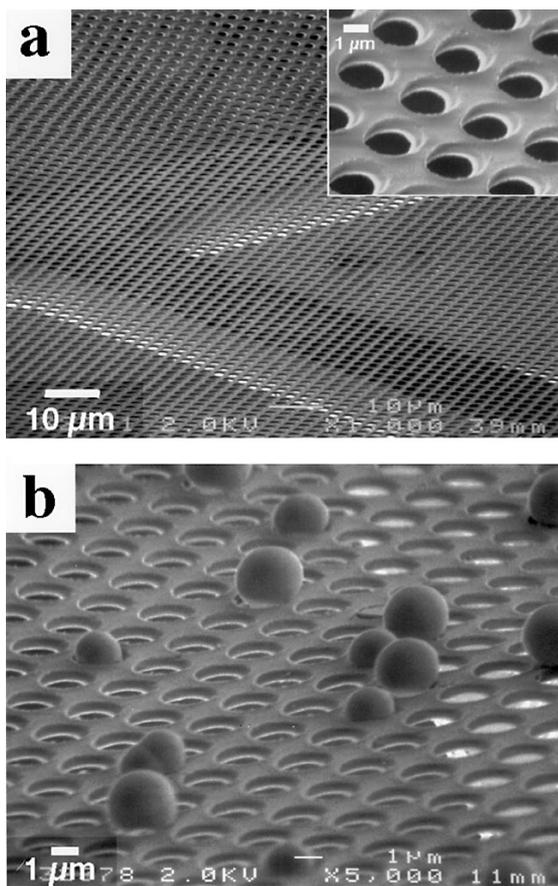


Fig. 3. a) Scanning electron micrograph of a membrane of titanosilicate glass (Ti/Si = 0.07) supported on a copper TEM grid. The thickness of the membrane is 0.2 μm . b) The same membrane, after passing an aqueous suspension of 2 μm silica beads through it.

step at a temperature where the viscosity is low enough to allow the relaxation of the roughness. This temperature can be reduced by adding boron oxide to the silica. Micro-contact molding could generate homogeneous ridge waveguides in a one-step process.

Figure 4a shows an array of aluminosilicate ridge waveguides. The composition of the glass, as given by XPS, is 8% atomic ratio Al:Si. The structure was annealed at 1100 $^{\circ}\text{C}$. The shrinkage of the lines was highly anisotropic, due to the good adhesion with the substrate. The bottom of the line remained undeformed and kept its original width of 2 μm . The width at the top of the line decreased by a factor 2 and the height of the line decreased from 2 μm to 1.4 μm during annealing. This value is consistent with the expected volume contraction due to the evaporation of the solvent and the elimination of the pores.^[5] A precise measurement of the index of refraction of the aluminosilicate glass could not be made because the growth of the underlying thermal silicon oxide layer was not controlled during the annealing.

The waveguiding behavior of the aluminosilicate lines was characterized by coupling a 633 nm light beam into one end of a 5 mm long line and imaging the other end.

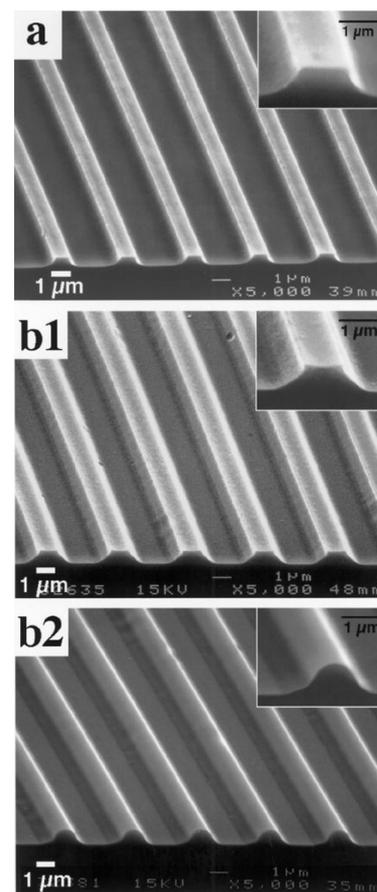


Fig. 4. Scanning electron micrographs of a) aluminosilicate (Al/Si = 0.09) ridge waveguides on Si/SiO₂; b) borosilicate (B/Si = 0.1) lines on Si/SiO₂ annealed for 10 min at 800 $^{\circ}\text{C}$ (b1) and 900 $^{\circ}\text{C}$ (b2).

