Miniature infrared gas sensors using photonic crystals

A. Lambrecht[a]*, S. Hartwig[a], S. L. Schweizer[b,c], R.B. Wehrspohn[b,c]
[a]Fraunhofer Institute for Physical Measurement Techniques (IPM),
Heidenhofstr. 8, D-79110 Freiburg, Germany
[b]University of Paderborn, Dep. of Physics, Warburger Str. 100, D-33098 Paderborn, Germany
[c]Martin-Luther-University Halle-Wittenberg, Institute of Physics,
Heinrich-Damerow-Str. 4, D-06120 Halle, Germany

ABSTRACT

The sensitivity of an infrared gas sensor depends on the interaction length between radiation and gas, i.e. a reduction in cell size generally results in a reduced sensitivity, too. However, low group velocity regions in the bandstructure of photonic crystals should enable the realization of very compact gas sensors. Using photonic crystals based on macroporous silicon experimental results with CO_2 show an increase of the gas sensitivity in the photonic crystal compared to an empty cell of same dimensions. For practical applications the results are compared with gas measurements using conventional multireflection cells and hollow fiber setups.

Keywords: Photonic crystals, gas sensors, infrared, macroporous silicon

1. INTRODUCTION

In many fields such as technical, environmental, automotive, and medical applications gas sensors are indispensable. The concentration of dangerous and/or air polluting gases such as O_3, NO_x, CO_2, CO, CH_4 etc., occurring in technical processes has to be monitored to prevent harm. In the medical sector it is, e.g., necessary to monitor and control respiratory gases. Ethanol breath testing is a common example, too. Several types of gas sensors are available on the market. One class of gas detectors measures the changes of the conductance or of the capacitance that are induced by the presence of certain gas atoms which are adsorbed onto the surface or which diffuse into the detector material. Most of these methods are only applicable to certain specific gases that influence physical properties of the detector materials. Another class of detectors are optical, or more specific, spectroscopic gas sensors which measure the change of reflection or transmission in the presence of gases. Here, characteristic absorption lines arising from rotational-vibrational excitations of the molecules in the mid-infrared (MIR) spectral range are monitored. The spectroscopic principle is a rather general approach applicable to a broad variety of gases, and is in addition highly selective due to the specific rotational-vibrational states (fingerprint) of every gas. The major drawback of such optical sensors is their relatively high cost due to the high demands on the optical components.

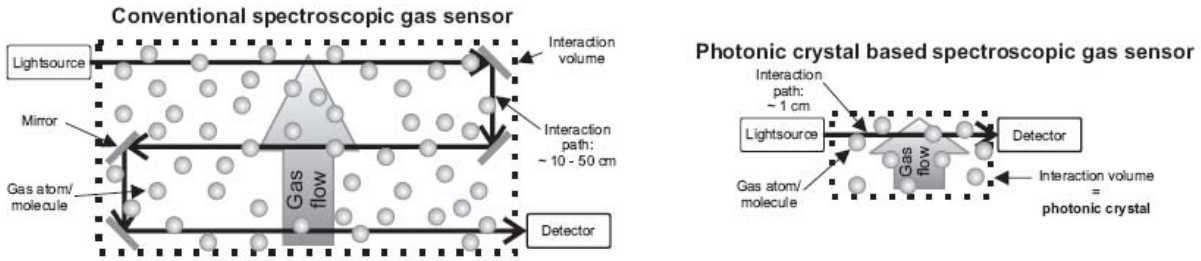

Figure 1: Comparison of a conventional (left) and a Photonic Crystal (PhC) based gas sensor (right). The gas sensor size could be drastically reduced using PhCs as interaction volume.

* armin.lambrecht@ipm.fraunhofer.de; phone: +49 761 8857-122; fax + 49 761 8857-224

A conventional spectroscopic gas sensor consists of three basic parts: the radiation source, the interaction volume and the radiation detector. Using e.g. laser sources and adapted detectors, very sensitive, selective and fast instruments can be built.[1,2,3] Employing tunable laser spectroscopy, a monochromatic intense laser emission line is precisely tuned across gas absorption lines. Highly collimated laser beams can be combined with efficient Harriott multireflection cells, yielding interaction lengths of 100 m and above.[2] Thus e.g. with quantum cascade lasers (QCL) in the MIR sensitivities in the ppt range can be achieved.[1,2] Using cavity ring down or cavity leak out setups effective interaction lengths of several km have been demonstrated yielding ppt sensitivity, too.[4] However, in most cases the high price of lasers and other system components is prohibitive, and limits this techniques to nice applications. For the majority of optical gas sensors low cost thermal emitters and thermopile or pyroelectric detectors are used as radiation sources resp. detectors with adapted optical components. Therefore we focus our work on this case.
We suggest the use of Photonic Crystals (PhCs) to obtain compact, robust and low-cost spectroscopic gas sensors. We only consider the replacement of the interaction volume in such a conventional sensor by a PhC as shown in Fig.1. But one could also think of replacing the thermal radiation source by a PhC emitter that shows enhanced emission in the spectral region of interest due to the redistribution of the photonic density of states (PhDOS) within the PhC.[5,6,7] Due to the dilute nature of gases their interaction with light is rather weak (compared to liquids), which in turn necessitates relatively long interaction paths in the range of 10 to 50 cm to determine concentrations in the ppm range. Such long interaction paths and the resulting large interaction, i.e. sample volumes, are rather impractical because first, they result in relatively large sensor devices and second, it is often impossible to fill such large volumes with gas, as, e.g., in the case of baby breath monitoring. Furthermore it is usually necessary to keep the interaction volume at a certain temperature to avoid condensation, and to guarantee reproducible measurement conditions. This is energy consuming, especially for large volumes. A reduction of the interaction volume can be achieved by increasing the effective interaction of the radiation and the gas. Mirrors are used to reflect the light back and forth within the interaction volume and thereby multiplying the interaction between radiation and gas which allows to reduce the interaction volume. However, the emission properties of the thermal sources are a severe limitation, and the necessary alignment of the mirrors in such cells (s. Fig.1) increases overall cost.

