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Chemical sensor based on a long-period fibre grating modified by a functionalized polydimethylsiloxane coating

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A chemical sensor based on a coated long-period grating has been prepared and characterized. Designer coatings based on polydimethylsiloxane were prepared by the incorporation of diphenylsiloxane and titanium cross-linker in order to provide enhanced sensitivity for a variety of key environmental pollutants and optimal refractive index of the coating. Upon microextraction of the analyte into the polymer matrix, an increase in the refractive index of the coating resulted in a change in the attenuation spectrum of the long-period grating. The grating was interrogated using ring-down detection as a means to amplify the optical loss and to gain stability against misalignment and power fluctuations. Chemical differentiation of cyclohexane and xylene was achieved and a detection limit of 300 ppm of xylene vapour was realized.

Introduction

With an ever-increasing need to monitor chemical changes in the natural or industrial environment, the demand on chemical sensors has reached an unprecedented high point. For example, every municipality in the industrialized world needs to analyze samples from dozens of monitoring wells several times per year. Typically, this analysis is done off-site at considerable cost and infrequently enough that a breach of containment may remain undetected for weeks or months. Permanently installed chemical sensors could be useful in applications such as these. Although their use as early warning devices decreases the demands on chemical specificity and even detection limits, such sensors need to be very robust, easy to service and inexpensive.

Long-period gratings (LPGs) have been proposed as platforms for chemical sensors because of their ability to record minute changes in the optical properties, such as the refractive index, of their environment.^{1–5} These devices consist of a periodic variation in the refractive index of the core of a single-mode optical fibre. The periodicity of the refractive index variation is typically between 100 and 1000 μm . While the related fibre Bragg gratings are also sensitive to the environmental stimuli, LPGs are particularly promising as detector heads since they are capable of sensing small changes in refractive index ($\Delta n = 10^{-4}$). The shift in the LPG's attenuation spectrum may be detected by measuring the optical loss with a narrow band laser at a fixed wavelength or by recording the entire attenuation spectrum.

LPGs were originally developed as band rejection filters for use in the telecommunications industry,⁶ since the introduction of an LPG into a fibre-optic cable results in a series of attenuation bands that correspond to phase matched couplings of the fibre

core mode to co-propagating cladding modes. Light traveling in these cladding modes is quickly dissipated, leading to a decrease in the waveguide transmission at characteristic wavelengths. The phase matching condition is strongly influenced by environmental factors such as mechanical strain, temperature and the ambient refractive index of the medium surrounding the LPG.^{7,8} Changes in these parameters produce changes in the attenuation spectrum, making LPGs good candidates for physical and chemical sensor elements.

For example, aromatic compounds in a hydrocarbon matrix have been detected with LPG-based sensors. In this particular example, a shift of the LPG attenuation peak by ~ 0.4 nm was observed for a concentration of xylene of 0.5% (vol) in a paraffin solution.⁹ The detection limit was reported as 0.04% (~ 400 ppm). Similarly, LPGs submersed in gasoline were used to determine the ethanol content with a detection limit of about 8%.¹⁰

The fact that all species have a refractive index has the advantage that chemical derivatization is unnecessary. On the other hand, chemical speciation is one of the most significant challenges in detection *via* refractive index. This can be accomplished by applying coatings to the LPG that introduce selectivity *via* chemically-selective solid-phase microextraction (SPME). SPME provides a useful means to select and preconcentrate the analyte of interest. By introducing different substituents into the extraction phase, selective detection of key classes of molecules can be achieved.

SPME based on polymer coatings for optical fibres has been used previously for the detection of extracted compounds through absorption of the evanescent radiation in the SPME coating.^{11–14} The main drawback of these approaches has been the need for direct absorption of radiation by the extracted compounds. This places significant limitations on the light sources and detectors which can be used. However, SPME in combination with LPG-based detection schemes permits the detection of the analyte through the refractive index and not

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through optical absorption, while retaining the advantage of chemical selectivity offered by the extraction phase.

Peshko *et al.* have recently reported the use of commercial polydimethylsiloxane (PDMS) to coat LPGs for the detection of toluene.¹⁵ PDMS is a popular phase for SPME and shows excellent compatibility with optical fibre materials. A detection limit of 100 ppm of toluene in water was realized using custom-fabricated LPGs, with a comparably short pitch of 120 to 180 μm .

