

Reconfigurable diffraction gratings based on elastomeric microfluidic devices

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Abstract

This paper describes the fabrication and operating principles of a reconfigurable diffraction grating based on a microfluidic device. The device consists of an array of microscopic channels (50 μm wide and 20 μm deep) defined by the conformal contact between a transparent elastomeric material that has an embossed surface relief and a flat glass substrate. The microchannels can be filled reversibly with fluids (gas, aqueous solutions, or organic solutions). The difference in index of refraction between the fluid in the array of microchannels and the structural elastomeric solid generates a difference in the phase of the light passing through the device; absorption by the fluid changes the amplitude of the light. Both of these effects give rise to diffraction. The gratings are reconfigured by pumping liquids with different indices of refraction and optical densities through the microchannels. In these experiments, the devices exhibited maximum depths of modulation of ~ 20 dB and switching times of ~ 50 ms; the volume of liquid sampled by the incident light was about 8 nl. The potential application of these devices as sensing elements in micro total analysis systems (μTAS) and as actuators is evaluated. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Devices for spatial light modulation that are based on liquid crystals [1], colloidal crystal hydrogels [2], materials showing photochromic [3] and photoelastic effects [4], and micromachined structures [5–7] have been reported: these devices have applications in both sensing and actuating. Here, we describe the fabrication and characterization of reconfigurable diffraction gratings based on microfluidic devices. These gratings consist of arrays of parallel 50- μm wide channels that can be filled with fluids. The diffraction of light from these gratings is controlled by the optical properties of the fluids in the microchannels. Changes in the index of refraction of the fluid cause changes in the phase of the light passing through the microchannels; variations in the optical density of the fluid cause changes in the amplitude of the light transmitted by the microchan-

nels. Both phase gratings and amplitude gratings can be prepared by this approach; the gratings are reconfigured simply by pumping different liquids through the microchannels.

We believe that optical microfluidic devices have potential application in sensing [8–11] (e.g., real-time monitoring of the variation of the index of refraction and absorption of a fluid) and actuating [12] (e.g., wavefront engineering, reconfigurable optical filters, and modulators). For instance, microfluidic diffraction gratings might serve as sensing elements in micro total analysis systems (μTAS) [8–11]. These systems are chip-based microfluidic devices containing manifolds of microchannels and elements that pump, mix, separate, and detect fluids: the dimensions of the microchannels are compatible with the microfluidic device described here.

Most microfluidic devices have been fabricated in silicon and glass by multi-step procedures from conventional microfabrication techniques [8,13,14]. We fabricate microfluidic devices by defining microchannels in polymers: a polymer (polydimethylsiloxane, PDMS) is cast on thin

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films of photoresist patterned by photolithography [15,16]. The depth of the surface relief on the resulting PDMS molds is controlled by the thickness of the photoresist film: this depth can, in principle, be varied between 1 and 1000 μm . The width and separation of the surface features are determined by the size of the features of the mask used in photolithography: these dimensions can be as small as 1 μm . Sealing of a PDMS mold against a planar substrate generates enclosed channels of micron-sized dimensions that can be filled with fluids [17,18]. The sealing procedure we have developed to bond PDMS to glass—plasma oxidation of the surface of the PDMS followed by room temperature contact with the glass—is especially straightforward, and can be carried out at room temperature; by contrast, the anodic and fusion bonding processes that are used to seal devices fabricated in silicon and glass require combinations of high temperatures, pressures, and voltages [19,20]. As the fabrication method used here is based on replica molding, it is convenient, rapid, and allows the preparation of numerous (> 20) gratings from one master. PDMS is transparent in the visible and near-UV regions of the spectrum (down to 300 nm) [21]; this property, when coupled with simple fabrication methods, also makes it a suitable material for fabricating optical devices [22–25]. We believe that the ease with which complex designs of microfluidic channels can be fabricated and sealed [26], together with the favorable physical and optical properties of PDMS, also make the methods described here broadly applicable to the development of microfluidic optical devices [27].

2. Experimental section

Elastomeric diffraction gratings were prepared by casting PDMS prepolymer (Sylgard 184, Dow Corning) onto a patterned photoresist surface relief (the master) generated by photolithography [15,16]. The fabrication procedure is illustrated in Fig. 1. The pattern of photoresist consisted of an array of 20 parallel lines, 20 μm thick, 50 μm wide, and separated by 50 μm . The lines of photoresist were ~ 2.5 cm long, and connected to a 4×4 mm² pad at each end: the pads defined outlines for reservoirs to which fluids could be added. The photoresist was passivated by gas-phase silanization with (tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane (Gelest, Tullytown, PA) to facilitate mold release. Glass tubing was positioned at each end of the array of lines to define reservoirs for liquids. After curing for 1 h at 65°C, the polymer was removed from the master to give a free-standing PDMS slab with an array of microchannels embossed on its surface: this array serves as a diffraction grating.

The choice of the critical dimensions (depth and width) of the microchannels requires comment. The depth of the channels is determined by the thickness of the photoresist on the master: this thickness can be controlled by adjusting

the speed of spin-coating of the photoresist in the photolithographic step. We used Shipley 1110 photoresist (Marlborough, MA) coated at 1500 rpm to produce films 20 μm thick; using different spin speeds and photoresists, channels ranging in thickness from 1 μm to 1000 μm could be produced easily. In particular, channels thicker than 20 μm can be generated using SU-8 50 or SU-8 250 (Microlithography Chemical Newton, MA). The width of the microchannels is determined by the mask used in photolithography: we used a high resolution transparency as a mask that places a lower bound of 20 μm on the width of the lines [28]. By using commercial chrome masks, however, microchannels with widths and separations as small as 1 μm can be fabricated. We chose to fabricate devices with relatively wide channels (50 μm) because the production of transparencies is much cheaper and faster than that of chrome masks [28], and because it enables faster flow of fluid that reduces the switching time of the device.