2. THEORY

Photonic Crystals (PhCs) are the optical analog to electronic semiconductors. The concept of PhCs was introduced independently in 1987 by Sajeev John[8] and Eli Yablonovitch.[9] In electronic semiconductors like Si or GaAs the bandstructure for the electrons arises from the periodic arrangement of the atoms that make up the crystal lattice. Electron waves travelling through the electronic semiconductor are scattered at the periodic electrostatic potentials of the atoms and their interference leads to the replacement of the free electron dispersion relation by the electronic bandstructure. In PhCs the photonic bandstructure (PhBS) results from scattering and interference of electromagnetic waves at periodic arrangements of materials with different refractive indices $n = \sqrt{\varepsilon}$, where ε is the materials dielectric constant. The PhBS replaces the dispersion relation of photons $\omega = (c/n)\cdot k$ in a homogenous dielectric medium with refractive index n and frequency ω along the direction k, where c is the speed of light in vacuum.
The PhBS depends on several parameters. One important parameter is the geometry of the lattice of the PhC such as a hexagonal or square lattice. A typical example of a PhC-structure is macroporous Si, with a regular lattice of air pores in Si. Assuming that the diameter of the air pores does not change along the z-axis, such a structure is called a two-dimensional (2D) PhC. If the pore diameter is varied along the z-axis in such a way, that there is in addition to the periodicity in the x-y-plane also a periodicity l_z along the z-direction, such a structure would be called a 3-dimensional (3D) PhC. Another important parameter that influences the PhBS is the so-called dielectric contrast $\Delta\varepsilon = \varepsilon_1 - \varepsilon_2$ which is significant in the case of the air/Si material system where one has $\Delta\varepsilon_{air,Si} = \varepsilon_{Si} - \varepsilon_{air} = 11.6 - 1 = 10.6$. As a rule of thumb the photonic bandstructure shifts to higher frequencies and the photonic bandgap (PhBG) increases when the dielectric contrast is increased.
The PhBS depends furthermore on the so-called r/a-ratio, the ratio of the radius r of the pores and the lattice constant a of the PhC. This is a very important feature which will be very useful for the gas sensor application, because it is possible to adjust the PhBS to the different resonance frequencies of various gases by simply changing the pore diameter. A closer look on the PhBS reveals that the slope of the PhBS represents the group velocity $v_g = \partial\omega/\partial k$ for electromagnetic waves of frequency ω within the PhC, where k is a vector in the reciprocal lattice of the PhC. Consequently, in regions where the photonic bands are flat, the group velocity $|v_g|$ is low. Such a reduction of the group

velocity down to about 0.02c and 0.05c has been experimentally verified for line defects in PhCs by Notomi et al.[10] and Asano et al.,[11] respectively. This means that light travelling through the PhC at a lower speed $v_g < c$ interacts longer with the gas, i.e., the interaction time t_{int} is increased and therefore the length of the interaction path l_{int} can be reduced while keeping the total interaction constant.
In another intuitive picture the low group velocity can be interpreted as a result of the many reflections due to the many scattering surfaces in the PhC. As a consequence the fields of the scattered waves superimpose coherently and interact several times with the gas atoms and this gives the enhanced interaction. From this argument one can deduce that the light absorption A in the gas $\propto 1/v_g \propto E^2$ where E is the electric field of the incoming plane wave. Furthermore one has to consider the redistribution of the field energy within a PhC. In a conventional gas sensor the mode that interacts with the gas is more or less a plane wave. In a PhC in contrast, due to the interference of the multiply scattered electromagnetic waves travelling through it, a lot of mode profiles strongly differing from plane wave field distributions can be observed. For certain frequencies, i.e. in certain photonic bands, some of the modes have the maximum of their field intensity in the high ε region, e.g., in the Si matrix, while other modes have their field intensity maxima in the low ε regions, e.g., in the air pores. Details are described elsewhere.[12]
Thus, by reducing v_g and increasing the field intensity E in the gas filled pores of a PhC, a reduction of the interaction volume of a gas sensor should be possible. However, there is a drawback of such a simple PhC gassensor. In a classical picture a low group velocity v_g corresponds to a high refractive index n_{eff}. This makes in- and out coupling of radiation difficult. This problem could be overcome by the design of an appropriate taper or an anti-reflection layer taking into account the impedance and the modal mismatch. This has been realized in the 2D design by using specially designed surface modes that couple with very high efficiency plane waves to low-v_g modes.[12,13,14,19]
Because suitability of PhC in gas sensor devices only depends on the specific band structure of the PhC, one can take into account either 2D or 3D PhCs, which will be discussed in the following.

