

# Microstructured optical fiber coated with thin films for gas and chemical sensing

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**Abstract:** We propose the use of tapered microstructured fibers with collapsed air-holes coated with thin layers for gas sensing. The collapsing of the holes allows having access to the evanescent fields which can be absorbed or attenuated with gas-permeable thin films. On the other hand, a section of the holey fiber is transformed into a solid multimode fiber. The beating between the multiple modes of the latter makes the transmission spectra of the device to exhibit an oscillatory pattern. This evanescent-fields-plus-modal-interferometer structure may offer interesting properties for gas and chemical sensing. As an example we demonstrate a hydrogen sensor.

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## References and links

1. T. M. Monro, W. Belardi, K. Furusawa, J. C. Bagget, N. G. R. Broderick, and D. J. Richardson, "Sensing with microstructured optical fibers," *Meas. Sci. Technol.* **12**, 854-858 (2001).
2. Y. L. Hoo, W. Jin, C. Shi, H. L. Ho, D. N. Wang, and S. C. Ruan, "Design and modeling of a photonic crystal fiber gas sensor," *Appl. Opt.* **42**, 3509-3515 (2003).
3. T. Ritari, J. Tuominen, H. Ludvigsen, J. C. Petersen, T. Sørensen, T. P. Hansen, and H. R. Simonsen, "Gas sensing using air-guiding photonic bandgap fibers," *Opt. Express* **12**, 4080-4087 (2004).
4. G. Pickrell, W. Peng, and A. Wang, "Random-hole optical fiber evanescent-wave gas sensing," *Opt. Lett.* **29**, 1476-1478 (2004).
5. J. M. Fini, "Microstructure fibers for optical sensing in gases and liquids," *Meas. Sci. Technol.* **15**, 1120-1128 (2004).
6. V. Matejec, J. Mrázek, M. Hayer, I. Kašík, P. Peterka, J. Kaňka, P. Honzátko, and D. Berková, "Microstructure fibers for gas detection," *Mater. Sci. Eng. C* **26**, 317-321 (2006).
7. Y. K. Lize, E. C. Magi, V. G. Ta'eed, J. A. Bolger, P. Steinvurzel, and B. J. Eggleton, "Microstructured optical fiber photonic wires with subwavelength core diameter," *Opt. Express* **12**, 3209-3217 (2004).
8. E. C. Magi, H. C. Nguyen, and B. J. Eggleton, "Air-hole collapse and mode transitions in microstructured fiber photonic wires," *Opt. Express* **13**, 453-459 (2005).
9. V. P. Minkovich, A. V. Kiryanov, A. B. Sotsky, and L. I. Sotskaya, "Large-mode-area holey fibers with a few air channels in cladding: modeling and experimental investigation of the modal properties," *J. Opt. Soc. Am. B* **21**, 1161-1169 (2004).
10. V. P. Minkovich, J. Villatoro, D. Monzón-Hernández, S. Calixto, A. B. Sotsky, and L. I. Sotskaya, "Holey fiber tapers with resonance transmission for high-resolution refractive index sensing," *Opt. Express* **13**, 7609-7614 (2005).
11. A. W. Snyder, "Coupling of modes on a tapered dielectric cylinder," *IEEE Trans. Microwave Theory Tech.* **MTT-18**, 383-392 (1970).
12. D. T. Cassidy, D. C. Johnson, and K. O. Hill, "Wavelength-dependent transmission of monomode optical fiber tapers," *Appl. Opt.* **24**, 945-950 (1985).
13. S. Lacroix, R. Bourbonnais, F. Gonthier, and J. Bures, "Tapered monomode optical fibers: understanding large power transfer," *Appl. Opt.* **25**, 4421-4425 (1986).
14. M. A. Buttler, "Optical fiber hydrogen sensor," *Appl. Phys. Lett.* **45**, 1007-1009 (1984).