To form enclosed microchannels, the microfluidic devices were sealed in the following way. First, the PDMS mold and a glass slide were placed in a plasma oxidation chamber and oxidized for 1 min [26]. The PDMS structure was then placed on the glass slide with the surface relief in contact with the glass. The conformal contact between the mold and glass resulted in an irreversible seal between the two substrates: the bond between the two substrates was so strong that the PDMS mold could not be peeled from the glass substrate without damaging the elastomer. We believe that the irreversible seal is a result of the formation of bridging siloxane bonds (Si–O–Si) between the two substrates that result from a condensation reaction between silanol (SiOH) groups that are present at both surfaces after plasma oxidation. B–O–Si bonds may also be formed between borosilicate glass and oxidized PDMS. Fig. 2 shows a picture of a PDMS mold, with an array of microchannels defined on its surface (inset), sealed against a glass slide.

Diffraction of light by the microchannels was controlled by filling them with different solutions of either inorganic salts or dye. The microchannels were filled by placing a drop of fluid in one reservoir and pulling vacuum from the other end of the microchannels. The microchannels were emptied by applying vacuum and were thoroughly rinsed with deionized water between measurements. Solutions of sodium chloride (NaCl, EM Science), potassium thiocyanate (KSCN, Aldrich), and Azure A (Aldrich) were prepared in deionized water and thermally equilibrated at room temperature prior to use; solutions of dye were filtered to remove particulates. The ranges of concentrations were as follows: NaCl: 0–20% (w/w); KSCN: 30–55% (w/w); Azure A: 0–100 mM. The index of refraction of the solutions of inorganic salts (n_f) was estimated using tabulated data: n_f ranges from 1.333 to 1.386 for the NaCl solutions, and from 1.393 to 1.452 for the KSCN solutions [29]. The indices of refraction in these tables were mea-