3. TECHNOLOGY OF SILICON PHOTONIC CRYSTALS

2D and 3D photonic crystals can be prepared by pore etching in silicon. Macroporous silicon has been pioneered in the early 1990s by V.Lehmann and H.Föll.[15,16] Macropores can be obtained either by anodization of p-type Si in hydrofluoric acid or in n-type Si, which is used here. Since in n-type silicon holes (necessary for the dissolution reaction) are minority carriers, they have to be generated by backside illumination. Then, they diffuse to the etch front through the wafer to promote dissolution of silicon mainly at the pore tips. This technique has high requirements on the minority carrier diffusion length so that normally float-zone (FZ) wafers are used. Since in this technique the holes move by diffusion and not by drift as in the p-type case, the strong boundary condition of a fully depleted pore wall is relaxed and thicker walls can be obtained up to 10 times the space-charge region width.[16] It is even possible to change the pore diameter during pore growth which is hardly possible with p-type silicon in a controlled manner.[17,18] To obtain ordered arrangements of pores, a n-type silicon wafer with (100) orientation is first prepatterned by standard photo-lithography. Subsequent alkaline etching produces inverted pyramids acting as initial pores. Under anodic bias and backside illumination the wafer is then etched in hydrofluoric acid. As a result pores grow straight along the (100) direction with a very high aspect ratio. The arrangement of these pores can be controlled by the lithographic mask and the pore diameter by the illumination intensity. By controlling these parameters, unintentional variations of the pore diameter with depth can be made negligible. Interpore distances in the range of a = 500 nm to a few tens of microns are possible.[20]
Straight and 350 µm deep pores can be fabricated on a routine basis using automatic etching techniques (s. Fig. 2 left). With appropriate backside processing porous membranes can be achieved, too. Modulation of the illumination intensity during the etch process yields a modulation of the pore diameter which results in a 3D-PhC (s. Fig. 2 right). Such 3D photonic crystals have been realised by fixing the lattice constant of the lithographically defined 2D lattice at a = 1.5 µm and varying the modulation period and amplitude of the macropores with depth. [22]
For coupling light into 2D-PhC samples the quality of the end faces is crucial. It turned out, that cleaving, etching, polishing etc. of the edges of a macroporous Si slab to obtain suitable side faces is far more difficult than with bulk Si. Experimentally, we obtained the best results, i.e. smoothest faces when separating the PhC samples via etch trenches during the pore etching process itself. Furthermore the necessary antireflection region can be implemented in the similar way by a pore -free region of well defined thickness between the porous PhC and the separating trench. Trenches and AR- regions can be predefined by photolithography and are well transferred into a vertical structure by the etching process (see Fig. 3).[21]

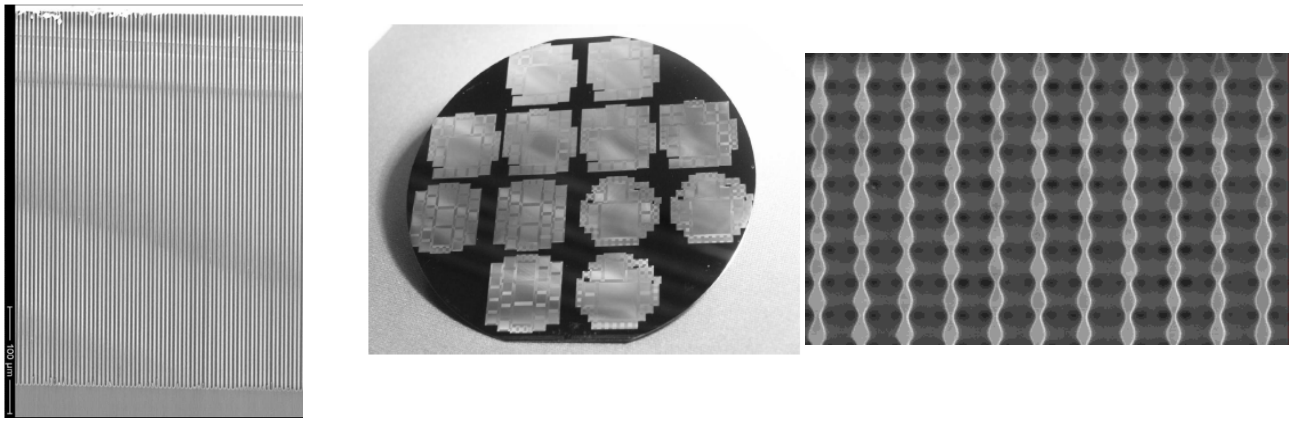

Figure 2: Scanning electron microscope (SEM) cross section of a macroporous silicon 2D-PhC having a depth of 350 µm and a pore diameter of 3 µm (left). 4 inch silicon wafer with 10 PhC gas sensor structures (middle). 3D-PhC obtained via modulated etching. The pores have a horizontal period of 1.5µm and a vertical modulation period of 1.69 µm (right).

