Integration of polymer waveguides for optical detection in microfabricated chemical analysis systems

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Multimode polymer waveguides and fiber-to-waveguide couplers have been integrated with microfluidic channels by use of a single-mask-step procedure, which ensured self-alignment between the optics and the fluids and allowed a fabrication and packaging time of only one day. Three fabrication procedures for obtaining hermetically sealed channels were investigated, and the spectrally resolved propagation loss (400–900 nm) of the integrated waveguides was determined for all three procedures. Two chemical absorbance cells with optical path lengths of 100 and 1000 μm were furthermore fabricated and characterized in terms of coupling loss, sensitivity, and limit of detection for measurements of the dye bromothymol blue. © 2003 Optical Society of America

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1. Introduction

The interest in microfabricated devices for biochemical sensing has increased rapidly during the past decade. This is mainly because of the enticing prospect of performing a total chemical analysis with a single device.1,2

The vast majority of devices for chemical analysis that rely on optical detection schemes have so far used bulk optical elements for control of the light path. This is a drawback in terms of packaging because of alignment problems and shock stability. Free-space optical elements are, furthermore, often difficult to miniaturize. Planar optical waveguides monolithically integrated with microfluidic channels may offer a viable solution to these problems. Insertion of optical fibers in etched grooves has also been done by a number of groups, but this approach allows only a single detection point per fiber and is thus of limited use for complex devices.3–5

Devices based on integrated silicon nitride or doped silicon dioxide waveguides have been presented in recent years. They were fabricated by use of silicon micromachining techniques such as thin-film deposition and anisotropic etching with the use of two to four photolithographic mask steps.6–8 The fabrication procedures were relatively complicated and took at least a couple of weeks. The motivation for the study presented here is therefore to significantly reduce the system costs by use of polymer waveguides instead of waveguides based on silicate glass.

Integration of polymer waveguides with microfluidic channels has previously been reported by McMullin9 and Lee et al.10 McMullin used UV laser writing of optical adhesive spun onto a glass substrate for waveguide and microfluidic channel fabrication. The waveguides in the study of Lee et al.10 consisted of a photoresist (SU-8; MicroChem, Massachusetts, U.S.) core layer and a cladding layer of spin-on glass. The buried channel waveguides were fabricated when a prefabricated silicon-channel network was filled with both materials.

In this study the negative photoresist SU-8 was chosen as the structured layer because it has been widely used for fabrication of microfluidic devices.9,11–13 Layers with a thickness of approximately 100 μm can also be readily fabricated with a high aspect ratio by use of standard equipment.14,15

The emphasis in this paper is on the design, fabrication, and optical characterization of the integrated planar waveguides in terms of propagation loss by employment of different fabrication schemes. Two chemical absorbance cells were, furthermore, fabricated and characterized in terms of coupling loss, sensitivity, and limit of detection for measurements of the dye bromothymol blue.
2. Design

The bottom and top substrates were used as waveguide buffer and cladding layers, respectively (Fig. 1), to make the process as simple as possible. The SU-8 layer was surrounded by air on two sides and glass or polymer substrates on the top and bottom. Waveguidance by means of total internal reflection was therefore obtained in the SU-8 layer \((n = 1.59 \text{ at } 633 \text{ nm})\) because of a higher refractive index. The mask design consisted of microfluidic channel walls, optical planar waveguides, and fiber-to-waveguide coupler structures (Fig. 2).

A. Microfluidic Channels

The channel network was designed for capillary electrophoresis experiments\(^{16,17}\) and consisted of an injection cross, a separation channel, and two types of absorbance cell. The first type used the width of the channel as the optical path length. For the second type of absorbance cell (lower part of Fig. 2), the length of a 1000-\(\mu\)m microfluidic channel segment was used for detection, in order to increase the path length.