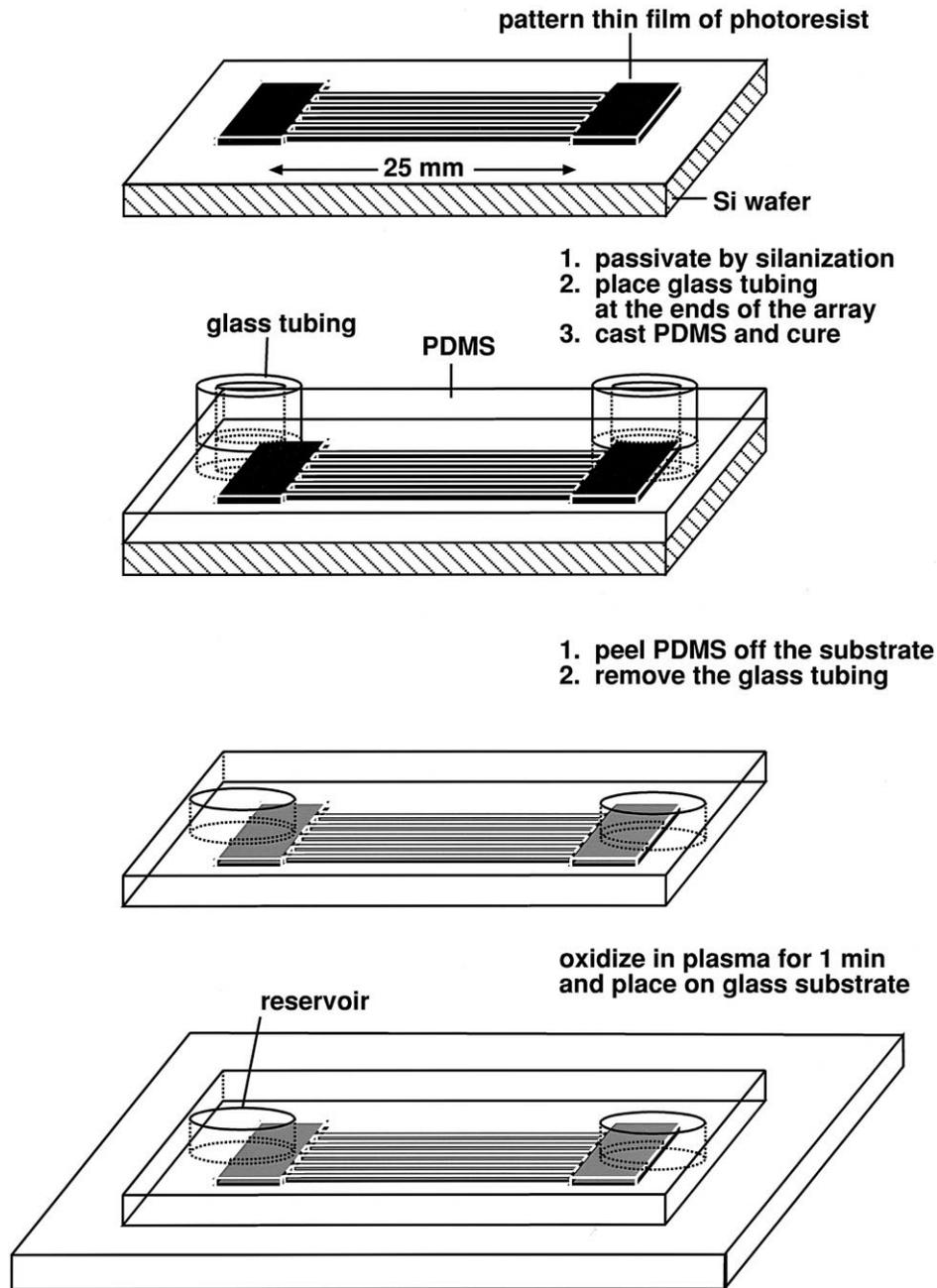


Fig. 1. Preparation of microfluidic diffraction gratings. A thin film of photoresist patterned by photolithography is passivated by gas-phase silanization. The pattern consists of a periodic array of lines ($50\ \mu\text{m}$ wide spaced by $50\ \mu\text{m}$) and is, therefore, a diffraction grating. Glass tubing is placed at the ends of the array to allow the fabrication of inlet and outlet reservoirs for the liquids used to fill the channels. PDMS is cast against the passivated film of photoresist. Once cured, the PDMS is removed from the photoresist master and the glass tubing is removed from the PDMS slab. The photoresist master can be used multiple times to generate PDMS structures. The PDMS slab embossed with the diffraction grating and a clean glass slide are oxidized by plasma treatment and brought into contact. The plasma treatment activates the PDMS surface and enables fluid-tight sealing of the PDMS on the glass slide to generate an array of closed channels that can be filled with fluids.

sured at $589\ \text{nm}$ and 20°C . The diffraction experiments were performed at $633\ \text{nm}$ and at room temperature ($\sim 22^\circ\text{C}$): the index of refraction in the experiments and the tabulated data may therefore differ by $0.002\text{--}0.004$. We are concerned, however, with differences in phase rather than absolute values of phase so small errors in n_f do not effect greatly the interpretation of our data.

Characterization of the devices as diffraction gratings was performed with a He–Ne laser ($633\ \text{nm}$). The incoming laser beam was centered on the array of microchannels, and the intensity of the diffracted beams was recorded using a photodiode (Newport, Model 818-SL) and a power meter (Newport, Model 1830-C) positioned $\sim 2\ \text{m}$ from the grating; this distance allowed spatial resolution of the

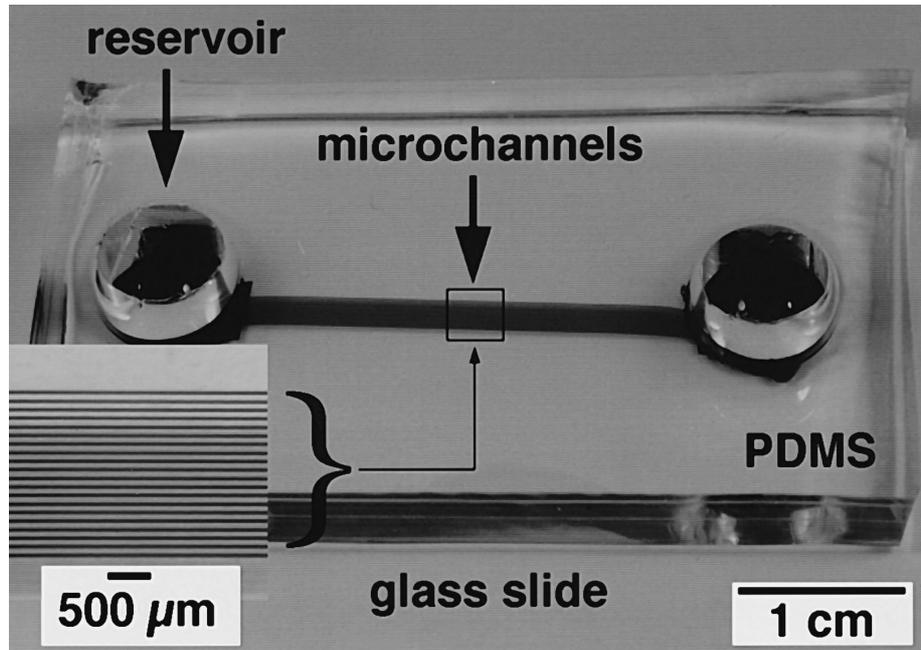


Fig. 2. A microfluidic diffraction grating. A PDMS mold containing an array of 20 parallel microchannels (50 μm wide, 20 μm deep, spaced by 50 μm) was sealed against a glass substrate. A dye was pumped through the channels from the reservoirs to provide contrast. The inset shows a magnified image of the channels; the width of this array is ~ 2 mm. In the diffraction experiments, the diameter of the laser beam at the grating was ~ 1 mm: approximately 10 microchannels and a volume of liquid of 8 nl were therefore sampled.

diffracted beams. The diameter of the laser beam at the grating was ~ 1 mm: approximately 10 microchannels (Fig. 2) and a volume of liquid of ~ 8 nl were sampled in the diffraction experiments.

3. Theory

Fig. 3 illustrates the mode of operation of the microfluidic diffraction grating. Light passing through the grating is diffracted by the periodic array of microchannels defined by the contact between the PDMS mold and a glass slide. The optical properties (index of refraction; absorption) of the fluid filling the channels dictate the appearance of the diffraction pattern produced by the grating. The period of the grating determines the angular position of the diffracted beams, while the thickness of the channels and the optical properties of the fluid determine their relative intensities.