The lines appeared to be single-mode waveguides with slight coupling between adjacent lines.^[17]

Figure 4b shows a borosilicate line at different stages of sintering. The composition of the glass was found by XPS to be 9% B₂O₃ and 91% SiO₂. Whereas pure sintering seemed to occur at 800 $^{\circ}\text{C}$, the cross-section of the line changed dramatically after annealing at 900 $^{\circ}\text{C}$, due to the melting of the glass. In this case, we expect the edge of the waveguide to be much smoother and scatter the light less than the unsmoothed waveguides. Since the index of refraction of borosilicate is lower than that of the silica substrate, those lines did not have waveguiding properties.

By molding a sol-gel precursor solution between a substrate and an elastomeric mold, we were able to fabricate microstructures made of different glasses; the procedure typically required a few hours, not counting the time required for thermal consolidation and annealing. This method can reproduce features present in the mold that are as sharp as 50 nm in radius. Free-standing membranes have been fabricated and have shown good mechanical properties. Supported waveguides have also been produced. Provided that the structures were small enough (smaller than 2 μm) and the adhesion with the substrate was good, breakage did not occur during the annealing step. In the case of supported

structures, the shrinkage was anisotropic and changed the shapes of the features. By contrast, free structures were annealed with an isotropic shrinkage that did not perturb even very small features of the pattern.

In summary, this method seems promising as a complement to conventional combinations of photolithographic and reactive ion etching (RIE) methods for production of glass micro- and nanostructures. It is, however, limited to structures with an aspect ratio between ca. 0.5 and 2, because of the compliance of the mold. Furthermore, the deformability of the elastomeric mold may make it difficult to control the long-range order of the structures. The real limits to registration and achievable pattern resolution have, however, not been quantified yet.

Experimental

Materials: Silicon wafers (Silicon Sense, MA) were cleaned briefly in a O_2 /plasma cleaner before use. Aluminum (99.99 %, Alfa) coated wafers were prepared by electron-beam evaporation. Tetramethylorthosilicate and di-*sec*-butoxyaluminumoxytriethoxysilane (United Chemicals), titanium isopropoxide and boron trioxide (Aldrich), oxalic acid and acetonitrile (Fisher) were used as received. The elastomeric molds were prepared by casting the silicone precursor (Sylgard 184, Corning, NY) on masters prepared by regular photolithography [18].

Patterned Solid: A 50 nm thick gold film was prepared on a (100) silicon wafer primed with 2 nm of titanium by electron-beam evaporation. A monolayer of hexadecanethiolate was patterned on the wafer using micro-contact printing so that the resulting pattern presented uncovered $2 \mu\text{m}$ squares [18]. The unprotected gold was removed with a cyanide etch [18]. The native silica oxide layer was then removed by etching in 2 % HF for 30 s. The silicon was etched in a 40 wt.-% solution of KOH in water and isopropanol; this anisotropic etch generated pyramidal pits. The remaining gold was removed with aqua regia. The surface of the resulting textured solid was treated by putting the wafer under static vacuum with a drop of (tridecafluoro-1,1,2,2-tetrahydro-octyl)-1-trichlorosilane for 30 min. This compound polymerized on the surface and made a layer that reduced adhesion to the surface.

A mixture of 6.5 g TMOS and 1.5 g of water acidified to pH 1 by adding oxalic acid was stirred for 1 min and left at room temperature for 1 h. (We will refer to this solution as sol A throughout the paper. This solution can remain fluid and clear for days.) The mold was prepared by putting a 1 cm^2 piece of the textured wafer in a plastic petri dish. Just before casting in the mold, 5 drops of aqueous ammonia (pH 11) were added to 3 g of sol A. The wafer was covered with 0.5 mL of this solution. The preparation was then placed in a closed 100 cm^3 container for 24 h. The solid structure was not adhering to the mold at this point and was carefully removed. It was then dried slowly at room temperature for a week, then at 60°C for 2 days. It was finally annealed at 1100°C for 10 h.

Membrane: We allowed 3 g of sol A to react at room temperature for 12 h. A solution of 0.34 g of titanium isopropoxide in 0.5 g of acetylacetone and 3 g of acetonitrile was added. One drop of this solution was placed on a freshly cleaned, aluminum-coated silicon wafer and the 1 cm^2 elastomeric mold was immediately pressed against the surface. The whole structure was placed in a closed 100 cm^3 container with one drop of aqueous ammonia (30 %). The ammonia vapors diffused slowly through the elastomer into the sol and induced gelation. The mold was removed after 12 h. The glass film remained on the wafer and was annealed at 400°C for 10 min. The aluminum support was then removed by etching in a 8:1 mixture of phosphoric acid and nitric acid to release the membrane.

