proceedings

Proceedings

Enhancement of the Sensitivity of a Volatile Organic Compounds MOF-Sensor by Means of Its Structure †

Diego Lopez-Torres [1,*], Aitor Lopez-Aldaba [1,2], Cesar Elosua [1], Jean L. Auguste [3], Rapahel Jamier [3], Philippe Roy [3], Manuel Lopez-Amo [1,2] and Francisco J. Arregui [1,2]

[1] Electric and Electronic Engineering Department, Public University of Navarre, Pamplona, Spain; aitor.lopez@unavarra.es (A.L.-A.); cesar.elosua@unavarra.es (C.E.); mla@unavarra.es (M.L.-A.); parregui@unavarra.es (F.J.A.)
[2] Institute Of Smart Cities (ISC), Public University of Navarre, Pamplona, Spain
[3] Photonics Department, Umr Cnrs/University of Limoges, Limoges CEDEX, France; jean-louis.auguste@xlim.fr (J.L.A.); raphael.jamier@xlim.fr (R.J.); philippe.roy@xlim.fr (P.R.)
* Correspondence: diego.lopez@unavarra.es; Tel.: +34-948169841
† Presented at the Eurosensors 2017 Conference, Paris, France, 3–6 September 2017.

Published: 16 August 2017

Abstract: In this paper, we experimentally compare several core structures of Microstructured Optical Fibers (MOFs) for low-finesse Fabry-Pérot (FP) sensors. These sensors are designed for Volatile Organic Compounds (VOCs) measurements. We deposit Indium Tin Oxide (ITO) thin films by sputtering on the MOFs and different optical phase responses of the FP were measured for saturated atmospheres of ethanol. The sensitivity of the developed sensors is demonstrated to depend on the geometry and the dimensions of the MOF-cores. The sensors show recovery times under 100 s and the baselines are fully recovered after exposure to VOC.

Keywords: microstructure optical fiber (MOF) 1; low-finesse fabry-pérot (FP) 2; volatile organic compounds (VOCs) 3; indium tin oxide (ITO) 4

1. Introduction

Nowadays, the development of applications related to VOCs is experiencing a considerable growth due to their toxicity for humans and the hazard that they suppose for the environment, among others reasons. Optical fiber sensors based on different operating principles such as Lossy Mode Resonances (LMRs), fiber etching or tapering of fibers, have been used in the development of devices for these applications [1–5]. Another interesting case are the sensors based on MOF, which have attractive features to detect VOCs. MOFs present relatively large air holes surrounding a small core (typically few μms of diameter) which seem to be suspended along the fiber length and maintained by small silica bridges which facilitates the absorption and desorption of VOC molecules and increases the evanescent field of the guided light. Some papers confirm this assumption and encouraged us to carry out a study of different cores geometries of MOFs to improve the sensitivity of previous demonstrated devices [6].

2. Experimental Details

Three different sensors were fabricated by splicing a single mode fiber to ~1 mm of a new rectangular-shape core MOF developing a Low-finesse Fabry Pérot interferometer. Those fibers were fabricated using the stack and draw process [7]. They are formed by four large air holes divided by a rectangular core with different dimensions and structures. MOF-1 and MOF-2 showed a solid rectangle core of 2.62 μm by 1.02 μm and 3.1 μm by 4.4 μm, respectively. The third sensor, MOF-3, also showed a rectangle core (2.73 μm by 4.2 μm) with another hole (with a diameter of 761.1 nm, Figure 1B) in its center (see Figure 1).