The Fraunhofer (far-field) diffraction pattern can be calculated by Fourier transformation of the transmission function of the grating. The transmission function, $\tau(x)$, of the microfluidic diffraction grating is given by Eq. (1), where $\delta\phi$ is the difference in the phase of light that passes through the microchannels and the light that passes through PDMS only, T is the transmittance of the fluid in the microchannels, w is the width of the microchannels, and p is the period of the grating:

$$\tau(x) = \begin{cases} \sqrt{T} e^{i\delta\phi} & kp < x < kp + w \quad k \text{ integer} \\ 1 & \text{otherwise} \end{cases} \quad (1)$$

Eq. (1) indicates that the transmission function and hence, the diffraction pattern can be changed by either modulating the phase or changing the amplitude of the light that passes through the microfluidic channels. The modulation of the phase is determined by the profile of the index of refraction of the grating. The phase difference is given by Eq. (2), where λ is the wavelength of the light, d is the depth of the channels, and $\Delta n = n_p - n_f$, i.e., the difference between the index of refraction of PDMS ($n_p \sim 1.41$) and that of the fluid filling the channels (n_f):

$$\delta\phi = \frac{2\pi}{\lambda} d \Delta n. \quad (2)$$

By filling the channels with fluids that have different indices of refraction, the phase of a given microfluidic device can therefore be modulated. For examples: if empty channels are filled with water, the phase shift $\Delta\phi$ between the two states (filled vs. empty) is $\delta\phi_{\text{filled}} - \delta\phi_{\text{empty}}$: this difference is equal to 21π or about 10 modulation cycles at 633 nm for 20- μm thick channels; if the index of refraction of the fluid filling the channels matches that of PDMS, then the phase will not be modulated and the device will transmit light without diffracting it. Eq. (2) shows that the modulation of phase is effected by the thickness of the microfluidic channels: to illustrate this effect, $|\delta\phi/2\pi|$ is plotted as a function of the index of refraction of the fluid filling channels for three different channel thicknesses in Fig. 4A. Each unit on the y-axis of this plot represents one cycle in the modulation of the phase of the microfluidic diffraction grating as the index of refraction of the fluid changes. Fig. 4A shows that diffrac-

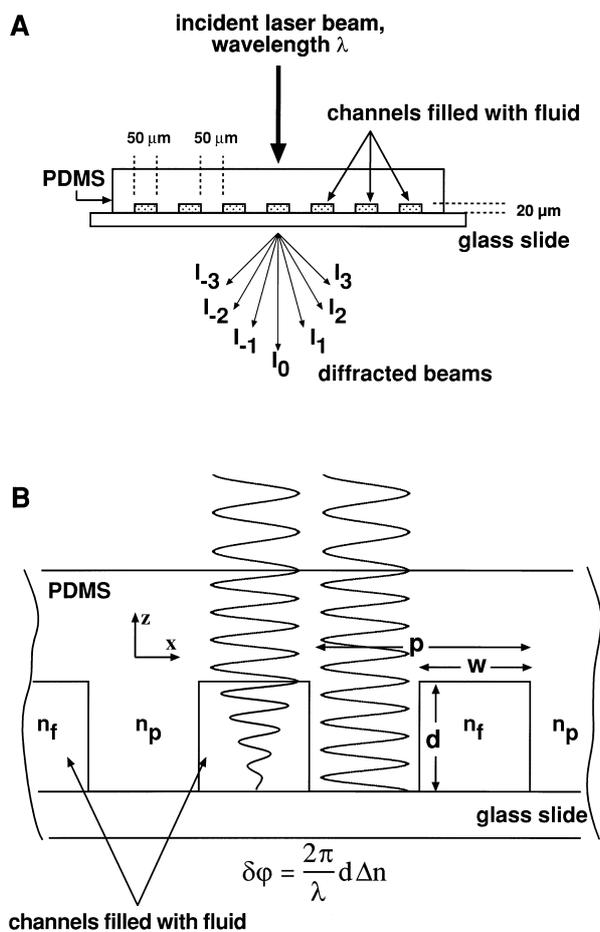


Fig. 3. (A) Channels of microscopic dimensions are formed by sealing a PDMS mold, with a surface relief pattern consisting of an array of parallel lines, on a glass slide. The array of microchannels can be filled with fluids and behaves as a microfluidic diffraction grating. (B) The optical properties of the diffraction grating change as the index of refraction and the absorption of the fluid filling the microchannels vary. If the fluid is non-absorbing, only the phase of the light is effected by changes in the index of refraction: the phase is proportional to the thickness of the microchannels and the difference in index of refraction between the PDMS and the fluid. If the fluid absorbs light, both the phase and the amplitude of the light passing through the microchannels change (as shown). Diffraction results from the interference of light passing through PDMS and light passing through the microchannels: changes in phase and amplitude modulate the relative intensities of the diffracted beams.

tion gratings with thicker channels will be more sensitive than thinner channels to small changes in the index of refraction of a fluid.

If the channels of a microfluidic diffraction grating are filled with a fluid that absorbs light, then the amplitude, as well as the phase of the light passing through the microchannels is effected. Eq. (1) indicates that, in this case, the intensities of the diffracted beams will depend on both the difference in phase and the amount of light that is absorbed by the fluid [12]. For example, a difference in phase of π results in total extinction of the 0th order diffracted spot only when the beams that interfere destruc-

tively have the same amplitude; if the amplitude of the light passing through the fluid is changed due to absorption, then there will not be complete destructive interference and the intensity of the 0th order diffracted spot will be non-zero even though the difference in phase is π [12].

The influence of the geometry of the microchannels filled with an absorbing liquid on the transmittance, T , is illustrated by the Beer–Lambert law (Eq. (3)) that de-

