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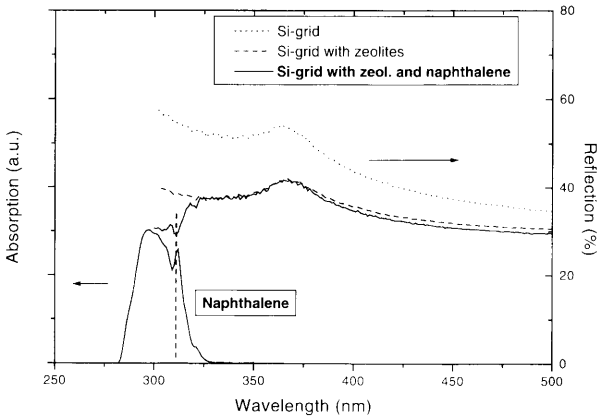

Fig. 3. UV/vis reflectance spectra of filled and unfilled ZSM-5 zeolites aligned in silicon grids. For reference, the absorption spectrum of naphthalene dissolved in toluene is also shown.

spectrometer[28] with an integrating sphere was used to perform reflection experiments.

The reference (absorption) spectra of naphthalene dissolved in toluene is shown in the lower part of Figure 3. The absorption peak at 311 nm is consistent with the literature value.[29] The upper three curves represent the reflection spectra of the silicon grid, the silicon grid with fixed zeolites and the silicon grids with filled zeolite channels, respectively. The fixation procedure of zeolites leads to a decrease in reflection of about 5–10 %, but qualitatively there is no observable difference between the empty and filled silicon grid in reflectance.

On the other hand, an additional absorption at 311 nm can be seen when the zeolites are filled with naphthalene. We attribute this absorption to the naphthalene in the channels. This clearly shows that the pores of the zeolite crystals are not clogged by the fixation process with tetramethoxysilane.

In conclusion, we have developed a suitable technique to uniquely order large numbers of zeolite crystals by means of artificially produced surface structures. This method provides the possibility of aligning small zeolites with the advantage of a dense two-dimensional packing comparable to a single crystal layer. The ordering method is of great universality and can be used to order micrometer-sized particles or crystals. The only restriction is that the particles must not stick together.

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Fabrication of Arrays of Channel Waveguides by Self-Assembly Using Patterned Organic Monolayers as Templates**

By *Enoch Kim, George M. Whitesides,* Larry K. Lee, Stephen P. Smith,* and *Mara Prentiss**

Optical waveguides[1,2] are structures that confine and guide light waves. They are important in a range of applications: communication lines, photonic sensors (bio-,[3] chemo-,[4,5] and fluoro-sensors[6]), and components of optical devices[7] such as couplers, splitters, and interferometers. In particular, channel waveguides[8] allow high integration density, unambiguous sensing field, and spatial multiplexing in optical systems. These channel (or strip) waveguides are fabricated by dry etching,[9,10] localized ion exchange,[11] laser-densification of sol-gel films,[12] direct laser writing,[13] and conventional photolithographic techniques.[14–16]

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In this Communication, we suggest a new approach to the fabrication of channel waveguides based on self-assembly, and we demonstrate this approach by the fabrication of multi-mode optical waveguides. This approach is based on the self-assembly of a polymer (as a liquid prepolymer) on a template, which in turn is prepared by microcontact printing (μCP)[17–19] of self-assembled monolayers (SAMs) of alkanethiolates on a thin gold film. The procedure thus uses self-assembly at two scales: the formation of SAMs on gold at the molecular scale and the fabrication of the polymeric waveguide that forms on these patterned SAMs[20] at the mesoscopic scale. Strategies based on this self-assembly offer the potential of substantial simplification of fabrication and reduction of cost, relative to most existing procedures that involve multiple steps and longer fabrication time.