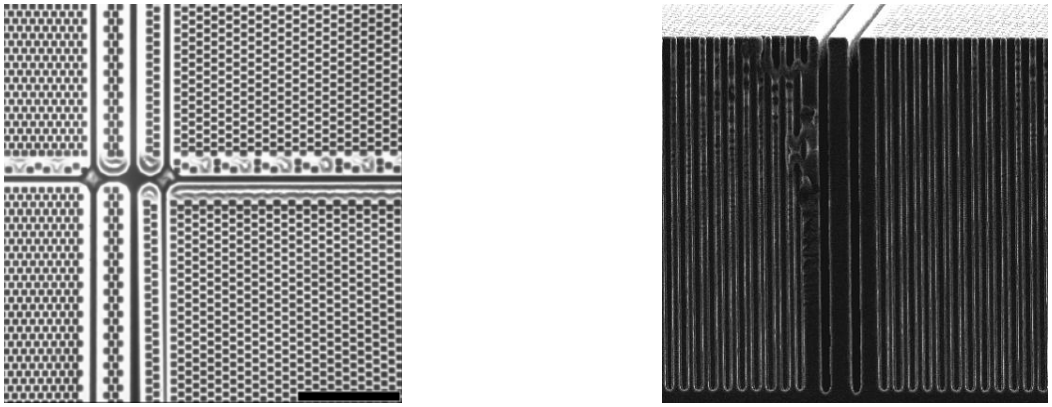

Figure 3: Top view of a photolithographically patterned Si-wafer (left). The black bar at the right lower corner is 50 µm long. The pattern shows separating trenches and antireflection regions with no pores. During electrochemical etching smooth faces of the PhC elements are formed simultaneously together with the pores. The corresponding SEM cross section shows pores and trenches extending straight through the wafer (right).

4. EXPERIMENTS AND RESULTS

3D- Photonic Crystals

First measurements were performed with 3D-PhCs as shown in Figure 2 (right). This had the advantage, that the beam direction of the probing light and the gas flow are perpendicular to the plane of the macroporous Si wafer (i.e. in the paper plane of Fig. 3), and the sample cell could be easily introduced into the sample compartment of a standard FTIR instrument (Bruker IFS 66v/S). The design and a photograph of the gas cell are shown in figure 4. The illuminated sample area is larger than 1 cm^2 and the surface quality of the PhC is sufficient and not critical in this case.

However, with this setup no enhancement of the gas absorption in the PhC compared to an empty cell was observable. The main problem was that the 100-300µm gap between window and sample (i.e. the dead gas volume in front of the PhC) was too large compared with the thickness of our 3D-PhC-samples of some 35 µm to observe any reliable effect. Additionally, when changing samples the gap between window and sample could not be maintained at a sufficiently fixed value. Further details on these measurements are described elsewhere.[12]

Therefore we moved to the 2D-PhC setup where longer measurement paths and less experimental uncertainties are anticipated.

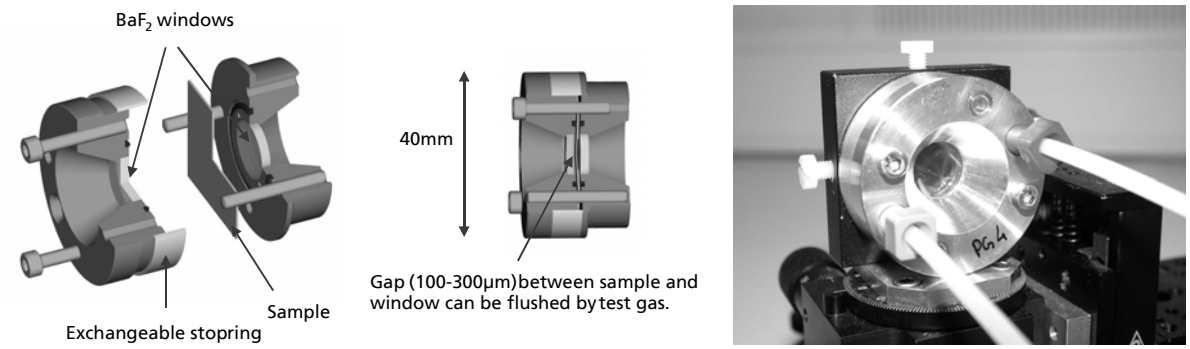

Figure 4: Design(left) and image (right) of the gas cell used for 3D Photonic crystals.

2D- Photonic Crystals

Following the technology described in chapter 3 2D-PhC samples with lengths from 100µm to 1mm were obtained. Thickness and width of the samples were approximately 330µm and 1mm, respectively. Transmission measurements indicate an optical attenuation of less than 2dB/mm showing the high quality of the structure. Losses are probably mainly due to residual scattering. Analysing the pore diameter and interpore distance variation by SEM yields an average value of 1-2 %, mainly due to doping variation in the starting silicon material. Unfortunately the overall transmission of the samples is still quite small, and longer samples could not be used with our thermal radiation source setup.