15. A. Bearzotti, C. Caliendo, and E. V. A. D'Amico, "Integrated optic sensor for the detection of H<sub>2</sub> concentrations," *Sens. Actuators B* **7**, 685-688 (1992).
16. C. Wang, A. Mandelis, and J. A. Garcia, "Detectivity comparison between thin-film Pd/PVDF photopyroelectric interferometric and optical reflectance hydrogen sensors," *Rev. Sci. Instrum.* **70**, 4370-4376 (1999).
17. J. Villatoro, A. Diez, J. L. Cruz, and M. V. Andres, "In-line highly sensitive hydrogen sensors based on Pd-coated single-mode tapered fibers," *IEEE Sensors J.* **3**, 533-537 (2003).
18. A. Ortigosa-Blanch, A. Diez, A. González-Segura, J. L. Cruz, and M. V. Andrés, "Wavelength-codified fiber laser hydrogen detector," *Appl. Phys. Lett.* **87**, 201104 (2005).
19. J. Villatoro and D. Monzón-Hernández, "Fast detection of hydrogen with nano fiber tapers coated with ultra thin palladium layers," *Opt. Express* **13**, 5087-5092 (2005).
20. Z. Zhao, M. A. Carpenter, H. Xia and D. Welch, "All-optical hydrogen sensor based on a high alloy content palladium thin film," *Sens. Actuators B* **113**, 532-538 (2006).
21. H. Lin, T. Gao, J. Fantini, and M. J. Sailor, "A porous silicon-palladium composite film for optical interferometric sensing of hydrogen," *Langmuir* **20**, 5104-5108 (2004).
22. T. Xu, M. P. Zach, Z. L. Xiao, D. Rosenmann, U. Welp, W. K. Kwok, and G. W. Crabtree, "Self-assembled monolayer-enhanced hydrogen sensing with ultrathin palladium films," *Appl. Phys. Lett.* **86**, 203104 (2005).

## 1. Background and motivation

The advent of microstructured optical fibers (MOFs) has opened up a new range of possible photonic applications. Currently, there are different groups around the world investigating the use of different types of MOFs for the development of novel fiber-based sensors. It is well known that in a solid-core MOF a fraction of the modal field is located within the air-holes of the cladding. This allows the direct interaction of the guided light with different gases, liquids or biological samples via evanescent field effects. Filling the air-holes of a MOF with gases gives a possibility to design sensors with long interaction lengths with the advantage that only a small quantity of gas is required to fill the microscopic holes. Several types of MOFs have low bending losses; therefore they can be coiled to a small-size spool to realize compact gas sensors. To date several sensors that exploit the direct interaction of the evanescent fields with the target gas within the holes of unmodified MOFs have been proposed or demonstrated [1]-[5]. The walls of the air-holes of a MOF can also be coated with thin layers for the selective detection of specific gases [6].

In spite of the above advantages of MOFs for gas sensing the filling of the air-holes with the target gas may represent an inconvenient since it can take a long time. Theoretical and experimental studies have shown that the time for a gas to diffuse into the holes of a MOF is between tens of seconds to several minutes depending on the fiber length [2]. Such a long time is an issue in gas sensing and it is the main drawback of the above approach. To the time needed for a gas to diffuse into the holes of a MOF one has to add the time needed to detect, analyze, and process the signal. Leaving the microscopic holes open in a MOF is also an inconvenience since they can be infiltrated with undesirable micro-particles that can block the holes. The air-holes can also be infiltrated with moisture which may be misinterpreted as signal. There are some situations in which the response time of the sensor is crucial. In potentially explosive or flammable environments, for example in hydrogen environments, fast gas sensors are desirable. In such environments the rapid response of a sensor may be crucial.

The referred inconveniences of MOFs for gas sensing motivated the work presented here. Instead of filling the air-holes we propose the use of tapered MOFs coated with thin layers permeable to the target gas -or chemical parameter- for optical sensing. To taper a MOF we stretch it slowly while the fiber is heated with an oscillating high-temperature flame torch. This non adiabatic tapering process causes that for certain taper diameters the air-holes of a MOF collapsed allowing the access to the evanescent fields of the guided light. The collapsing of the air-holes also transforms a section of the MOF into a solid unclad multimode optical fiber which can support multiple modes. This transformation gives rise to mode coupling and beating as we will discussed later on. As a result, the transmission spectrum of a tapered MOF exhibits interference ripples. When exposed to the gas of interest the thin film deposited on



the solid section of the taper will absorb or attenuate the guided modes and, consequently, the output interference pattern will be modified. In particular if the solid region of the taper is coated with a thin palladium layer then the selective and fast detection of hydrogen is possible. With adequate thin films other chemical or physical parameters can be sensed.

It should be pointed out that the tapering of MOFs to access the evanescent fields have been already proposed [7], [8]. However, to our knowledge this is the first demonstration of gas sensing with MOFs coated with thin films.