Figure 1 outlines the procedure used to prepare the multimode organic waveguides using μCP.[17–19] An elastomeric stamp made of poly(dimethylsiloxane) (PDMS) was "inked" with $HS(CH_2)_{15}CH_3$ (1 mM in ethanol). After the solvent had evaporated, the thiol was transferred to a gold film (250 Å on silicon primed with 10 Å of Ti) by bringing the stamp and the gold into contact, and a patterned SAM of hexadecanethiolates formed. After the stamp had been removed, the surface was washed with an ethanolic solution of $HS(CH_2)_{15}COOH$ (1 mM, 2 mL) to render the rest of the surface hydrophilic by forming a SAM from this carboxylic acid-terminated thiol. A drop of prepolymer of polyurethane (J-91, Summers Optical) was placed on the patterned gold surface. When the excess polymer was removed (either by tilting the surface to drain off the excess or by blowing it off using a gentle stream of nitrogen), the remaining polymer selectively wetted and covered the hydrophilic regions (–COOH) of the surface[21] and left the hydrophobic regions ($-CH_3$) bare.[22] This simple procedure of dewetting was reproducible and fabricated waveguides on >95% of the patterned surface.

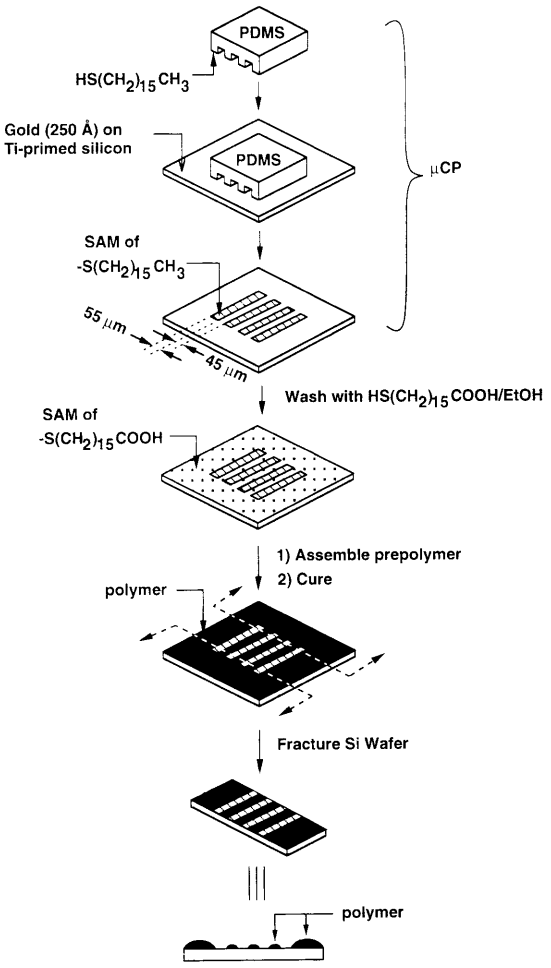

Fig. 1. Schematic representation of the fabrication of channel waveguides on the hydrophilic (carboxylate-terminated) regions of the patterned SAM.

The prepolymer was cured by exposing it to UV light (from a Hg vapor lamp, 450 W, medium pressure) at 5 cm for 30 min. During curing, the volume of the prepolymer changed only slightly (< 1%), and the overall shape and the contact angle (the angle at which the liquid prepolymer wetted the surface) were retained. This process created an array of 1.5 cm long waveguides, approximately 45 μm wide and 3 μm high. After the polymer was cured, we cleaved the substrate in the direction perpendicular to the long axes of the waveguides by scoring and then stressing the silicon.

The electron micrograph in Figure 2 shows a number of nearly identical structures (Fig. 2a; typically, we prepared 50–100 waveguides of the same size in a single set of steps).

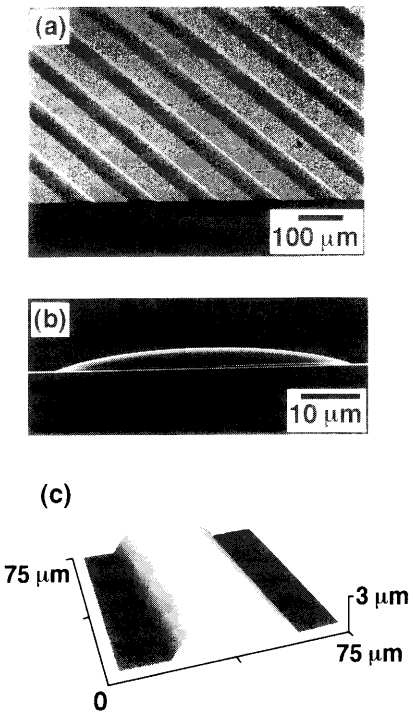

Fig. 2. SEM and AFM images of waveguides. Polymeric waveguides were sputtered with gold before analysis by scanning electron microscopy. Images (a) and (b) are both of the same structures; (b) is a high resolution image of one of the fractured ends. Image (c) is by AFM, and confirms the dimensions inferred from (b).