The PhC membranes are fixed between two BaF_2 light guiding rods (12mm x 1mm x 400µm), which couple the IR-radiation in and out of the PhC sample. The fragile rods are firmly fixed within a groove (20 mm x 1mm x 400µm) in a plastic holder. To account for varying lengths of the PhC- samples the BaF_2 rods are pressed against the PhC. A flat plastic top plate seals the setup airtight. Two tiny holes in the center at the position of the PhC enable a gas flow through the PhC sample. A schematic view and the open cell is shown in Fig. 5 (left and right). The assembled gas cell is mounted between a thermal radiation source and a pyrodetector with an IR bandpass filter centered at 4.24 µm for CO_2. No further optical elements are necessary for this compact setup (s. Fig. 6).

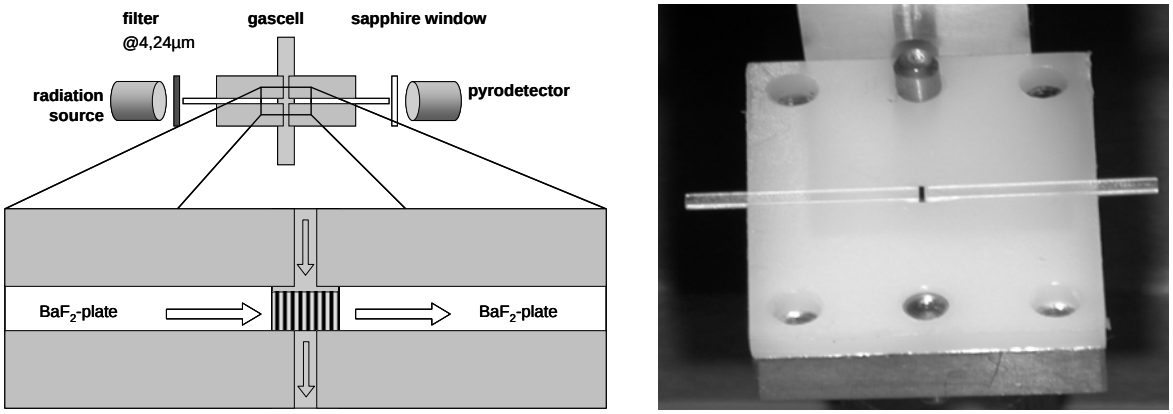

Figure 5. Schematic design (left) and image (middle) of the gas cell used for 2D-photonic crystals.

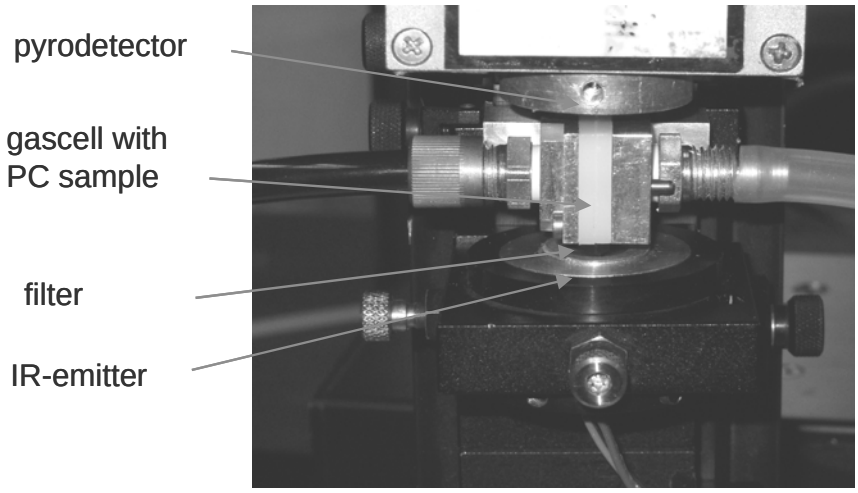

Figure 6: Image of the closed cell assembly with gas supply hoses in the measurement setup.

The radiation intensity of the IR emitter was modulated via the operating voltage with a frequency of 10 Hz. The signal of the pyrodetector was measured using a digital lock-in amplifier with a time constant of 2 s. In the course of the experiments the gas cell was filled with dry N_2, then filled with CO_2, and rinsed with N_2 again. This cycle was repeated several times. After measurement of a sample the PhC could be removed from the plastic holder without changing the positions of the BaF_2- rods. Thus measurements of the empty cell with the same length were possible. The results are shown in Figure 7.