## 2. Device fabrication and working mechanism

To fabricate the tapers we employed a home-made large-mode-area MOF consisting of a solid core surrounded by four rings of air-holes in the cladding arranged in a hexagonal pattern [9]. An atomic force microscope image of the cleaved end of our MOF before the tapering is shown in the top-left image of Fig. 1. The parameters of our MOF are: outer diameter = 125  $\mu\text{m}$ , core diameter = 11  $\mu\text{m}$ , average hole diameter = 2.7  $\mu\text{m}$ , average hole spacing (pitch) = 5.45  $\mu\text{m}$ . The fiber is single-mode from 600 nm and can be easily spliced to conventional single-mode optical fiber with minimal losses. The fiber was tapered by gently stretching it with two translation stages while it was heated with an oscillating flame torch. With such a process one gets a tapered MOF with the shape shown schematically in Fig. 1. The taper waist has a constant diameter ( $\rho_w$ ) over a length  $L_0$ . The length of oscillation of the flame torch and the elongation of the fiber can be easily adjusted. Thus, tapers with virtually any value of  $\rho_w$  and  $L_0$  can be fabricated.

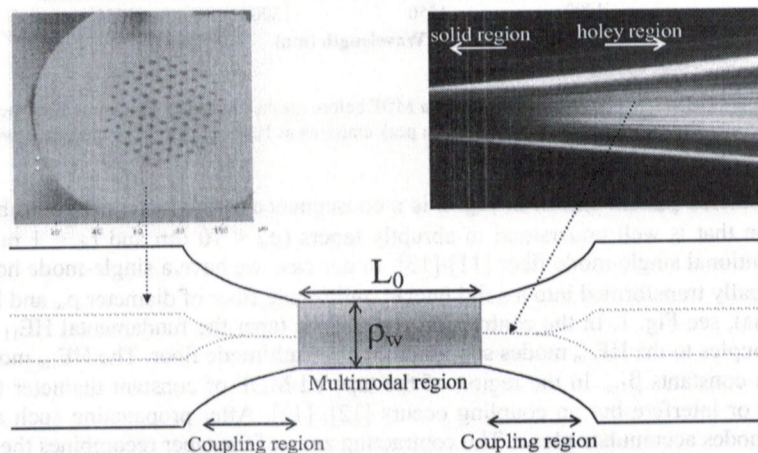


Fig. 1. Images of the cross section of an untapered MOF (top left) used to fabricate the tapers and of the expanding zone of the taper (top right). The draw illustrates a tapered MOF. The shadowed area represents the gas-permeable thin film.  $L_0$  is the length of the solid multimodal section and  $\rho_w$  is the taper waist diameter.

To study the tapers we followed two approaches. One consisted of destructive tests in which the tapered section of the MOF was inspected under an optical microscope. An image of the expanding (or contracting) zone of one of our tapers is shown in Fig. 1. The horizontal lines of different colors that appear in the right-hand side of the image indicate the presence of the air-holes. We can note that these horizontal lines converge and disappear indicating the collapsing of the air-holes. An inspection of the tapers with an atomic force microscope -after cleaving them in middle- confirmed the collapsing of the air-holes, see Ref. [10]. The other approach consisted of non destructive tests in which we launched light from different light-emitting-diodes (LEDs) to the MOF and analyzed the output pattern with an optical spectrum

analyzer (OSA). Figure 2 shows the normalized transmission spectra before and after thinning our MOF to a diameter of 15  $\mu\text{m}$ . Note that the spectrum before the tapering is basically the output pattern of the LED whereas the spectrum after the tapering exhibits a series of maxima and minima.

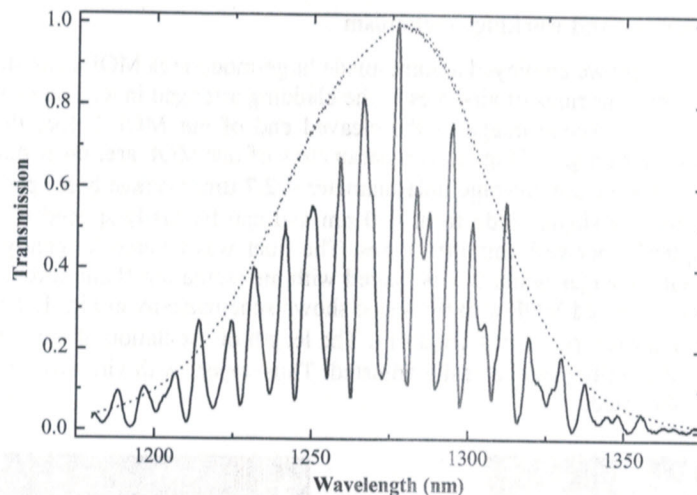


Fig. 2. Normalized transmission spectra of a MOF before (dashed line) and after (solid line) the tapering. The light source was an LED with peak emission at 1280 nm. Taper parameters:  $\rho_w = 15 \mu\text{m}$  and  $L_0 = 15 \text{ mm}$ .