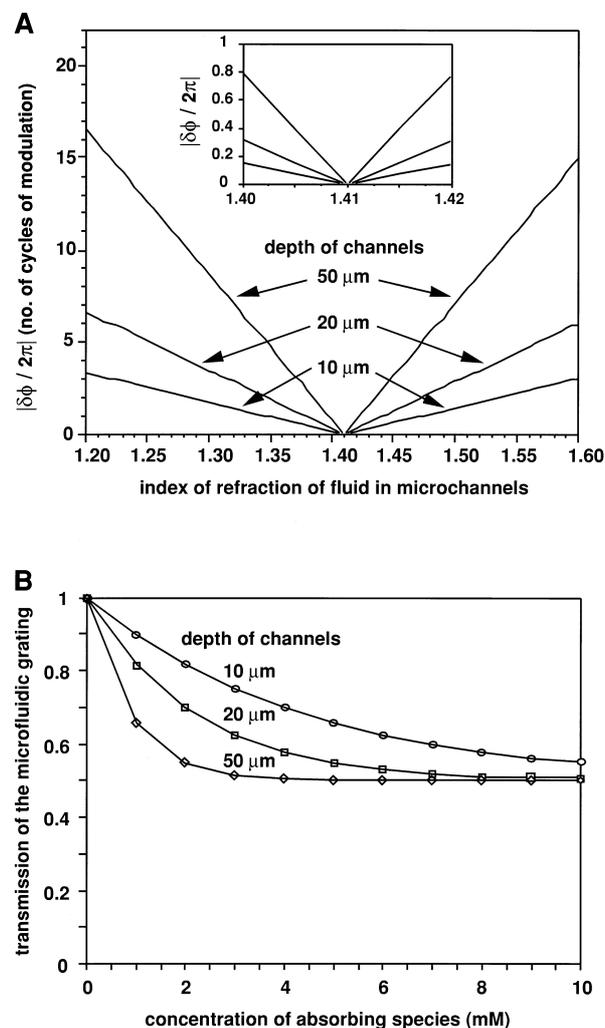


Fig. 4. (A) Modulation of the phase difference, $\delta\phi$, as a function of the index of refraction of the fluid for diffraction gratings with channels that are 10, 20, and 50 μm thick at 633 nm: a change in $\delta\phi$ of 2π represents 1 cycle of modulation. When the index of refraction of the fluid matches that of PDMS ($n_p \sim 1.41$), the device is completely transparent and no diffraction takes place. The sensitivity of the device to changes in index of refraction of the fluid increases with the thickness of the microchannels. The inset shows how the phase difference varies with small changes in index of refraction. (B) Variation of the transmission coefficient of the microfluidic diffraction grating, from values of T (the transmittance of the channels) calculated using the Beer–Lambert law (Eq. (3)), as a function of the concentration of an arbitrary absorbing species, assumed to have $\epsilon \sim 10^5 \text{ M}^{-1} \text{ cm}^{-1}$, in the microchannels. As the thickness of the microchannels increases, the transmission decreases: Eq. (1) indicates that this decrease will change the relative intensity distribution of the diffraction pattern.

describes the effect on T of an absorber at low concentrations [30]. In Eq. (3), I_0 and I are the intensities of the incident and transmitted beams, respectively, ε is the molar absorption coefficient, $[C]$ is the concentration of absorbing species in the solution, and d is the thickness of the microchannels:

$$\frac{I}{I_0} = T = 10^{-\varepsilon[C]d} \quad (3)$$

Eq. (3) shows that the transmittance decreases exponentially as ε , $[C]$, or d increases. Fig. 4B illustrates the variation of the transmission of microfluidic diffraction gratings as a function of concentration of an absorbing fluid and the thickness of the microchannels. Small changes in concentration (at low values of concentration) have a

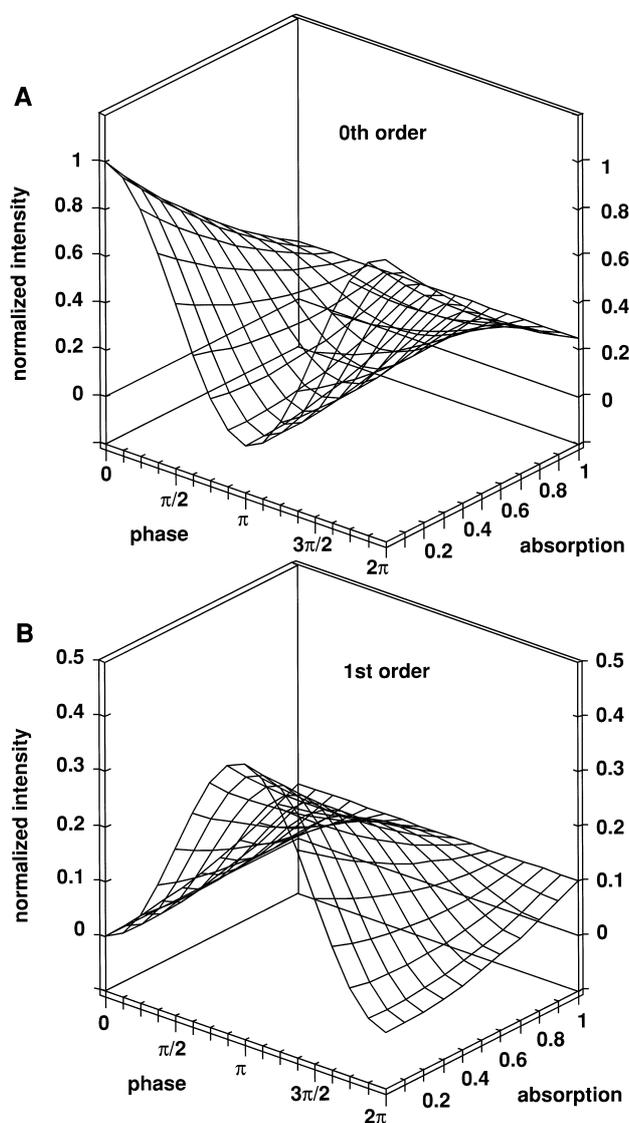


Fig. 5. Variation in the intensities of the 0th (A) and 1st (B) order diffracted beams as a function of the phase and absorption ($1 - \sqrt{T}$) of the microchannels filled with fluid. These plots were generated by Fourier transformation of Eq. (1).

strong effect on the transmission of the device, and hence, on the diffraction pattern, for thick microchannels.