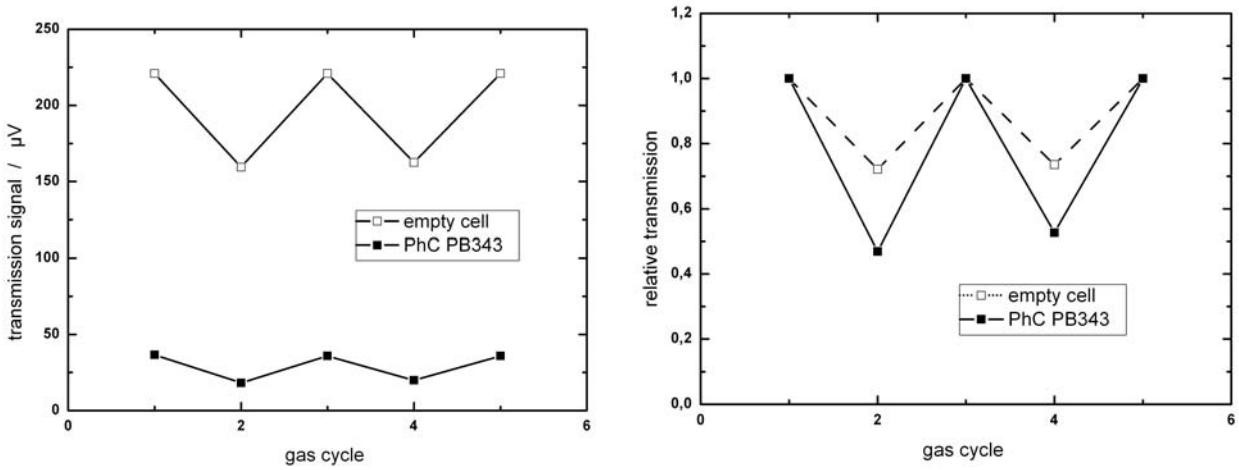

Figure 7: Infrared transmission signal at 4.24 µm of the empty gas cell and the cell with a 250 µm long PhC- sample during gas filling cycles with N_2 (cycle 1,3,5) and CO_2 (cycle 2,4) (left). Normalized transmission of the empty gas cell and the PhC-sample (right).

In Fig. 7 (left) the IR absorption of CO_2 is obvious. The transmission of the PhC sample (length 200 pore rows i.e. 250 µm, thickness 330µm) is only 8,6%. First measurements with other samples with 1 mm PhC length yield transmission values of approximately 4%. The normalized data of Fig. 7 (right) show that with the PhC the absorption by CO_2 is more than twice the value of the empty cell. This is the first evidence that in PhCs enhancement of absorption can be achieved.

5. ALTERNATIVE METHODS

Multireflection cells

Though promising, the investigated PhC cells are still not suitable for practical applications in gas sensors. In this section we report on results with more conventional compact gas cell solutions. The results may be compared with the PhC approach. For this reason we define a dimensionless cell figure of merit C = optical pathlength/(cell volume)$^{1/3}$.

The usual multipass cell for use with broadband thermal emitters is the White cell. The principle of this cell is based on multiple reflection between three spherical concave mirrors, all having the same radius of curvature.[23] The optical set-up features a high light transmission where radiation losses are caused only by absorption and scattering on the reflecting surfaces. The optical path, i.e. the number of reflections is dependent on the adjustment of the mirrors, but limited by the diameter of the active area of the source. The design of our cell with adapters for radiation source and detector is shown in Figure 7. Here an optical path length of 1.6 m is implemented in a volume of 11 x 5 x 6 cm^3. The body of the cell is machined from aluminum. For mirrors, gold-coated convex glass lenses were employed.[24]

CO measurements have been performed using the White cell, a micromachined IR-emitter,[25] and a commercial pyrodetector with two filters, a reference-channel at 3.95 µm and a CO-channel at 4.6 µm. The micromachined IR-emitter was heated with 2.3 W to an operation temperature of about 850°C. The radiation of the IR-emitter was modulated with a chopper at a frequency of 2 Hz. The time constant of the Lock-in-amplifier was 10 s. A significant change in signal for 100 ppm CO is observed.

Figure 7: exploded view of 1.6 m White cell (left), image of the cell (middle), result of a CO measurement (right).

Using typical thermal emitters the cell figure of merit C is limited by optical crosstalk between the reflecting beams inside the cell. In our case C≈23. Using an improved optomechanical design C values of up to 100 can be achieved. C > 1000 is possible with highly collimated laser sources, which are not in the scope of this paper aiming at compact low cost sensors.

Hollow fibers

Another alternative way is the use of a hollow fibers where the light is guided in the air core and is absorbed by gas inside the fiber core itself. Using a 1 m hollow fiber with inner diameter of 1mm C= 1084 results, neglecting dead volumes of gas fittings and coupling pieces. With hollow fibers of smaller core diameters, which are commercially available much higher C- values are feasible. However, available infrared fibers have rather high transmission and bending losses which limits their use for compact devices with long optical pathlengths using thermal emitters. Using laser sources, very sensitive instruments have been demonstrated.[26]

A typical setup using a thermal radiation source, and a 10 cm infrared hollow fiber from Polymicro, Inc. is shown in Fig. 8 (left). Using a 25 cm long fiber, a micromachined IR emitter[25] with a modulation of 34.5 Hz, an optical filter at 9.3µm for the measurement of Ethanol vapor, and a lock-in amplifier with a time constant of 500ms a significant change in signal for 500 ppm Ethanol in N_2 is demonstrated in Fig. 8 (right).