An alternative approach to detection with LPGs is to employ materials with refractive indices higher than that of the cladding as the SPME/detection phase as long as the thickness of the coating is controlled within narrow tolerance limits.^{16–18} For example, with a 160 nm coating of syndiotactic polystyrene, Cusano *et al.* were able to quantify low-ppm concentrations of chloroform in water.¹⁷

The next challenge, then, in the design of an LPG-based sensor, is an improvement of the sensitivity and detection limit. We have approached this in two ways. Firstly, by matching the refractive index of the coating to that of the cladding a significant increase in sensitivity can be achieved. Secondly, the placement of the LPG element in a fibre-loop allows for amplification of the optical loss due to the fact that each photon injected into the loop experiences multiple passes through the detector head.

This technique, called fibre-loop ring-down spectroscopy (FLRDS), is a sensitive and robust technique for measuring small optical losses within a loop of optical waveguide.^{19,20} The method takes inspiration from the cavity ring-down spectroscopic technique (CRDS) widely used in gas-phase absorption spectroscopy.^{21–24} In both methods, losses are inferred by the exponential decay of light intensity circulating within an optical cavity. If a short laser pulse is injected into the cavity, the decay rate of the pulse intensity exiting from the cavity, after successive traversals, determines the net optical loss. Alternatively, a continuous-wave (cw), intensity-modulated light source can be used. The finite optical lifetime of the cavity generates a phase lag between the modulated source and the light leaking from the cavity. The observed phase-shift, ϕ , is related to the angular modulation frequency, Ω , and the optical lifetime, τ , of the cavity through the relation, $\tan\phi = -\Omega\tau$. This technique, first described by Engeln *et al.*, is known as phase-shift cavity ring-down spectroscopy.²³ The phase-shift approach, applied to FLRDS, has been used to measure absorbing species in picoliter volumes of solution contained within a small gap in the loop.²⁵ Phase-shift fibre-loop ring-down spectroscopy (PS-FLRDS) is used in the present context to monitor the transmission of an LPG contained within a loop of optical fibre.

Thus the three components of the sensor platform: (1) the long-period grating, which responds to changes in refractive index, (2) the polymer coating, which concentrates the analyte of interest near the grating using SPME and, (3) the optical fibre-loop ring-down system, are all necessary to accomplish the selective and sensitive detection of analytes, such as volatile organic compounds (VOCs). In particular, we have examined a high refractive index analyte (xylene) and a low refractive index analyte (cyclohexane) and demonstrate that the sensor described above is capable of distinguishing between the two. In addition, a ten-fold increase in sensitivity is observed by tuning the refractive index and chemical make-up of the PDMS coating.

Preparation of the sensor system

LPG sensor element

The wavelengths, λ_i , at which a long-period grating induces coupling between the core mode and co-propagating cladding modes of an optical fibre are given by the equation:

$$\lambda_i = A[n_{\text{core}}^{\text{eff}}(\lambda, n_{\text{core}}, n_{\text{clad}}) - n_{\text{clad},i}^{\text{eff}}(\lambda, n_{\text{core}}, n_{\text{clad}}, n_a)] \quad (1)$$

where A is the periodicity of the refractive index modulation in the core, and $(n_{\text{core}}^{\text{eff}} - n_{\text{clad},i}^{\text{eff}})$ is the difference in the effective refractive index of the core mode and i^{th} cladding mode.⁸ The effective refractive index of the core mode depends upon the refractive indices of the core and cladding material of the fibre. Similarly, the effective refractive index for a given cladding mode of order i depends on the refractive indices of the cladding material (n_{clad}), the core material (n_{core}), and also the ambient refractive index, n_a , adjacent to the LPG.

The effective refractive index depends on the extent to which the mode field is present in the three different media. High order cladding modes that have a large evanescent field, *i.e.* much of their mode field penetrates the environment of the fibre waveguide, have the lowest effective refractive index, whereas the single core mode has the highest effective refractive index. From eqn (1), a change in n_a will lead to a change in $n_{\text{clad},i}^{\text{eff}}$ and consequently, a shift in the peak positions of the LPG spectrum. For $1 < n_a < n_{\text{clad}}$, the effective cladding index increases as n_a increases, leading to a shift in peak positions to shorter wavelengths, *i.e.* $d\lambda_i/dn_a < 0$. As the ambient refractive index approaches n_{clad} , the magnitude of the shift increases dramatically (Fig. 1). When $n_a > n_{\text{clad}}$ the cladding modes become leaky, resulting in $d\lambda_i/dn_a > 0$.