The mask design consisted of devices with channel widths of 30 and 100 \(\mu\)m. The channels were defined on each side by bonding regions (1–2 mm wide) of the remaining SU-8. This design strategy was chosen because it permits fabrication of all fluidic and optical elements in a single patterning step, which significantly reduces the fabrication time compared with other approaches, such as the filling of prefabricated channels with a high refractive-index material.\(^{19}\) A similar approach has been presented a few times previously. Foquet \textit{et al.}\(^{18}\) fabricated a device with silicon dioxide waveguides intended for single-molecule detection. Friis \textit{et al.}\(^{19,20}\) and Mogensen \textit{et al.}\(^{21}\) used doped silicate glass waveguides for applications in the visible and UV range. McMullin\(^9\) integrated laser-written polymer waveguides in microfluidic devices. No chemical measurements with the integrated waveguides were presented for the devices of Foquet \textit{et al.}\(^{18}\) and McMullin.\(^9\)

B. Planar Waveguides

The waveguides in this study are used for absorbance detection based on intensity modulation. It is therefore not necessary to use single-mode waveguides. The waveguides were made as wide as feasible to increase the transmitted optical power in the devices because this increases the signal-to-noise ratio (see Section 5). An additional advantage of multimode waveguides is that the alignment tolerances are relaxed, thereby reducing the packaging costs. A chip size of 3.0 cm \(\times\) 4.0 cm made a bend radius of 1.5 cm reasonable for the desired waveguide structures (Fig. 2). Bends of 20 deg were included to ensure that mainly guided light would be collected by the output fiber. As a rule of thumb, the ratio between the bend radius and the half-waveguide width was chosen to be 1000, so radiation losses would not be dominating.\(^{22}\) These considerations were the basis for choosing a waveguide width of 30 \(\mu\)m. The waveguides had air as the side cladding, which is advantageous in terms of bend loss, because a high refractive-index contrast reduces the radiation loss in the bend and hence allows smaller bend radii.\(^{22}\) This makes it possible to make more compact devices, compared with systems based on buried channel silicate glass waveguides.\(^6,8\) A disadvantage is that an increase in the refractive-index contrast results in an increase in scattering loss.\(^{22}\)

C. Fiber-to-Waveguide Coupler Structures

Fiber-to-waveguide couplers designed for accommodation of commercially available fibers were, furthermore, defined in the same exposure step to facilitate easy optical packaging. The fiber-to-waveguide couplers consisted of a tapered groove, which was aligned to a planar waveguide to ensure self-alignment between the fiber and the waveguide. A similar fiber-coupling design has previously been used by Eldada \textit{et al.}\(^{22}\) and by McMullin.\(^9\) Figure 3
shows a microscope picture of two coupler structures, one with an inserted optical fiber.

The covering lid would always extend over the coupler regions, to ensure that the fibers were also aligned in the vertical direction. The minimum thickness of the polymer pattern, and hence the height of the waveguides and the depth of the channels, was determined by the outer diameter of the optical fiber because otherwise it would not be possible to insert a fiber into the coupler groove. The couplers were therefore designed to fit a thin commercially available fiber, which had an outer diameter of only 68 μm and a core diameter of 50 μm (FVP050055065, Polymicro Technologies, Phoenix, Arizona, U.S.). The coupler groove was 80 μm wide toward the planar waveguide and 200 μm wide at the end where the fiber was inserted. The length of the taper was 5 mm.

3. Fabrication and Packaging

The device fabrication was carried out on 4-in. (1 in. = 2.54 cm.) substrates and relied on standard photolithography. The procedures for the fabrication of the devices are shown in Fig. 4. The fabrication procedures can be divided into three steps as depicted in Fig. 4. These steps, which are described in more detail below, are (a) preparation of the substrate, (b) patterning of the SU-8 photoresist, and (c) bonding of a lid. The steps, including packaging of the device, can be finished in a single day. Steps (a) and (b) were the same for all devices, but three procedures in step (c) were investigated because bonding of a lid was the most difficult part of the fabrication.

A. Preparation of the Bottom Substrate

Borofloat glass wafers or silicon wafers with thermally grown silicon dioxide were used as the bottom substrate. The Borofloat glass wafers (Pyrex, Corning) had a refractive index of \( n = 1.474 \) (at 589 nm) and were transparent in the visible range. They could therefore be used directly as the waveguide buffer layer, in contrast to the silicon wafers, for which a 2.5-μm-thick silicon dioxide layer was grown by annealing at 1100 °C in water vapor for 16 hr (\( n = 1.46 \) at 633 nm). The Borofloat glass wafers were cleaned in a Piranha solution (\( \text{H}_2\text{O}_2:\text{H}_2\text{SO}_4 = 3:1 \)) for 10 min and subsequently baked at 200 °C for 2 hr to remove water from the glass, which improved the adhesion of the photoresist.