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Figure 2b shows the profile of one waveguide at a higher magnification. More detailed information about the profile of the waveguide was obtained by atomic force microscopy (AFM) of one of these waveguides (Fig. 2c). It is approximately 45 μm wide and 3 μm high. By controlling the dimension of the stamped pattern and the free energy of the liquid–vapor (or liquid–liquid, if the waveguides are formed in a second liquid phase) interface, these dimensions can be controlled over a wide range (< 1 μm to 1 mm). A waveguide with these particular dimensions should be able to support approximately upwards of 200 modes in the plane parallel to the substrate and 10 modes in the plane perpendicular to the substrate when using 633 nm light.[23]

To demonstrate optical guiding, we first coupled a He-Ne laser (633 nm) into a single-mode glass fiber (3.7 μm diameter) and butt-coupled the fiber against the cleaved end of the waveguides. An index-matching fluid was used to reduce reflection from both the output end of the fiber and the input end of the waveguide. With a beam block above and the silicon substrate below the waveguides to block off light, only the light passing through the waveguide was projected onto a diffuser in the far field.

When the laser beam was viewed alone, a circularly symmetric Gaussian output was observed as expected (Fig. 3a). In contrast, Figure 3b shows the multi-mode asymmetric output from one of the waveguides, and indicates that the beam is indeed being guided through this waveguide. The approximately 15:1 (vertical:horizontal) asymmetrical output is in good agreement with the 45:3 (μm; horizontal:vertical) dimensions of the waveguides. Different transverse modes of propagation could be selected by changing the relative orientation of the fiber and waveguide slightly (Fig. 3c).

A more graphic demonstration of these waveguides is shown in Figure 4a, where a significant angle was introduced between the axes of fiber and waveguide. Figure 4b shows the same set-up with the only source of light being the optical fiber; the beam turns a sharp (7°) corner when it leaves the fiber and enters the waveguide. Mismatch in the modes of the fiber and the waveguide led to initial propagation of lossy modes in the waveguides and resulted in scattering in the initial section (~ 2 mm) of the waveguide. Once these lossy modes scattered out, however, there was very little visible scattering from the waveguide, indicating that the waveguides are low loss.

Due to the metallic layer underneath these waveguides, only the waveguide modes with electric fields parallel to the metallic underlayer were transmitted with low loss. The polarization mode perpendicular to the metallic layer experienced a very large loss, and thus, the output of the waveguide is nearly linearly polarized, independent of the input state of polarization. Total transmission efficiencies (i.e., the coupling efficiency times the transmission efficiency across the waveguide) as large as 25 % have been observed. The output from the polymeric waveguide can be further coupled into another fiber (a multi-mode glass fiber having

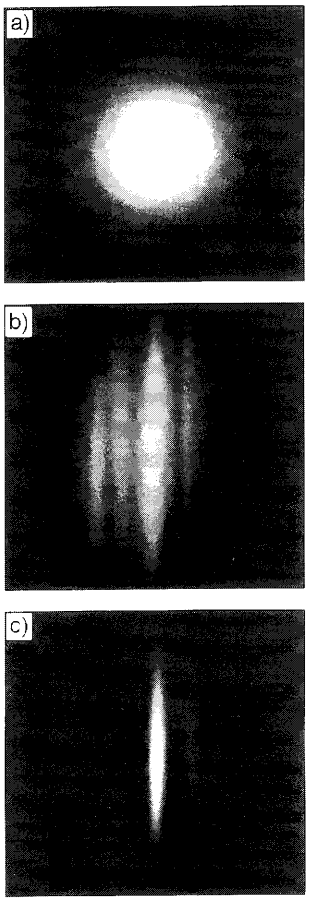

Fig. 3. Laser output from waveguides. The outputs were projected on a diffuser 30 cm away from the source. a) The output from a single-mode fiber. b) The output from a waveguide, after the beam from the fiber has propagated through the waveguide (1 cm). c) Another output from a waveguide, at a different relative orientation of the fiber and waveguide.