The channeled pattern shown in Fig. 2 is a consequence of mode coupling and beating, a phenomenon that is well understood in abruptly tapers ( $\rho_w < 10 \mu\text{m}$  and  $L_0 < 1 \text{ mm}$ ) made from conventional single-mode fiber [11]-[13]. In our case we have a single-mode holey fiber that is gradually transformed into a solid unclad multimode fiber of diameter  $\rho_w$  and length  $L_0$  (or viceversa), see Fig. 1. In the contracting zone of the taper the fundamental  $\text{HE}_{11}$  mode of the MOF couples to the  $\text{HE}_{1m}$  modes supported by the multimode fiber. The  $\text{HE}_{1m}$  modes have propagation constants  $\beta_{1m}$ . In the region of the tapered MOF of constant diameter the  $\text{HE}_{1m}$  modes beat or interfere but no coupling occurs [12], [13]. After propagating such a beating length the modes accumulate phase. The contracting zone of the taper recombines the multiple modes of the solid fiber to core modes of the MOF. Therefore, a tapered MOF with collapsed air-holes can be considered as an interferometer. The contracting and expanding zones are equivalent to couplers or beam splitters and the modes of the beating region can be considered as arms of the interferometer. The transmission of this modal interferometer is similar to that of a Michelson or Mach-Zehnder interferometer [13]. In our case, however, to calculate the propagation constants  $\beta_{1m}$ , and consequently the phase difference between the beating modes, one has to take into account the geometry of the MOF: number of rings, diameter of the air-holes, the pitch, and obviously the wavelength, and the indexes of the waveguide and the external medium. The coupling coefficients between the  $\text{HE}_{11}$  mode and the  $\text{HE}_{1m}$  modes depend also on the quoted parameters. A detail theoretical calculation of the  $\beta_{1m}$ 's, the coupling coefficients, and the accumulated phase difference between the beating modes is beyond the scope of the present paper. It should be pointed out that in the recombining process some energy is lost. In the samples we fabricated such losses were found to be typically below 3 dB. We also like to mention that the normalization was done with respect to the highest peak of the interference pattern.



In the waist of the taper the external medium plays the role of cladding and the solid section plays the role of core. Therefore, a thin layer deposited on the region with collapsed air-holes will attenuate or absorb the evanescent fields of the different propagating modes. As a consequence, the interference pattern of the taper will also be modified. Thus, the interferometric sensing of different gases or any other chemical parameter is feasible. As a proof of principle we demonstrate here the sensing of hydrogen. To do so, we deposited an ultra thin palladium layer on the solid section of a tapered MOF, i.e., on the beating region. It is well known that a thin palladium (or palladium alloy or composite) film has the property of selectively and reversibly absorbing hydrogen [14]-[22]. When a thin Pd or Pd-alloy thin film is exposed to hydrogen it is converted to PdH. The hydration of the thin film causes an increase of the Fermi level which makes the real and imaginary part of the film dielectric constant to decrease [15, 17, 20]. Such changes in the Pd film can be monitored with optical methods [14]-[22]. We chose an ultra-thin palladium film for its rapid response time to hydrogen that can range from a few seconds to several milliseconds [19, 22].

It is important to point out that the structure proposed here for gas or chemical sensing is based on the interaction between the gas, or any other parameter of interest, and the evanescent fields via an intermediate thin layer. This indirect interaction perturbs the beating modes and makes the gas to be codified in an interference pattern. We believe that this dual behavior of the structure, evanescent fields plus modal interference, may offer some advantages for gas sensing. We next discuss some results.

### 3. Experimental results and discussion

An eight nanometer thin film was deposited on the waist of a tapered MOF with  $\rho_w = 28 \mu\text{m}$  over a length of 10 mm. The palladium film was deposited in a high-vacuum chamber by thermal evaporation at a rate of  $\sim 1 \text{ \AA/s}$ . The thickness of the film was monitored with a conventional quartz-crystal thickness monitor. Once the palladium coating was carried out the sensor was tested -at normal conditions- in an aluminum gas chamber which had an inlet and outlet to allow the hydrogen or the hydrogen/carrier mixture to flow in and out. As a carrier gas we used nitrogen. The flow of nitrogen (set to 750 sccm) and hydrogen were controlled individually with mass flow controllers. The optical and detection components consisted of a low-power LED with peak emission at 1280 nm and 80 nm of spectral width and an OSA. The spectra of the device were recorded and analyzed in a personal computer as the sensor was exposed to different concentrations of hydrogen. The MOF was fusion spliced to standard fiber and the tapered section was held straight and secured in a mechanical mount in all the experiments.