B. Patterning of the SU-8 Layer

A 90-μm SU-8 layer (SU-8-2075, MicroChem) was spun onto the wafers with a rotational speed of 1800 rpm for 30 s. The wafers were subsequently baked at 95 °C for 25 min before exposure. The exposure was done at a wavelength of 365 nm with a lamp intensity of 8.5 mW/cm². The exposure was performed as 15-s illuminations with a break of 10 s between each illumination step. This was done seven times to obtain a total dose of 892.5 mJ/cm² without overheating the chip. A postbaking step of
25 min at 95°C was carried out before development for 6 min in a propylene glycol-monomethylether-acetate solution (MicroChem).

C. Bonding

Three types of bonding procedure were investigated (Fig. 4). The first procedure was UV-activated adhesion bonding of a Borofloat glass lid with the use of a thin film of SU-8 as an intermediate layer. This type of bonding was investigated because it has been widely used for microfluidic devices with SU-8 channel sidewalls. A 5-µm-thick SU-8 layer (SU-8-2025, MicroChem) was spun onto a Borofloat glass wafer with prefabricated throughholes after the wafer was rinsed in a Piranha solution for 10 min and treated in an oxygen plasma for 15 min at 500 W. The wafer was subsequently prebaked at 80°C and a slight pressure was applied to bring the substrate with the SU-8 layer toward the waveguide W. The lid was carefully placed onto the bottom substrate by a 5-min oxygen plasma treatment at 200 W. The bottom substrate was made hydrophilic prior to bonding by a 5-min oxygen plasma treatment at 200 W. The lid was carefully placed onto the bottom substrate with the SU-8 layer toward the waveguide pattern, and a slight pressure was applied to bring the wafers into contact. The assembled wafer pair was subsequently prebaked at 80°C for 15 min. Cross linking of the resist was achieved by UV exposure through the lid for 30 s and postbaking at 95°C for 15 min.

The second procedure, which also employed adhesion bonding, was the fastest. In this case, a 60-µm-thick laminating foil (GHQ120 crystal clear laminating film, GMP, Germany) with CO2-laser-fabricated throughholes was placed onto the substrate. The lid was laminated onto the substrate at 120°C–125°C with a lamination speed of 5 mm/s. In both these procedures the parameters were chosen as a trade-off between achieving a strong bond and avoiding clogging of especially, narrow channels (<100 µm). In the case of SU-8 bonding, increasing the hydrophilicity of the surfaces and increasing the thickness of the SU-8 adhesion layer (on the lid) results in a better bond but also increases the risk of SU-8 being dragged into the channels owing to capillary forces. This becomes increasingly problematic for narrower channels because blockage can already occur with less material and because the capillary forces are stronger. Similar concerns must be taken into consideration for the lamination process in which an increase in temperature and a decrease in the lamination speed result in improved bonding but also in a higher risk of blockage. It was, however, possible with both methods to fabricate 100-µm-wide sealed channels that were not blocked.

No clogging of the channels was experienced with the third method, in which polydimethylsiloxane (PDMS) was used as the lid material. A 10:1 mixture of Sylgard 184 (Dow Corning, Michigan, U.S.) and its curing agent was spun on a 15-mm-thick (poly)methyl methacrylate substrate with CO2-laser-machined throughholes. The layer thickness was approximately 100 µm and was achieved via spinning at a rotational speed of 600 rpm for 30 s. The PDMS was subsequently cured at 70°C for 2.5 hr. The SU-8 pattern of the bottom substrate was made hydrophilic by an oxygen plasma treatment at 200 W for 5 min before assembly of the lid. The bond strength was improved by clamping the two substrates together in a metal holder with spring-mounted screws.

The devices were finally packaged, which involved insertion of optical fibers into the coupler structures and gluing of liquid reservoirs over the inlet holes. The presence of the fiber-to-waveguide coupler structures made it possible to insert the fibers without the use of a micropositioner, which significantly reduced the packaging time.