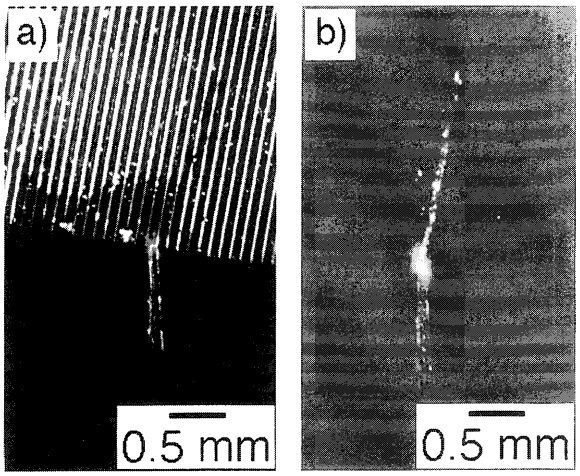

Fig. 4. Coupling of the fiber and waveguide at an angle. a) End-to-end coupling of the fiber and waveguide at an angle, with the light illuminating the region directly above the waveguides. b) The same set-up as (a), except the light is turned off.

50 μm core diameter), with about 40 % efficiency. The major loss in optical power in our experiments came from scattering due to inefficient coupling, and we expect the overall efficiency to be much higher with optimal coupling between the fiber and waveguide.

The waveguides fabricated by self-assembly can be used as sensors. As one demonstration of principle, we used the waveguide to detect the difference in index of refraction between the waveguide and the region surrounding it. First, light (He-Ne laser, 633 nm) from a single-mode fiber was butt-coupled into a polymeric waveguide, and the output from the waveguide was butt-coupled into a multi-mode fiber that deposited the light onto a remote photo-detector. When air surrounded the waveguide, the detector voltage reflecting the transmitted intensity was 1.2 ± 0.05 V. When water replaced the air, the detector voltage fell to 0.43 ± 0.03 V: a change in external index from 1.0 to 1.3 thus reduced the intensity of the transmitted light by 65 %. The transmission intensity returned to 1.2 V when the water was removed from the surface of the waveguide. If the refractive index of a medium that surrounds the waveguide is closer to that of polyurethane (1.492), the change in transmission intensity should be even larger.

Microcontact printing and self-assembly of solid, three-dimensional polymeric structures from liquid precursors suggest a new approach to the fabrication of waveguiding structures. Preliminary results suggest that this technique can be extended to smaller dimensions for the fabrication of single-mode waveguides. Because μCP is a flexible technique, it is possible to generate the patterned surface on which the waveguide forms with a high level of control over dimensions and shapes; generating complex arrays of waveguides is also straightforward. Fabrication of optical waveguides on a metallic substrate is not ideal, however. Since μCP can be used to pattern SAMs on glass and Si/SiO_2, this process may even be extended to insulating substrates. We have so far fabricated and demonstrated the properties of multi-mode waveguides only with polyurethane, but this strategy for fabrication can certainly be extended to many different organic polymers, including those with nonlinear optical, electrooptical and mechano-optical properties. The ability to form waveguides from organic polymers may also make possible the fabrication of other classes of useful structures that combine the surface functionalization of the organic polymer with waveguiding, such as evanescent wave sensors and directional couplers.

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Continuous Yttria-Stabilized Zirconia Fibers**

By *Bernd Clauss*, *Andrea Grüb*, and *Wilhelm Oppermann**

The availability of continuous ceramic fibers has had a major impact on the development of new high performance materials. Ceramic fibers can be used in metal matrix as well as in ceramic matrix composites, as high temperature insulation materials or as components in microstructural applications. Although many research activities have recently been focused on non-oxide fibers of the Si-C-N-O type[1–4] or the Si-Ti-C-O type[2–5] and on single-crystal oxide fibers[3] for temperatures above 1400 °C, the potential of polycrystalline oxide fibers has not yet been sufficiently examined. There is a demand for different types of fibers in order to check their properties for the applications mentioned above. Currently there are only a few continuous polycrystalline oxide fibers on the market, and these are all based on Al_2O_3.[2–4]

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