In general, the microfluidic diffraction grating will not operate as a pure phase or amplitude grating: the variation in the intensities of the diffracted beams will be determined by changes in both $\delta\phi$ and T . We determined numerical solutions of the Fourier transformation of Eq. (1) to model the behavior of the gratings as a function of the optical properties of the fluid. The variations in the intensities of the 0th and 1st orders diffracted beams as a function of both phase and absorption are plotted in Fig. 5. The intensity of the 0th (1st) order beam is maximum (minimum) when the depth of modulation of the phase is 0 or 2π , and minimum (maximum) when the depth of modulation of the phase is π . If the index of refraction of a non-absorbing fluid filling the channels varies over a sufficiently wide range so that the resulting shift in phase is $\sim \pi$, the optical response of a microfluidic diffraction grating is switched between two extremes: i.e., from a state in which the 0th order beam is fully illuminated to one in which it is fully extinct. If the absorption of the fluid in the microchannels changes, the relative intensities of the various diffracted orders change: for example, the maximum contrast between 0th and 1st order diffracted beams decreases as the absorption increases.

4. Results and discussion

4.1. Controlling microfluidic diffraction using solutions of inorganic salts

We investigated the influence of the index of refraction of a solution on the diffraction pattern generated by the microfluidic device. The intensities of 0th and 1st order beams of the diffraction pattern from an array of microfluidic channels filled with solutions of NaCl are plotted in Fig. 6 as a function of the concentration of salt. The diffraction pattern of the empty PDMS grating remained constant throughout the experiments, indicating that the PDMS was not swelled by aqueous solutions. The insertion loss of ~ 0.1 dB shows that absorption and reflection by PDMS and glass have a small effect on the performance of the device. These data show a modulation of the diffraction when the concentration of NaCl increases. The changes in intensity of the 0th and 1st diffracted orders are large, i.e., ~ 20 dB; this depth of modulation compares favorably to that (16 dB) of an electrostatically actuated diffraction grating that was micromachined in silicon [6]. The solid lines in Fig. 6 represent a fit to these data using the plots generated in Fig. 5 and assuming zero absorption. The good agreement between theory and experiment indicates that the modulation of the diffraction pattern is consistent with changes in the phase as the index of refraction of the liquid in the microchannels was varied, i.e., the device operated as a phase grating. The overall

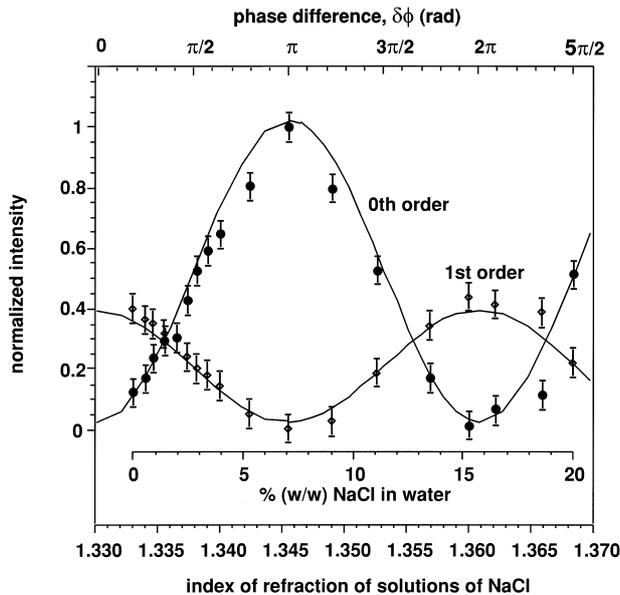


Fig. 6. Variation in the intensities of the 0th (filled circles) and 1st (open diamonds) order beams of the diffraction pattern from a microfluidic grating as a function of the concentration of NaCl in solutions filling the microchannels. The measurements were carried out at 633 nm. The data for the 1st order beams are an average of the positive and negative beams; both sets of data were normalized to the total intensity of light transmitted through the device. A second x -axis is labeled that shows the index of refraction of the solutions determined from tabulated values [27]. The index of refraction varies linearly with concentration from 1.333 for pure water to 1.3684 for a 20% NaCl solution: this difference in index of refraction corresponds to ~ 1.1 cycle of modulation (Eq. (2)). The solid lines show the variation of the intensities of the 0th and 1st orders for a pure phase grating as a function of the phase difference (top x -axis) calculated from Eq. (1). The change in phase over the range of concentrations determined from the fit is $\sim 2.3\pi$, i.e., ~ 1.2 cycles of modulation. The modulation of the microfluidic diffraction grating is therefore consistent with a change in phase induced by a variation solely in the index of refraction of the fluid filling the microchannels. The deviation in the experimental data from the fits probably arises from instabilities in the He–Ne laser and detector that result in errors of $\pm 5\%$ in the measurements.

modulation was 1.1–1.2 cycles (i.e., 2.3π in phase angle) for NaCl solutions varying from 0–20% (w/w).

A similar experiment was carried out using aqueous solutions of KSCN. In this case, index-matching of PDMS was achieved when the microchannels were filled with a solution containing $\sim 38\%$ (w/w) KSCN: this solution has an index of refraction of ~ 1.41 [29].

4.2. Controlling microfluidic diffraction using solutions of dye

The influence of absorption on the diffraction pattern generated by the microfluidic device was investigated by filling the microchannels with aqueous solutions of a dye, Azure A, that has a maximum in absorption ($\epsilon \sim 10^5 \text{ M}^{-1} \text{ cm}^{-1}$) at 633 nm [31]. The variations in the intensities of the 0th and 1st order beams of the diffraction pattern as a

function of the concentration of dye are shown in Fig. 7A. Fig. 7A shows that the modulation of the intensity of the diffracted beams was only partial: neither the 0th nor the 1st order diffracted beams became totally illuminated or extinct as the concentration of dye was changed. This behavior is consistent with differences between both the amplitude and phase of the light passing through PDMS and the fluid in the microchannels (Fig. 5).