4. Waveguide Propagation Loss

The different bonding procedures had a strong influence on the waveguide properties because the lid also served as the waveguide cladding layer. The spectrally resolved propagation loss was determined for all three types of bonding procedure. The results are shown in Fig. 5 for waveguides with a width of 30 µm, a height of 100 µm, and a refractive index of n = 1.59 (at 633 nm).

Each graph was obtained by measurement of the transmission spectrum from 190 to 910 nm (Spectro 320, Instrument Systems, Munich, Germany) of waveguides with lengths of 2.52, 3.52, 4.02, and 4.52 cm that were otherwise identical in terms of materials and fabrication conditions. The spectra were normalized to a reference spectrum of the light source, and the total waveguide insertion loss was calculated. A linear fit of the insertion loss versus the waveguide length was subsequently calculated for each data point to obtain the propagation loss as a function of the wavelength. The error on the fit is included at intervals of 100 nm (Fig. 5).

It is seen from Fig. 5 that the waveguides with a PDMS top cladding layer (n = 1.43) had the lowest propagation loss. The loss was 1.4 dB/cm at 633 nm and 0.8 dB/cm at 850 nm. Two other groups have presented measurements on the propagation loss of SU-8-based channel waveguides. Lee et al. achieved a propagation loss of 4 dB/cm at 633 nm, and Curtis et al. reported a loss of 6.2 dB/cm at 850 nm. McMullin achieved a propagation loss of 5
dB/cm at 633 nm for integrated waveguides based on a UV-curable optical adhesive.

Figure 5 also shows that the waveguides with a lamination foil as the cladding layer had a higher propagation loss below approximately 800 nm than the waveguides with the PDMS cladding layer. The difference between the two types of waveguide is also seen to be getting larger for shorter wavelengths. The reason for the increased propagation loss is attributed to thermal degradation or “yellowing” during the lamination process because the substrate was heated to 120°–125°C compared with a maximal processing temperature of 95°C for the waveguides with a PDMS cladding. Because thermal degradation is a well-known problem for polymer waveguides, the thermal stability was initially tested when the wafer was postbaked at 180°C for 35 min after development of the SU-8 pattern. A PDMS cladding layer was subsequently bonded on top of the waveguides, and the propagation loss was determined.

Figure 6 shows that baking the wafer at 180°C before bonding significantly increases the propagation loss compared with the waveguides baked at 95°C. The increase is also larger for shorter wavelengths, which is in accordance with the result for the laminated waveguide in Fig. 5. The thermal stability of the SU-8 waveguides in this study is very poor, at least compared with waveguides fabricated with other types of resist, for which a thermal degradation rate at 840 nm of only 9.22×10^{-5} dB/(cm hr) was achieved. The degradation rate at 840 nm derived from Fig. 6 is 3.4 dB/(cm hr). The high value might be due to increased cross-linking of the resist.

Figure 5 shows, furthermore, that the waveguides with the Borofloat glass lid (bonded by use of a 5–10-μm-thick SU-8 adhesion layer) had approximately a 3-dB/cm higher propagation loss across the entire wavelength region. This is attributed to increased radiation loss because light was unguided in the upper part of the waveguide, where the SU-8 adhesion layer was used for bonding [see Fig. 4(c), left]. Some of the SU-8 from the adhesion might also be present on the sidewalls of the waveguide core, which would reduce the optical confinement even more. This is very likely the case because the waveguides were made hydrophilic before bonding by treatment in an oxygen plasma.

The propagation loss of 0.8 dB/cm at 850 nm for the integrated waveguides with the PDMS cladding is more than an order of magnitude larger than the loss obtained by other groups for single-mode waveguides developed for telecom applications. The high value is partly attributed to an increased contribution from scattering loss because high-order modes in multimode waveguides typically exhibit a higher scattering loss. A major fraction of the loss, especially below 700 nm, is also believed to be due to absorption in the SU-8 material. This can probably be significantly improved by use of a different type of polymer.