Fig. 1 Transmission peak shift due to reduction in cladding diameter during ammonium bifluoride etching of long-period grating. The (red) dotted curve shows the attenuation spectrum of the uncoated LPG before etching in air and the (blue) dashed curve shows the coated and etched LPG in air. The solid curves were recorded with the LPG submersed in the etching solution at 0, 5, 10, 15 and 18 min (from left).

From eqn (1), it is apparent that any physical, mechanical, or environmental parameter will lead to a change in the attenuation spectrum of the LPG, if it is capable of changing (1) the effective refractive indices differentially, *e.g.* through

the refractive index of the surrounding medium, or (2) the period of the grating, *e.g.* through mechanical strain. Given proper calibration, one can use the attenuation spectrum shift to interrogate an environmental parameter of interest.⁸ This measurement principle has led to considerable interest in using LPGs as inexpensive, robust and sensitive sensors.^{2–5,7–9,26–28}

Here, different solutions of dimethyl sulfoxide (DMSO) in water were used to calibrate the sensor. The refractive indices of these solutions were calculated using the Lorentz–Lorenz equation²⁹ together with previously reported refractive index values for DMSO and water of $n_a = 1.4666$ ³⁰ and $n_a = 1.31499$,³¹ respectively, at 1.55 μm and 25 $^{\circ}\text{C}$.

For most applications, the peak shift of the attenuation peak for a given change in ambient refractive index, $d\lambda_i/dn_a$, increases with increasing mode order.^{1,7} Thus, for sensor applications, it is desirable to work with the highest-order cladding mode that falls within the bandwidth of the light source used to interrogate the grating. The wavelength at which a given cladding mode will appear is a function of the physical parameters of the LPG such as its periodicity, refractive index modulation depth and the fibre radius. The fibre radius can be easily reduced through chemical etching, making it possible to adjust the phase-matching wavelength of a given cladding mode.^{32,33} The wavelengths of the attenuation maxima, λ_i , shift to longer wavelengths as the fibre diameter is reduced, leading ultimately to a more sensitive detector.

In addition, for a given mode, the response of an attenuation peak at λ_i to a change in the refractive index of the surroundings, n_a , also depends strongly on the radius of the fibre, R_{clad} . This may be expressed by

$$\frac{d\lambda_i}{dn_a} = \frac{d\lambda_i}{d\Lambda} \times \frac{1}{R_{\text{clad}}^3} \times \Gamma \left(n_{\text{core}}^{\text{eff}}(\lambda, n_{\text{core}}, n_{\text{clad}}), n_{\text{clad},i}^{\text{eff}}(\lambda, n_{\text{clad}}, n_a), n_a, \lambda_i \right) \quad (2)$$

This expression shows that the sensitivity of the LPG increases when the fibre radius is reduced. Here Γ is a function of the optical properties of the waveguide which is independent of the waveguide radius, R , and LPG pitch, Λ .

The laser employed to monitor the LPG has a tuning range from 1520 to 1620 nm. Therefore, to stay within this tuning range, while allowing for peak shifts resulting from the polymer coating and analyte absorption within the polymer, the selected attenuation band must be around 1600 nm before application of the polymer. These LPGs were supplied by ITF Labs (Montréal, QC, Canada) with a periodicity of 320 and 236 μm . The sixth cladding mode (LP_{06}) for the 320 μm grating appeared at 1520 nm. To shift this mode to approximately 1600 nm, the fibre cladding was etched in a saturated aqueous solution of ammonium bifluoride. The fibre was suspended in a Teflon[®] trough containing the etching solution while the grating transmission was monitored using an optical spectrum analyzer (Agilent 86142B, Santa Clara, CA). Upon initial addition of the etching solution the LP_{06} attenuation peak shifted slightly to shorter wavelengths due to the increased refractive index of the solution relative to air. As the cladding was progressively eroded, the peak shifted to longer wavelengths (Fig. 1). After 18 min of etching, the mode was shifted from its original position to 1608 nm. At this point, the fibre was removed from the etching solution, and repeatedly washed with distilled water.