6. CONCLUSION AND OUTLOOK

The feasibility of gas sensors based on the classical Non Dispersive Infrared (NDIR) technique using thermal emitters and ultracompact photonic crystal gas cells was demonstrated. Enhancement of the CO_2 infrared absorption inside a PhC by a factor of 2.2 was observed compared to an empty cell. However, our PhC cell with an effective optical length of 2.2 x 250µm has a rather low C-value of 1.3. As C increases with the length of a cell, recent results with 1mm long samples yield C values around 3.[14]

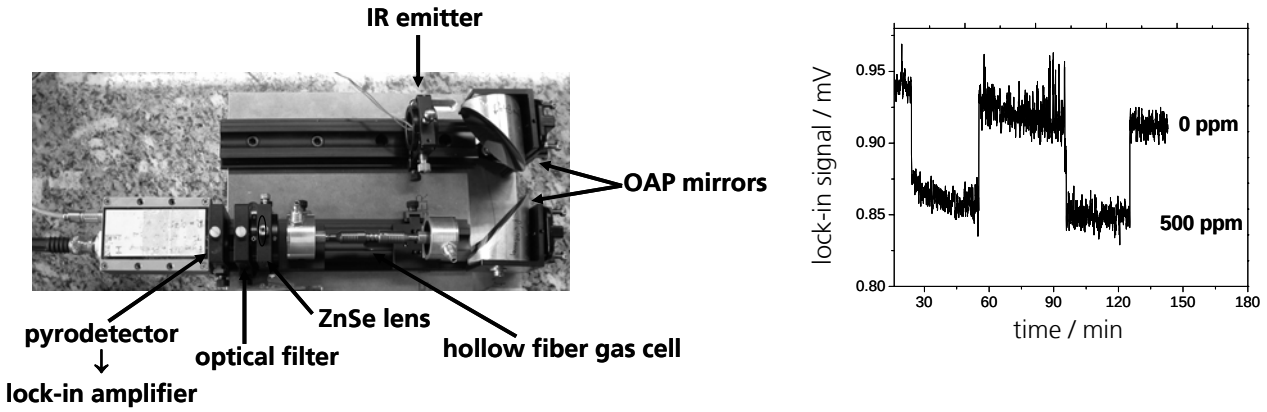

Figure 8: Setup used for measurements with hollow fibers (left). Result of an Ethanol measurement (right).

From theoretical considerations enhancement factors up to 30 seem possible.[14] The difference to the experimental value probably results from a not optimum anti-reflection layer thickness which needs a fabrication precision of a few percent. Technological irregularities are supposed to be the major reason for the observed low transmission values of our PhC samples, limiting the actual length of the cells to approximately 1 mm. By technical improvements 10 mm PhC length seems within reach. Thus taking a 10 mm PhC of 1mm width and 400µm thickness with an enhancement factor of 30, a gas cell with a figure of merit C = 189 would result. Further work in this field will pave the way to ultracompact optical gas sensors. Additionally, novel infrared light sources with better emission properties will further improve the quality of these devices.[7,27]

The actual PhC cells are still inferior to conventional techniques. To illustrate the situation, a simple 10 mm long tube with 1 mm^2 cross section has C = 4.6, and one folding mirror doubles this value. Thus hollow fibers thus may be a promising alternative. Especially, hollow photonic crystal fibers (PCF) could be the ideal solution. They might offer high light and gas transmission, spectral filtering, and optimized dispersion control which could also lead to an enhanced absorption in a single element. It could be a key technology for gaseous trace detection, too.

Because fiber technology in the MIR is still at the beginning, and many practical details are unknown, substantial effort to develop hollow PCF in this spectral range would be greatly appreciated.

ACKNOWLEDGEMENTS

Many thanks to J. Hildenbrand, J. Fuss (Fraunhofer IPM), T. M. Geppert, D. Pergande, and A. v. Rhein (University Paderborn and University Halle). The authors would like to acknowledge financial support by the BMBF and by Drägerwerk AG within the project PHOKISS (13N8525). Work on hollow fibers and multireflection cells was partly supported by the European Commission (Project GOODFOOD, FP6-IST-1-508744-IP).