Both the absorption and the phase of the light passing through the diffraction grating can be determined simultaneously. Fig. 7B shows the variation of the transmission of the device, determined by summing the intensity of the first six diffracted orders (0 to ± 5), as a function of concentration. As expected, the transmission decreased as the concentration of dye in solution was increased but, since the microchannels that contain the absorbing fluid

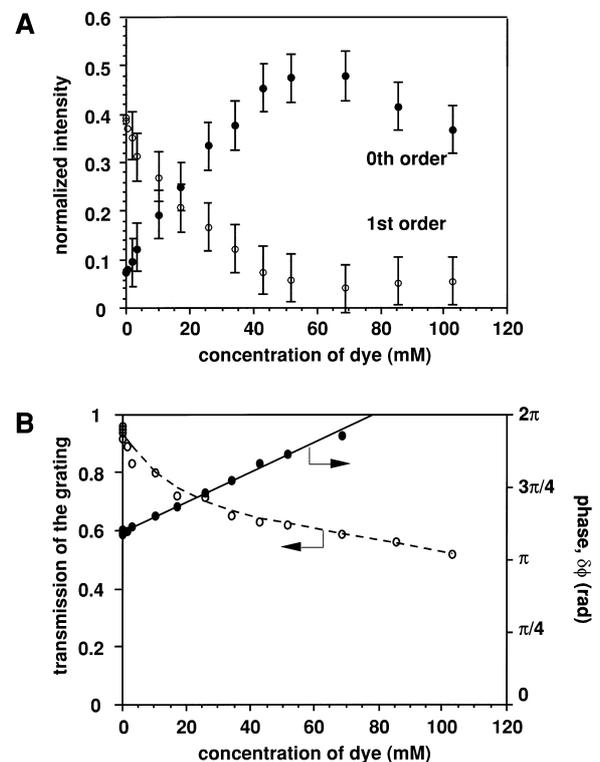


Fig. 7. (A) Variation in the intensities of the 0th (closed circles) and 1st (open circles) orders of the diffraction pattern from a microfluidic grating as a function of the concentration of Azure A in aqueous solutions. (B) Variation of transmission of the microfluidic device (open circles) and phase (closed circles) as a function of concentration of Azure A. The phase was determined from fits to Eq. (1) of the diffraction pattern for each solution of dye; the solid line through these data represent a linear fit. The dotted line is a guide to the eye for the transmission of the device. The transmittance of the liquid in the channels was fitted to the Beer–Lambert law (not shown). The low value of ϵd ($\sim 11 \text{ M}$) produced by this fit compared to the value estimated from the coefficient of extinction of Azure A and the thickness of the microchannels ($\epsilon d = 200 \text{ M}$) can be explained by the deviation from the ideal behavior described by the Beer–Lambert law at high concentrations ($> 10 \text{ mM}$) of an absorbing species [28].

represent only half of the surface area of the grating, the lower value of transmission of the device was only 0.5. The phase can be determined from the relative intensity of the 0th and 1st order diffracted beams, the measured transmittance of each solution, and the calculated plots shown in Fig. 5: the phase determined for each solution is shown in Fig. 7B. The phase, determined with an ambiguity of $\text{mod } 2\pi$, increases linearly with the concentration of dye in solution.

4.3. Evaluation of the microfluidic diffraction grating as an optical element for sensing and actuating

The results presented in this section indicate that this optical microfluidic device could be used to monitor changes in the index of refraction and absorption of a fluid. This device could potentially be useful in applications that require dynamic, real-time monitoring of the evolution of the properties of a liquid, for example, during chemical reactions in μTAS . In the device presented here, for a laser beam diameter of ~ 1 mm, a volume of liquid of 8 nl was sampled: this volume approaches those encountered in μTAS . This grating is amenable to several methods of pumping the liquids through the microchannels that would provide time resolution during a dynamic measurement of the diffraction pattern: application of vacuum and pressure, and electro-osmotic pumping [26].

Several issues, such as sensitivity and switching time, must be considered, however, to evaluate whether this device would be useful in μTAS or other microfluidic devices. The microfluidic diffraction grating exhibited large modulations in intensity (20 dB), so was sensitive to small changes in index of refraction in small volumes of liquid (8 nl). For example, Fig. 6 shows that switching between the fully illuminated and fully extinct 0th order beam required a change in index of refraction of the fluid (Δn_f) of 0.015. We are confident that, by using a more stable laser and detector, changes in the phase of 1% of a full cycle of modulation can be detected, i.e., changes in index of refraction of < 0.0002 . Devices can be fabricated that would be more sensitive to changes in index of refraction: for example, by using channels 500 μm thick, say, $\Delta n_f < 0.00002$ could be detected. Such a diffraction grating would be sensitive to changes in glucose concentration, say, of 0.7 mM [29]. By improving the optical system by, for example, using reflection or multi-pass configurations [12], and by optimizing channel geometry, we believe a 10-fold improvement in sensitivity could be achieved easily. The sensitivity of this device is similar to conventional index of refraction detectors used in capillary electrophoresis and high performance liquid chromatography that can detect changes in index of refraction of $\sim 5 \times 10^{-5}$ [32]. The detection method presented here, however, is not as good as specialized detection techniques such as surface plasmon resonance (SPR), a technique that detects changes in the index of refraction of about 10^{-6} [33], or laser-in-

duced fluorescence (LIF), which is commonly employed in μTAS , that can detect concentrations of fluorescently labeled molecules down to 10^{-9} M in nl volumes [32]. The use of a microfluidic diffraction grating for detection in μTAS does have some potential advantages over specialized methods, however: this method does not require fluorescently labeled molecules, is inherently compatible with the manifolds of microchannels in μTAS , and employs simple optical and detection systems.