Examination of the etched fibre using an optical microscope indicated a reduction in diameter of 20%, yielding a final fibre diameter of about 100 μm . The response of the LP_{06} cladding mode of the etched LPG to ambient refractive index change is shown in Fig. 2.

Fig. 2 Shift of the attenuation peak of the LP_{06} cladding mode with changing ambient refractive index. Values are given with respect to its resonance wavelength of $\lambda = 1605$ nm in air. Here $\Lambda = 320$ μm , and the fibre diameter was etched to 100 μm . The insert shows a typical shift of the attenuation spectrum with a change of n_a for a different LPG.

Polymer coating

The polymer chosen to coat the etched LPG was based on PDMS due to its ease of use and demonstrated ability to absorb organic contaminants from liquid and vapour phases.^{34,35} In order to fine tune the polymer for absorption of aromatic hydrocarbons³⁶ and refractive index, a portion of the dimethylsiloxane groups were substituted with diphenylsiloxane, and titanium tetraisopropoxide was incorporated at 0.5% by weight (*vide infra*). For our initial examination of the LPG sensor, we chose volatile aromatic and hydrocarbon analytes. The polymer was synthesized by first using acid catalyzed co-condensation of dichlorodimethylsilane with varying amounts of diphenyldiethoxysilane,³⁷ followed by addition of titanium tetraisopropoxide. In addition to adjusting the refractive index of the material, the titanium isopropoxide also served as a cross-linking agent to strengthen the polymer composite.

Tuning the refractive index of the polymer coating is critical since optimum sensitivity to refractive index is achieved when the refractive index of the polymer coating is slightly below that of the cladding, *i.e.* between 1.423 and 1.438 at 1550 nm (Fig. 1). An Abbé-type refractometer capable of measuring refractive indices at 1550 nm was constructed to allow various polymer formulations to be assessed for refractive index and analyte uptake. Through adjustment of the proportions of diphenyldiethoxysilane and titanium tetraisopropoxide incorporated into the polymer, it was possible to tune the refractive index within relatively narrow limits (Fig. 3). The final optimized composition of the polymer was 8.5% diphenylsiloxane, 0.5% titanium cross-linker and 91% PDMS resulting in a measured refractive index of 1.4237.

Fig. 3 Refractive index at 1.5 μm of PDMS containing 8.5% diphenylsiloxane with different titanium cross-linker concentrations. The titanium concentration is given as a percentage of the repeat units of the polymer, *i.e.* 1% = 1 Ti per 99 repeat units.

The polymer coating was applied to the LPG using a 5 : 1 dilution of the pre-cross-linked polymer and cross-linker in hexanes. Without removing the LPG from the etching fixture, a droplet of the hexanes solution was pulled along the length of the LPG. During this process the transmission of the grating was monitored using the optical spectrum analyzer. As the polymer was applied to the grating, the position of the transmission peak shifted to shorter wavelengths, as expected. Additional coatings were applied to the LPG until no further shift in peak position was noted. The final coating thickness was estimated as 20 μm by optical microscopy. The optimum thickness of the coating depends on the penetration depth of the evanescent wave of the respective cladding mode (itself a function of the coating's refractive index) and on the time for equilibration of the analyte into the film. Since the LPG is only sensitive to the ambient refractive index within a few microns of the fibre surface, and thicker coatings would increase the time it takes for analytes to partition to within this range, the minimum thickness needed to provide a stable spectrum was employed. To fully cure the polymer coating, the LPG was placed in an oven at 84 $^{\circ}\text{C}$ for several days until the transmission peak position (and therefore the refractive index of the polymer) remained constant. Typically, eight days of annealing were required. The decrease in the polymer refractive index during this curing process was approximately 0.0026.

A fixture was designed to allow the polymer-coated LPG to be suspended within a cavity, exposed to a flowing gas stream containing the analyte vapour. The vapour stream was created by bubbling nitrogen through a gas washing bottle containing pure solvent. This vapour stream was combined with pure nitrogen in a mixing flowmeter to adjust the concentration between 0 and 50% of the saturation pressure. Assuming that the headspace is equilibrated with the liquid solvent, the saturation pressure can be used to calculate the concentration range in ppm, such that 50% saturation pressure of xylene is equivalent to 5360 ppm and 50% saturation pressure of cyclohexane is 62 670 ppm.³⁸ The gas mixture from the flowmeter passed through a Teflon[®] tube to the

inlet of the cavity surrounding the LPG. The cavity volume was 3.5 cm^3 and the net gas flow rate was maintained at 88 $\text{cm}^3 \text{min}^{-1}$.