REFERENCES

1. Y. A. Bakhirkin, A. A. Kosterev, R. F. Curl, F. K. Tittel, D. A. Yarekha, L. Hvozdara, M. Giovannini, J. Faist, "Sub-ppbv nitric oxide concentration measurements using cw thermoelectrically cooled quantum cascade laser-based integrated cavity output spectroscopy", App. Phys. B**82**, 149-154, 2006
2. D.D. Nelson, J.H. Shorter, J.B. McManus, M.S. Zahniser, "Sub part-per-billion detection of nitric oxide in air using a thermoelectrically cooled mid-infrared quantum cascade laser spectrometer", J. Appl. Phys. **B75**, 343, 2002.
3. A. Lambrecht, "Quantum cascade lasers, systems, and applications in Europe", Proc SPIE **#5732**, 122-133, 2005
4. G. v. Basum, D. Halmer, P. Hering, M. Mürtz, S. Schiller, F. Müller, A. Popp, F. Kühnemann, "Parts per trillion sensitivity for ethane in air with an optical parametric oscillator cavity leak-out spectrometer", Optics Lett **29**, 797-799, 2004
5. S. Y. Lin, J. G. Fleming, E. Chow, J. Bur, K. K. Choi, and A. Goldberg, "Enhancement and suppression of thermal emission by a three-dimensional photonic crystal," Phys. Rev. B **62**, R2243, 2000.
6. J. G. Fleming, S. Y. Lin, I. El-Kady, R. Biswas, and K. M. Ho, "All-metallic three-dimensional photonic crystals with a large infrared bandgap," Nature **417**, 52, 2002.
7. M. Pralle, N. Moelders, M. McNeal, I. Puscasu, A. Greenwald, J. Daly, E. A. Johnson, T. George, D. Choi, I. El-Kady, and R. Biswas, "Photonic crystal enhanced narrow-band infrared emitters," Appl. Phys. Lett. **81**(25), 4685, 2004.
8. S. John, "Strong localization of photons in certain disordered dielectric superlattices," Physical Review Letters **58**(23), 2486, 1987.
9. E. Yablonovitch, "Inhibited spontaneous emission in solid-state physics and electronics," Physical Review Letters **58**(20), 2059, 1987.
10. M. Notomi, K. Yamada, A. Shinya, J. Takahashi, C. Takahashi, and I. Yokohama, "Extremely large group velocity dispersion of line-defect waveguides in photonic crystal slabs," Phys. Rev. Lett. **87**(25), 253902, 2001.
11. T. Asano, K. Kiyota, D. Kumamoto, B.-S. Song, and S. Noda, "Time-domain measurement of picosecond light-pulse propagation in a two-dimensional photonic crystal-slab waveguide," Appl. Phys. Lett. **84**(23), 4690, 2004.
12. R.B. Wehrspohn, S.L. Schweizer, J. Schilling, T. Geppert, C. Jamois, R. Glatthaar, P. Hahn, A. Feisst, and A. Lambrecht in "Photonic Crystals," ed. by K. Busch et al., Wiley-VCH, Weinheim, Germany, ISBN 3-527-40432-5, 238-246, 2004
13. R.B. Wehrspohn, T.M. Geppert, S.L. Schweizer, A.v. Rhein D. Pergande, T. Beyer, A. Lambrecht, "Photonic crystal gas sensors", 17th International Conference on Optical Fibre Sensors, Marc Voet, Reinhardt Willsch, Wolfgang Ecke, Julian Jones, Brian Culshaw, eds., Proc SPIE **# 5855**, 24-29, 2005
14. T.M. Geppert, A.v. Rhein, S.L. Schweizer, S. Hartwig, J. Wöllenstein, A. Lambrecht, R.B. Wehrspohn, "Silicon-based Photonic Crystal Gas Sensors", Proc. MRS Fall meeting, Boston, MA 2006
15. V. Lehmann, H. Föll, "Formation mechanism and properties of electrochemically etched trenches in n-type silicon", J. Electrochem. Soc. **137**, 653-660, 1990
16. V. Lehmann, J. Electrochem. Soc. **140**, 2836, 1993.
17. H. W. Lau, G. J. Parker, R. Greef, M. Hölling, Appl. Phys. Lett. **67**, 1877, 1995.
18. J. Schilling, A. Birner, F. Müller, R. B. Wehrspohn, R. Hillebrand, U. Gösele, K. Busch, S. John, S. W. Leonard and H. M. van Driel, Opt. Mater. **17**, 7, 2001.
19. T. M. Geppert, S.L. Schweizer, J. Schilling, C. Jamois, A. v. Rhein, D. Pergande, R. Glatthaar, P. Hahn, A. Feisst, A. Lambrecht, R.B. Wehrspohn, "Photonic crystal gas sensors", Proc SPIE **# 5511**: 61-70, 2004
20. R.B. Wehrspohn and J. Schilling "A model system for photonic crystals: macroporous silicon," Phys. Stat.Sol. **197**, 673, 2003.
21. T. Geppert, S.L. Schweizer, U. Gösele, R.B. Wehrspohn, "Deep trench etching in macroporous silicon" Appl. Phys. **A 84**, 237-242, 2006
22. J. Schilling, F. Müller, S. Matthias, R.B. Wehrspohn, U. Gösele, K. Busch, "Three-dimensional photonic crystals based on macroporous silicon with modulated pore diameter". Appl. Phys. Lett.**78**, 1180-1182, 2001
23. J. U. White, "Long Optical Paths of Large Aperture", Esso Laboratories, Standard Oil Development Company, Linden, New Jersey, J. Opt. Soc. Am. **32**, 285-288, 1942.
24. S. Hartwig, J. Hildenbrand, M. Moreno, J, Fonollosa, L. Fonseca, J. Santander, R. Rubio, C. Cane, A. Lambrecht, J. Wöllenstein, "A highly sensitive IR-optical sensor for ethylene monitoring", Proc. SPIE **#5836**, 452-460, 2005.
25. W. Konz, J. Hildenbrand, M. Bauersfeld, S. Hartwig, A. Lambrecht, V. Lehmann, J. Wöllenstein, "Micromachined IR-source with excellent blackbody like behaviour", Proc. SPIE, **#5836**, 540, 2005.

26. Charlton, C., Temelkuran, B., Dellemann, G., Mizaikoff, B., “Midinfrared sensors meet nanotechnology: Trace gas sensing with quantum cascade lasers inside photonic band-gap hollow waveguides”, Appl. Phys. Lett. **86**, 194102, 2005.
27. A. Lambrecht, M. Braun, S. Hartwig, J. Nurnus, J. Wöllenstein, F. Weik, J.W. Tomm, " New infrared sources for breath analysis", Proc. SPIE #**6093**, 2006.