Optical Waveguides: We added 0.5 g of di-*sec*-butoxyaluminumoxytriethoxysilane to 3 g of sol A. After stirring for 6 h, 3 g of acetonitrile was added to the clear solution (sol B). A solution of 0.8 g of trimethylborate in 3 g of acetonitrile was added to 3 g of sol A and left at room temperature for 1 h (sol C).

One drop of the solution (sol B or C) was placed on a freshly cleaned silicon wafer bearing a $2 \mu\text{m}$ thick thermal oxide layer. The 1 cm^2 elastomeric mold was immediately pressed against the surface. The whole structure was placed in a closed 100 cm^3 container with one drop of aqueous ammonia

(30 %). After 18 h, the mold was removed and the structure was consolidated by annealing for 3 h at 1100°C (for sol B) and 15 min at 800°C or 900°C (for sol C).

Received: May 13, 1997

Final version: November 21, 1997

- [1] J. L. Wilbur, E. Kim, Y. Xia, G. Whitesides, *Adv. Mater.* **1995**, 7, 649.
- [2] Y. Xia, J. Tien, D. Qin, G. M. Whitesides, *Langmuir* **1996**, 12, 4033.
- [3] M. Toki, S. Miyashita, T. Takeuchi, S. Kanbe, A. Kochi, *J. Non-Cryst. Solids* **1988**, 100, 479.
- [4] J.-L. R. Noguès, R. L. Howell, *Proc. SPIE* **1992**, 1751, 214.
- [5] C. J. Brinker, G. W. Scherer, *Sol-Gel Science*, Academic, San Diego, CA **1990**.
- [6] H. Dislich, in *Transformation of Organometallics into Common and Exotic Materials* (Ed: R. M. Laine), Nijhof, Dordrecht, **1988**, Vol. 141.
- [7] T. Tani, D. A. Payne, *J. Am. Ceram. Soc.* **1994**, 77, 1242.
- [8] S. D. Ramamurthi, S. L. Swartz, K. R. Marken, J. R. Bush, V. E. Wood, *Mater. Res. Soc. Symp. Proc.* **1992**, 271, 351.
- [9] W. Peiyang, L. Meidong, R. Yunhua, Z. Yike, J. Nan, *Sens. Actuators A* **1995**, 49, 187.
- [10] R. P. Rao, *J. Electrochem. Soc.* **1996**, 143, 189.
- [11] Y.-M. Li, T. Kudo, *Sol. Energy Mater. Sol. Cells* **1995**, 39, 179.
- [12] S. Wallace, L. L. Hench, in *Better Ceramics Through Chemistry* (Ed: C. J. Brinker, D. E. Clark, D. R. Ulrich), Materials Research Society, Pittsburgh, PA **1984**, p. 47.
- [13] H. Schmidt, G. Rinn, R. Nass, D. Sporn, in *Better Ceramics Through Chemistry* (Ed: C. J. Brinker, D. E. Clark, D. R. Ulrich), Materials Research Society, Pittsburgh, PA **1988**, p. 743.
- [14] F. Brochard-Wyart, P.-G. de Gennes, *J. Phys.: Condens. Matter* **1994**, 6, A9.
- [15] I. Barycka, I. Zubeł, *Sens. Actuators A* **1995**, 48, 229.
- [16] A. S. Holmes, R. R. A. Syms, M. Li, M. Green, *Appl. Opt.* **1993**, 32, 4916.
- [17] C. Marzolin, S. P. Smith, M. Prentiss, G. M. Whitesides, unpublished.
- [18] A. Kumar, G. M. Whitesides, *Appl. Phys. Lett.* **1993**, 63, 2002.

The Use of Soft Lithography to Fabricate Arrays of Schottky Diodes**

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Soft lithography is developing rapidly as a new approach to microfabrication.^[1-8] Although it has been applied most actively to optical^[9,10] and microanalytical systems,^[11] it also has potential for application in microelectronic devices.^[12] While it is improbable that it will compete with photolithography-based techniques for conventional, planar silicon devices having feature sizes $>100 \text{ nm}$, it is attractive for less familiar device structures: non-planar and

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[**] This research was supported in part by the ONR and DARPA, and by APO Grant DAAH04-95-0102. It made use of MRSEC shared facilities supported by NSF Grant DMR-94-00396. The authors thank Dong Qin and Xiao-Mei Zhao for helpful discussions.