5. Chemical Absorbance Cells

Two types of absorbance cell were included in the chip design. In the simplest approach the channel width was used as the optical path length. This resulted in absorbance lengths of 30 and 100 μm. (Section 2). In the second approach a path length of 1000 μm was obtained by the coupling of light across a channel segment arranged in a turn. Figure 7(a) shows a photograph of light coupled across the width of a microfluidic channel, and Fig. 7(b) shows light coupled along a 1000-μm channel segment. The positions of the detection cells on the chip are indicated by circles on the mask design (Fig. 2).

Planar waveguides are present at both sides of the absorbance cell and were used for excitation and collection of the transmitted light. The microscope pictures were taken when the channel network was filled with a 170-μM fluorescein solution that was excited by the coupling of 488-nm light from an argon-ion laser into the excitation waveguide. The resulting fluorescence helps to visualize the light path.

Absorbance cells with lengths of 100 and 1000 μm were compared in terms of sensitivity and limit of detection for the dye bromothymol blue (Sigma-Aldrich, Denmark) at 633 nm when a calibration curve for each absorbance cell was acquired. The resulting plots are shown in Fig. 8. The absorbance values were calculated from the Lambert–Beer law \( A = \epsilon bc = \log(I_{ref}/I) \), where \( \epsilon \) is the molar absorptivity, \( b \) is the optical path length, \( c \) is the concentration of the absorbing solution, \( I \) is the transmitted optical power through the absorbing solution, and \( I_{ref} \) is the transmitted optical power with a nonabsorbing reference solution (such as water). The relatively large deviation on the fit for the 1000-μm-long absorbance cell is due to drift in the coupling between the He–Ne laser source and the fiber during the measurements. The values for the sensitivity and the limits of detection are collected in Table 1, together with the effective path length for each absorbance cell. The sensitivities, \( S \), are given by the slope of the calibration curves and were therefore obtained from the linear fit, and the limit of detection was defined for a signal-to-noise ratio of 3.
photometer was blue determined from measurements on the spectrophotometric molar absorptivity of the solution of bromothymol length that is shorter than the nominal length. The expected, which corresponds to an effective path results in a sensitivity of the detection lower than acted with the chemicals is unwanted because it re-

collection of stray light in the case of the 1000-
m-long absorbance cell. The coupling loss across the 1000-
m-long channel was smaller than for the 100-
m cell because of an increased coupling loss, which is the reason for the increase in baseline noise. The coupling loss across the 1000-
m-long absorbance cell was calculated by measurement of the transmitted optical power at 633 nm with water in the channel. The transmitted optical power through the device in this case was 5.5 nW. This value was compared with the transmitted power with a similar waveguide that was not interrupted by a channel (P = 500 nW), yielding a coupling loss of 20 dB (1% transmittance). The coupling loss

gating by comparison of the obtained sensitivities with measurements performed on a commercial spectrophotometer (negligible influence from collection of stray light). Collection of light that has not interacted with the chemicals is unwanted because it results in a sensitivity of the detection lower than expected, which corresponds to an effective path length that is shorter than the nominal length. The molar absorptivity of the solution of bromothymol blue determined from measurements on the spectrophotometer was \( \epsilon = 26,500 \, \text{M}^{-1} \, \text{cm}^{-1} \). The effective absorption lengths, \( b_{\text{eff}} \), were calculated from the Lambert–Beer law \( (S = \frac{dA}{dc} = \epsilon b) \) by division of the sensitivities with the value for the molar absorptivity, resulting in lengths of 113 and 906 \( \mu \text{m} \) (summarized in Table 1). A value higher than the nominal is possible when skew rays, which are reflected from the channel sidewalls, also get collected.\(^{28}\) The measurements shown in Fig. 8 indicate a minor influence from collection of stray light in the case of the 1000-\( \mu \text{m} \)-long absorbance cell.