Phase-shift fibre-loop ring-down device

A schematic diagram and a photograph of the fibre-loop device are shown in Fig. 4. A tunable diode laser (AQ4320D, ANDO, Yokogawa Electric Corp., Tokyo, Japan) was used as the light source for the loop. The laser was operated in narrow linewidth mode ($\Delta\nu = 200 \text{ kHz}$) at a power of 4 mW. This laser can be internally amplitude modulated to a maximum frequency of 300 kHz. A small portion of the laser output was coupled into the fibre-loop using a 99.5/0.5 2×2 directional coupler (Lightel Technologies Inc., South Kent, WA). Since only 0.5% of the light enters the loop, the remaining light may be used to supply other fibre-loops. A spool of 12 m of Corning SMF-28 single-mode optical fibre was fusion spliced between the coupler and an inline power monitor (M160, EigenLight Corp., Somersworth, NH). This detector was used to measure the circulating light intensity. A transimpedance amplifier with a gain of 500 V mA^{-1} was used to boost the photodetector output. The polymer coated, etched LPG sensor element was spliced between the power monitor and the directional coupler to complete the loop. The phase difference between the photodetector output and a modulation reference signal from the laser was measured using either a lock-in amplifier (SR844, Stanford Research Systems, Sunnyvale,

Fig. 4 Phase-shift fibre-loop ring-down apparatus containing polymer coated long-period grating within the loop.

CA) or a phase comparator integrated circuit (AD8302, Analog Devices, Norwood, MA). This latter circuit produces a DC output of 10 mV for each degree of phase difference between the two inputs. Use of the integrated circuit for phase measurements allows for a more compact and economical version of the fibre-loop device.

Prior to incorporating the LPG into the fibre-loop, the baseline optical lifetime for the unit was determined by measuring the modulation frequency dependent phase-shift of the photodetector output. For a single exponential decay, the ring-down time can be determined from the modulation phase angle between the light entering and exiting the fibre-loop through the relation $\tan(\phi - \phi_0) = -\Omega \tau$. One can then determine the ring-down time, τ , by measuring $\phi - \phi_0$ as a function of modulation angular frequency, Ω . Here ϕ is the phase angle measured at a given Ω with the loop intact and ϕ_0 is the phase angle measured with the loop cut beyond the photodetector. The latter value amounts to a frequency dependent phase offset resulting from propagation delays in the cables and electronics time constants. Fig. 5 displays the frequency dependent phase-shift data for the fibre-loop without the LPG installed. The slope of the plot indicates a ring-down time of $\tau = 522$ ns. The photon lifetime is determined by the net optical loss within the loop comprised of splice transmission losses, insertion losses for the various components, transmission loss in the fibre and coupler loss. The lock-in amplifier was used for these phase angle determinations due to its greater precision ($\Delta\phi = 0.05^\circ$ specified by the manufacturer) compared to the phase comparator chip.

Fig. 5 Determination of the ring-down time constant for a 12 m fibre-loop without the long-period grating installed. The solid line is a linear fit.

Results

Before inserting the grating into the fibre-loop, we recorded single-pass grating transmission spectra at different xylene and cyclohexane vapour concentrations using the optical spectrum analyzer. A mixture of all three xylene isomers was used (14.1% *ortho*, 61.3% *meta*, 24.6% *para*, determined by gas