The switching time of the device is equal to the time it takes for fluid in the volume illuminated by the laser beam to be displaced. Application of vacuum caused the fluid in the 2.5 cm long microchannels to be completely displaced in less than 1 s: this pumping rate therefore results in a switching time of about 50 ms in the region sampled by the laser beam. If the liquids were pumped by pressure or electro-osmosis, then the switching time would be longer for the experimental conditions common in μTAS : for example, electro-osmotic pumping in this device caused by applying an electric field of 500 V cm^{-1} across the 20 microchannels would result in a switching time of ~ 500 ms [26]. These switching times could be made shorter by using a narrower beam radius and focusing the beam with cylindrical lenses: this arrangement would ensure that the length of channel sampled was reduced while the number of channels spanned by the beam that is required for diffraction was maintained. By using such an arrangement, we believe that minimum switching times of \sim ms could be achieved. The switching times of this device will certainly be short enough to monitor variations in the concentration of chemical species in solution in μTAS . Short switching times would also allow this device to be used in actuation, for example, as a reconfigurable beam steering element. The switching time of the microfluidic device compares favorably with other reconfigurable diffraction gratings: a sensor based on a periodic array of colloidal crystals in a hydrogel [2] had an equilibration time of 30 s; a grating based on liquid crystals [1] had a switching time of 20 ms. The switching time of the microfluidic diffraction grating is, however, longer than that of a reconfigurable diffraction grating (0.5 ms) that was actuated electrostatically [6]. In Table 1, we summarize our evaluation of the device presented here as a sensor and actuator by comparing the critical performance parameters to those of other commonly used devices and methods.

Finally, the mechanical deformation of PDMS may also induce modulation of light and affect the response of a sensor or actuator based on an elastomeric grating. We have previously demonstrated the fabrication of photo-thermal [22] and pressure [23] sensors and optical modulators [24,34]: these devices take advantage of the compliant nature of PDMS to effect the modulation of light. We believe that the deformation of PDMS due to pressure pumping of fluids through the channels will only minimally affect the response of the device. In the unlikely

Table 1

The critical parameters of a microfluidic diffraction grating compared to other devices used commonly in sensing and actuating

Parameter	Microfluidic diffraction grating	Other devices	
		Value of parameter	Device
Volume sampled	8 nl	8 nl (same channel size)	LIF ^a
Limit of sensitivity	7×10^{-4} M ^b $\Delta n_f = 2 \times 10^{-5b}$	0.5 nl	SPR ^a
		10^{-9} M	LIF [32]
		$\Delta n_f = 10^{-6}$	SPR [33]
Switching time	1–500 ms	$\Delta n_f = 5 \times 10^{-5}$	Conventional index of refraction detector [32]
		0.5 ms	Electrostatically actuated grating
		20 ms	[6]
		30 s	Liquid crystal device [1] Hydrogel device [2]

^aLIF = laser-induced fluorescence; SPR = surface plasmon resonance.^bIn a sample volume of 8 nl.

case of deformation of PDMS, one should be able to separate the effects of deformation from those associated with changes in the optical properties of the liquid: the mechanical deformation will change the profile of the grating, whereas changes in the optical properties of the fluid will not. If high pressures are required to pump fluids through the channels, devices based on the same principle could be fabricated using non-compliant materials or thin layers of elastomeric PDMS bonded directly to a rigid backing. The pressure required to cause significant distortion of PDMS will increase with decreasing thickness of PDMS.

5. Conclusions

We have fabricated and characterized a diffraction grating based on a microfluidic device. The diffraction pattern produced by this device can be reconfigured by pumping fluids with different optical properties through the microchannels that define the grating. Differences in phase (due to differences in the index of refraction) and amplitude (due to differences in absorption) between light passing through channels filled with fluid and PDMS regions of the grating result in the modulation of diffraction.

The fabrication of these devices is based on molding a polymer against a master and is simpler and less expensive than silicon micromachining. The photoresist master can be used multiple times. Sealing of the polymer mold to glass to define closed microchannels is straightforward and is carried out at room temperature. The fabrication process is also rapid [28]: it takes less than 24 h to produce a functional device starting from an initial design for a diffraction grating.

The device we have presented had relatively wide (50 μm) and shallow (20 μm) channels with large separations (50 μm); the volume sampled by the laser beam was about 8 nl. Devices could be fabricated with narrower, more closely spaced microchannels (down to 1 μm): such de-

vices would have greater angular resolution of the diffracted beams and would be able to sample smaller volumes. Gratings with deeper microchannels (up to 1000 μm) would provide greater sensitivity at the cost of sampling a greater volume of liquid.

We believe this device could be used as a sensor. A sensor based on this device could monitor the variations in the optical properties (index of refraction and absorption) of a fluid by measuring the intensities of diffracted beams. The switching time of this type of device (determined by the speed at which fluids can be pumped through the channels) is in the range 1–500 ms and would allow it, for example, to be used in real-time monitoring of the evolution of a chemical reaction on a chip. Furthermore, the liquids in the microchannels can be pumped by electro-osmosis: this possibility makes this device compatible with many μTAS that use electric fields to pump liquids and to separate analytes. While detection of fluids by diffraction might not attain the very high sensitivity of LIF to labeled molecules, it is sufficiently sensitive to offer a simple and inexpensive alternative for detection that is inherently compatible with μTAS .

The microfluidic grating could also be employed as an actuator: fluids with different optical properties can be pumped through the channels to modulate the diffraction of light. Complex modulations of diffraction could be achieved if the channels were addressed independently and filled with fluids with different optical properties. Microfluidic devices based on this concept could find applications in spatial light modulation or wavefront engineering, and could be used in beam-steering devices or phase arrays: this type of device is complementary to electrostatically modulated diffraction gratings.

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