The improvement in limit of detection from 30 to 15 \( \mu \text{M} \) when going from the 100- to the 1000-\( \mu \text{m} \)-long absorbance cell was only twofold even though the sensitivity increased by a factor of approximately 8. The discrepancy of approximately a factor of 4 originates from increased baseline noise during measurements with the 1000-\( \mu \text{m} \) cell, which also can be seen by comparison of the size of the error bars in Fig. 8. The origin of the increased baseline noise of the long absorbance cell was investigated by consideration of the relation between the variation of the baseline signal measured in absorbance units, \( \Delta A \), and the variation of the input parameters. This relation was found by differentiation of the Lambert–Beer law with respect to \( I_c \) and \( I_{\text{ref}} \):

\[
\Delta A = \frac{1}{\ln(10)} \left[ \left( \frac{\Delta I_c}{I_c} \right)^2 + \left( \frac{\Delta I_{\text{ref}}}{I_{\text{ref}}} \right)^2 \right]^{1/2}
\]  

(1)

It is seen from Eq. (1) that the variation of the baseline is inversely proportional to the transmitted optical power, \( I_c \) and \( I_{\text{ref}} \), and directly proportional to the noise of the detection system, \( \Delta I_c \) and \( \Delta I_{\text{ref}} \). The optical power transmitted through the 1000-\( \mu \text{m} \)-long cell was smaller than for the 100-\( \mu \text{m} \) cell because of an increased coupling loss, which is the reason for the increase in baseline noise. The coupling loss across the 1000-\( \mu \text{m} \)-long absorbance cell was calculated by measurement of the transmitted optical power at 633 nm with water in the channel. The transmitted optical power through the device in this case was 5.5 nW. This value was compared with the transmitted power with a similar waveguide that was not interrupted by a channel (\( P = 500 \text{ nW} \)), yielding a coupling loss of 20 dB (1% transmittance). The coupling loss

<table>
<thead>
<tr>
<th>Path Length (( \mu \text{m} ))</th>
<th>Sensitivity ( \times 10^3 , \text{M}^{-1} )</th>
<th>Limit of Detection (( \mu \text{M} ))</th>
<th>Effective Path Length (( \mu \text{m} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.3 ( \pm ) 0.02</td>
<td>30 ( \pm ) 5</td>
<td>113 ( \pm ) 8</td>
</tr>
<tr>
<td>1000</td>
<td>2.4 ( \pm ) 0.1</td>
<td>15 ( \pm ) 5</td>
<td>906 ( \pm ) 40</td>
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Table 1. Sensitivity, Limit of Detection, and Effective Path Length for Absorbance Cells with Nominal Lengths of 100 and 1000 \( \mu \text{m} \)

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across the 100-μm-wide channel was measured in a similar way to 5 dB (34% transmittance). An improved sensitivity is often achieved at the cost of a lower transmitted optical power, which means that at some point an additional increase in the sensitivity is accompanied by a reduction in the signal-to-noise ratio. Hence the best strategy for fabrication of an optical measurement system for chemical analysis is to find the optimum sensitivity in terms of the signal-to-noise ratio and not merely to increase the sensitivity.

The absorbance cells have to be optimized in terms of transmitted optical power to take full advantage of the improved sensitivity. This can be done, e.g., by evaporation of a metallic mirror on the inner channel sidewalls in the detection region, so it acts as a multireflection cell.29 It might also be possible to integrate micro-optical elements at the end faces of the waveguide, so the light will be focused within the channel.

6. Conclusion

Multimode polymer waveguides based on the photoresist SU-8 have been integrated with microfluidic channels. The process involved only a single mask step, which allowed a fabrication and packaging time of one day. Three bonding procedures were investigated to obtain hermetically sealed fluidic channels. The spectrally resolved propagation loss of the integrated waveguides were determined for all three bonding procedures. A propagation loss of 1.4 dB/cm at 633 nm was achieved with the use of a PDMS lid.

Two chemical absorbance cells with optical path lengths of 100 and 1000 μm were characterized in terms of sensitivity, coupling loss, and limit of detection for measurements of bromothymol blue. The improvement in limit of detection for the 1000-μm-long absorbance cell compared with a path length of 100 μm was only 2, owing to an increased variation of the baseline signal.

Future developments of the devices involve investigations of other types of resist in order to reduce the thermal degradation rate and to increase the transparency at short wavelengths. Furthermore, the coupling loss across the absorbance cells needs to be reduced in order to reduce the variation of the baseline signal and thereby increase the signal-to-noise ratio.

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References