chromatography). These data are presented in Fig. 6. This composition of xylenes has a refractive index $n = 1.4802$ at 1550 nm, which is greater than that of the PDMS polymer. As the partial pressure of xylene is increased, more xylene partitions into the polymer, increasing the refractive index of the coating, and causing the LPG attenuation peak to shift to shorter wavelengths. The attenuation amplitude is governed by the coupling coefficient between core and cladding mode and is also observed to be influenced by the ambient refractive index. Cyclohexane has a refractive index of 1.4141 at 1550 nm and 25 °C and therefore absorption of this analyte shifts the attenuation peak to longer wavelengths for the phenyl-doped PDMS polymer ($n = 1.4237$). Interestingly, employing undoped, commercial PDMS, both xylene and cyclohexane shift the LPG attenuation peak to shorter wavelengths since undoped PDMS has a lower refractive index ($n = 1.3959$) than either analyte. In addition, as anticipated, the designer PDMS coating has a much greater sensitivity – by a factor of ten – to both xylene and cyclohexane, compared to the undoped PDMS where the refractive index has not been tuned. When an LPG with a shorter period of $\Lambda = 236$ μm (instead of $\Lambda = 320$ μm) was used, a higher cladding mode, LP_{08} , is accessible. This mode shows a greatly increased response upon uptake of xylene and cyclohexane into the modified PDMS films.

Attenuation measurements in the fibre-loop assembly were made at a single wavelength. Based on the spectrum analyzer results, the coated LPG was inserted into a fibre-loop and the tunable laser set to $\lambda = 1530$ nm. This wavelength coincides with the short-wavelength edge of the LPG peak at zero-analyte concentration (Fig. 6, middle left panel). Using this wavelength, one would expect to see a monotonic increase in LPG attenuation throughout the concentration range studied.

The highest modulation frequency attainable (300 kHz) was chosen for the laser since the observed phase angles scale with frequency. Fig. 7 shows the fibre-loop response for a succession of xylene vapour concentrations. A larger output voltage corresponds to a smaller phase-shift. As the xylene concentration increases, the polymer refractive index increases and the LPG peak shifts to shorter wavelengths, towards the laser wavelength of 1530 nm. This leads to a progressively greater loss being introduced into the loop and a corresponding reduction in the ring-down time and phase-shift. From Fig. 7, it can be determined that the detection limit is approximately 3% of the saturated vapour as determined by the standard deviation of the baseline or 320 ppm using the 320 μm grating. If employed for headspace analysis above aqueous xylene solutions, 18 ppm of dissolved xylenes is therefore detectable.³⁸ The detection limit of 320 ppm was deduced from the single wavelength measurement for our particular device. It is also possible to estimate the detection limit from the minimal detectable peak shift of the coated LPG, in the case of a device where the complete LPG spectrum is measured as with the optical spectrum analyzer. Considering that shifts of the attenuation spectrum by 0.25 nm are readily detectable and that we observe a 19 nm shift upon exposure to a xylenes vapour at 50% of the saturation pressure, we can estimate the detection limit to be 70 ppm in gas phase, corresponding to 5 ppm dissolved xylenes.

Fig. 6 Response of etched and polymer-coated long-period grating to xylene vapour (left panels) and cyclohexane vapour (right panels). Top row: commercial polydimethylsiloxane (PDMS) on LPG with $A = 320 \mu\text{m}$. Middle row: PDMS with 8.5% diphenylsiloxane/0.5% Ti/91% PDMS polymer on LPG with $A = 320 \mu\text{m}$. Bottom row: same polymer as for middle row but on LPG with $A = 236 \mu\text{m}$. The curves represent 0, 5, 10, 20, 30, 40 and 50% vapour saturation. The exposure time per concentration step was 15 min. The dashed curve indicates the reversibility of the spectrum after N_2 purging. The dotted vertical line indicates the change of attenuation at a laser wavelength of about 1530 nm.

Using the more sensitive shorter period grating, significantly larger shifts, on the order of 60 nm were observed for a 50% saturated vapour. The greater sensitivity would permit the detection of xylene concentrations in the vapour on the order of 100 ppm using the fibre-loop system, and 23 ppm using analysis of the entire spectrum.

The time response of the LPG sensor element is shown in Fig. 8. The system reaches 90% saturation in less than 2 min and has an equilibration time constant of $\tau_{\text{eq}} = 40\text{--}55 \text{ s}$. This time interval likely represents the diffusion time of the xylene through the polymer to the LPG surface. As can be seen, absorption is fully reversible when the vapour is removed. The reversibility and reproducibility of the responses are shown in the insert to Fig. 8 where the xylenes vapour flow was cycled with pure nitrogen.

Discussion

The choice of components for the LPG sensor platform was motivated by its intended future use as a compact and inexpensive sensor platform. The LPG and its response to environmental parameters such as temperature, strain, and refractive index have been extensively studied and numerous sensor types are commercially available.^{1,7} Given the extensive body of literature on LPGs and the comparably inexpensive near IR light sources and characterization equipment, the LPG appears to be a promising candidate for a sensor head.