In Fig. 3 we show some results of our experiments. The left-hand side plots of the figure are the spectra that the device exhibited when it was exposed to hydrogen concentrations between 0 and 5.6%. Some of the peaks of the spectra are numbered for convenience. The relative increment of the intensity of the peaks 1 to 4 as a function of hydrogen concentration is shown in the right-hand side of Fig. 3. Note that the intensity of the peaks increases in a non linear manner as the concentration of hydrogen augments. For concentrations between 6 to 15% the device exhibited spectra (not shown here) similar to that at 5.6% which indicated the saturation of the palladium film. The reason of the rise of the interference spectra is because the index of the thin palladium film decreases when it is exposed to hydrogen [15 17, 20]. Such a decrement of the index causes the absorption of the evanescent fields to decrease. It is worth noting the remarkable increment of the intensity of the peaks which demonstrates the high sensitivity of our sensor. The sensor response time (the time required for the sensor to reach 90% of transmission change) was approximately 10 s [19].

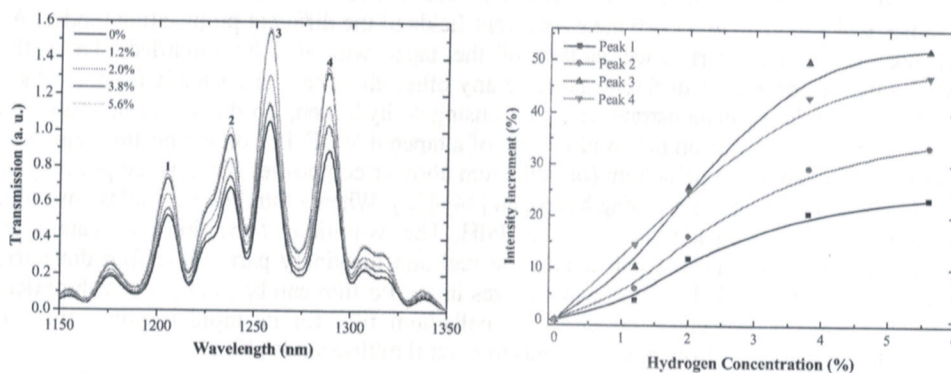


Fig. 3. Transmission spectra of a tapered MOF coated with an 8 nm-thick Pd film at different hydrogen concentrations (left) and relative increment of the peaks 1 to 4 as a function of hydrogen concentration (right). Parameters of the sensor:  $\rho_w = 28 \mu\text{m}$ ,  $L_0 = 10 \text{ mm}$ .

In Fig. 3 we can note that the intensity changes are more pronounced in the peaks or maxima than in the valleys or minima. It is expected that the changes are more remarkable at wavelengths at which constructive interference occurs. Note also that the changes at longer wavelengths, see peaks 3 and 4, are more intense than at shorter wavelengths, see peaks 1 and 2. This is owing to the fact that the attenuation of the palladium film increases with wavelength, according to the increase of the evanescent fields [17]. The interferometric hydrogen sensor reported here is more compact, simpler, and also faster than other interferometer-based hydrogen sensors reported in the literature [14]-[16], [21].

#### 4. Conclusions

In this paper we demonstrate the use of a tapered microstructured optical fiber with collapsed air-holes coated with gas-permeable thin films for gas sensing. The collapsing of the holes over a determined region of the fiber enables the access to the evanescent fields of the guided light. On the other hand, the collapsing of the holes transforms a section of the holey fiber into a multimode solid fiber. Owing to the beating between the modes supported by the solid region the transmission spectrum of a tapered MOF exhibits an oscillatory pattern. The presence of a thin film (a thin palladium layer in the example discussed here) causes absorption change of the evanescent fields and codifies the gas in the taper output interference spectrum. The evanescent fields plus modal interference behavior of the device discussed here is interesting for gas sensing, and for chemical sensing in general. Moreover, the sensor response time can be very fast since there is no need to fill the air-holes of the MOF with the gas of interest. In addition, the interaction length can be short without sacrificing the sensor sensitivity. In the proposed structure the air-holes are not open and exposed to undesirable particles or moisture. A hydrogen sensor is demonstrated to show the feasibility of our proposal.

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