The key to the development of effective, LPG-based chemical sensors is maximizing the interaction between the evanescent wave of cladding modes and the analyte. In order to accomplish this, the refractive index of the chemically selective coating

Fig. 7 Response of fibre-loop containing PDPS coated etched long-period grating to xylenes vapour (0–50% saturation). The laser wavelength is 1530 nm and the modulation frequency is $\Omega = 300$ kHz.

Fig. 8 Time response of the uptake and purging of xylene vapour (50% saturation pressure) into the PDPS coated long-period grating contained in fibre-loop. Laser wavelength is 1530 nm and modulation frequency is 300 kHz. The solid lines are fits to the rise and decay of the phase response ($\tau_{\text{rise}} = 53$ s and $\tau_{\text{decay}} = 41$ s). The insert illustrates the repeatability of the uptake and purging of the analyte. Here the xylenes vapour concentration was cycled between 0 and 30% saturation.

should be tuned such that it is close to that of the cladding. For example, in the extreme case where the refractive indices of cladding and coating are identical, the cladding loses its ability to guide light and will essentially be extended infinitely.⁸

As described herein, we were able to increase the detection sensitivity and chemical specificity by employing a custom-designed functional coating, which is matched to the refractive index of the cladding, and is capable of extracting organic contaminants from the surrounding medium by SPME. SPME normally makes use of the partitioning of the analyte of interest into a polymer matrix from a water or air medium. Partitioning coefficients from water (K_{fs}) for water-immiscible organic contaminants are typically larger than 100 and can reach 10^7 for some combinations of microextraction phase and analyte.³⁹ SPME therefore provides a means to not only increase

the concentration but also provide some level of chemical specificity for non-polar compounds.

The most popular SPME film material is the polymer PDMS, which extracts organic compounds from aqueous mixtures based on their hydrophobicity. There is a close correlation between K_{fs} for compounds in PDMS films and K_{ow} , the octanol : water partition constant.⁴⁰ Large values for K_{fs} indicate preconcentration of the analyte in the polymer matrix, with typical $\log K_{\text{fs}}$ values for organic compounds, such as polycyclic aromatic hydrocarbons (PAHs), in the range of 2–5.^{40,41} For volatile organic compounds, as long as the polymer matrix film is less than a few millimeters thick, the partitioning process reaches equilibration within minutes.

The selectivity patterns of polymer films such as PDMS can be tuned by doping the polymer. This may be accomplished by incorporating specific chemical functional groups into the polymer at various levels. For example, a PDMS film doped with phenyl groups was shown to have affinity for aromatic compounds such as toluene.³⁶ Consequently, polymers with affinities for particular classes of chemicals may be used, providing class-specific or greater chemical selectivity. In addition, the introduction of such functionalities can be used to tune the refractive index of the PDMS to within an optimal range. Multiplexing an array of such sensors, each with slightly different polymer selectivities, can then be used to determine the exact composition of an unknown sample using multivariate analysis.

A proof of principle measurement has been presented here. As is shown in Fig. 6, an eight-fold increase of sensitivity to xylene vapour detection, *i.e.* from $\Delta\lambda_{\text{max}} = 2.5$ nm/50% xylene to 19 nm/50% xylene, is obtained employing PDMS which has an optimized refractive index and functional group content complementary to the analyte *versus* commercial PDMS. The sensitivity increase observed is likely due in large part to refractive index matching, since an eight-fold increase in the sensitivity to cyclohexane is also observed. Further research is needed to determine whether the phenyl doping of the polymer also increases the partitioning coefficient by introducing specific aromatic interactions with xylenes, as has been suggested previously.⁴²

Furthermore, as shown in Fig. 6, the detector is able to differentiate xylene and cyclohexane by the direction of the shift of the attenuation peak. For example, xylene uptake results in a shift of the attenuation peak of interest to lower wavelengths while cyclohexane causes a blue shift in the same peak. This differential response allows us to distinguish between two important classes of VOCs, and would not be possible using commercial PDMS.

The temperature dependence of the measurement is an important concern, especially with regards to future field applications. Bathia has determined that the peak wavelength of a 320 μm LPG shifts by about $+60$ pm K^{-1} , which is mostly due to the change of the silica refractive index with temperature ($\sim 8 \times 10^{-7}$ K^{-1}) and to a much lesser extent due to the thermal expansion of the fibre.⁴³ In addition, the refractive index of the PDMS coating changes with temperature ($1.5\text{--}5.0 \times 10^{-4}$ K^{-1}) and further increases the effect on the spectrum. Using oil with a refractive index and thermo-optic coefficient comparable to that of PDMS ($n = 1.42$; $dn/dT = 4 \times 10^{-4}$ K^{-1}) Bhatia found

the attenuation maximum shifts by about +200 pm K⁻¹.⁴³ In the proposed application it will therefore be necessary to thermally stabilize the coated LPG to within a few degrees.

Recently, Peshko *et al.* have described the use of commercial PDMS to coat an LPG for the detection of toluene.¹⁵ Despite the fact that the PDMS coating was not doped and therefore its refractive index was likely lower than 1.42, toluene could be detected at levels comparable to those in our study (100 ppm). The high sensitivity achieved in this case is likely due to the use of customized gratings with very short periods of $\Lambda = 120\text{--}180\text{ }\mu\text{m}$ and an operating wavelength of 850 nm. As shown in Fig. 6, we also observed a dramatic increase in sensitivity by decreasing the period of the grating, even as little as from 320 to 236 μm . This decrease in the period of the grating allows us to interrogate a higher order mode which has inherently greater sensitivity [eqn (1)].¹⁸ It is likely, therefore, that employing even shorter gratings with our optimized coatings will provide an avenue for the development of highly sensitive fibre-optic gratings for the specific detection of chemical contaminants in the environment.

In all previous studies employing LPGs as sensors, the attenuation spectra were recorded with single pass measurements either using a tunable light source and a broadband detector or using a broadband light source and a narrow bandpass detector. These methods can be seriously affected by intensity fluctuations of the light source, the fibre alignment, coupling efficiency, and detector response curves. To correct for these effects, it is necessary to acquire the spectrum in the region of the maximum attenuation of the mode of interest and then infer the LPG response from, for example a shift of λ_r .

Cavity ring-down spectroscopy (CRDS), and the related phase-shift fibre-loop ring-down spectroscopy (PS-FLRDS), allow for measurements of optical loss that are largely independent of intensity fluctuations, since the ring-down time is a measure of the *rate* of intensity decay.¹⁹ The same optical light sources and detectors may be used as for the conventional measurement of the LPG spectrum, but without the constraints imposed by intensity fluctuations. This makes the sensor platform inherently more robust. Furthermore, since only a fraction of the light intensity is coupled into the loop, the remainder may be fed into identical sensor devices with differently coated LPG sensor heads. By sequential excitation of a series of sensor boards it is possible to parallelize the measurement and construct a sensor array – powered by a single light source. We note that CRDS is used in gas-phase spectroscopy mostly because of its greatly enhanced effective absorption pathlength, making it possible to detect extraordinarily weak transitions or, conversely, strong absorbers in very low ($\sim\text{ppt}$) concentrations.⁴⁴ In the present work CRDS was used primarily because it allows for a robust measurement of optical loss, and is not easily influenced by laser instability or detector alignment.

Conclusions

Long-period gratings have gained increasing popularity as chemical sensors, as indicated by the recent increase in related publications. Despite this fact, the commercial potential of LPG chemical sensors has not yet been exploited. For chemical LPG sensors to gain ground as robust devices suitable for field deployment, the optical interrogation system needs to

be simple, inexpensive and robust. With this publication we have demonstrated the utility of ring-down spectroscopy as a convenient and inexpensive way of measuring and enhancing the attenuation change of an LPG.

In order to enhance sensitivity and provide chemical specificity, we have developed a specialized PDMS polymer that has a refractive index matched to the cladding material. This particular polymer showed a differential response to two important classes of VOCs: aromatics and hydrocarbons. Finally, the sensitivity was improved by reducing the fibre diameter through fluoride etching. Further improvements are demonstrated to be possible by using an even higher mode of the LPG. This can be done by either changing the interrogation wavelength, or by changing the period of the LPG, and/or by changing its diameter. Modeling of the optical properties of the LPG will aid the further design of the interrogation scheme.

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