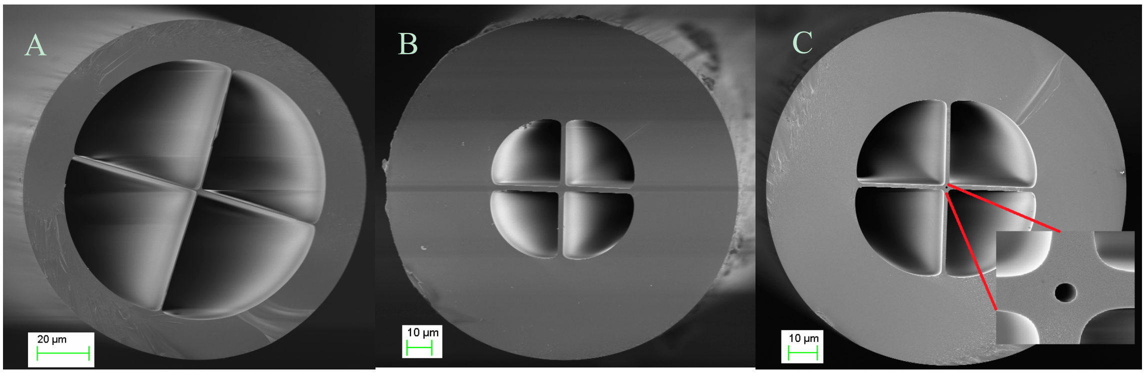

Figure 1. MOF-1 (**A**), MOF-2 (**B**) and MOF-3 (**C**) cross section. In the Figure (**C**), it can be appreciated a detail of the hole located in the center of the optical fiber.

Theoretically, when the fiber core is smaller, the interaction of the evanescent field with the surrounding external medium is stronger and this structure magnifies this effect. In the specific case of the MOF-1, this sensor shows high insertion losses when the light is coupled into its core, and the optical power obtained in the optical interrogator is lower than in the other two cases. Therefore, in terms of core size, there is a tradeoff between evanescent field interaction and optical transmitted power.

The sensing material selected was ITO because it has been previously used to detect successfully VOCs. This metallic oxide changes its refractive index in presence of different VOCs. Thus, an ITO thin film was deposited onto the head and into the walls of the MOF using a sputtering machine (Pulsed DC sputtering System, Nadetech Innovations) with a partial pressure of argon of 5×10^{-2} mb, a current of 160 mA and a voltage of 190 V during 10 min. The distance between the target of ITO and the head of the sensor was set at 5 cm. The interaction between the evanescent field of the guided light along the MOF and the ITO thin film deposited into the walls of the MOF is the main transduction mechanism which governs the behavior of this sensor [6]. The nanofilm obtained with 10 min ensures that this interaction is possible with high sensitivity [8].

The set up proposed to carry out the measurements was an in-reflection one using a commercial optical interrogator (Smartec SM 125) (see Figure 2). It was used both to illuminate the MOFs as well as to analyze the sensor responses; in this manner, it is possible to interrogate a sensor within one single channel. The responses of the sensors towards ethanol were performed placing the sensors in a metallic cell and injecting a volume of ethanol in order to achieve a saturated atmosphere of it.

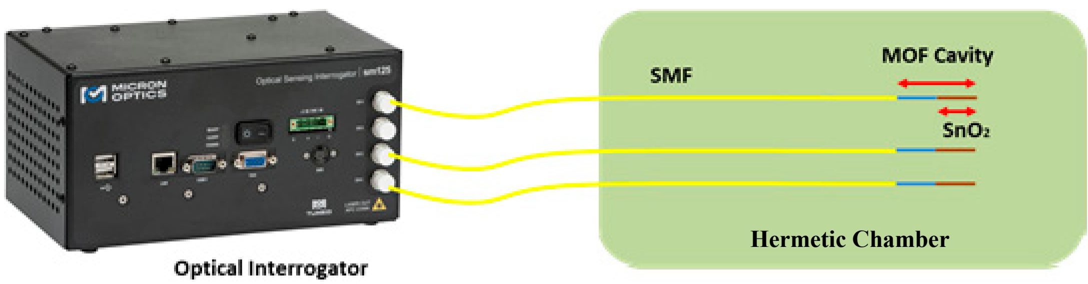

Figure 2. Experimental setup used to analyze the response of the sensors towards saturated atmospheres of ethanol.

Interrogation Technique

Sensors' response towards ethanol was measured using the Fast Fourier Transform (FFT); it is possible to work with this technique because the output optical signals of the 3 MOFs describe a periodic sinusoidal function (see Figure 3A). As it can be observed in Figure 3B, the FFT of the 3 MOFs optical spectrum present a principal component in the transformed domain, the main FP interference frequency. The sensors' responses were analyzed by monitoring the phase variations of this component; in the Figure 3B these components are encircled with a red dotted line. Also using the FFT the wavelength shifts in the optical spectrum can be monitored without the noise influence or signal amplitude variations.

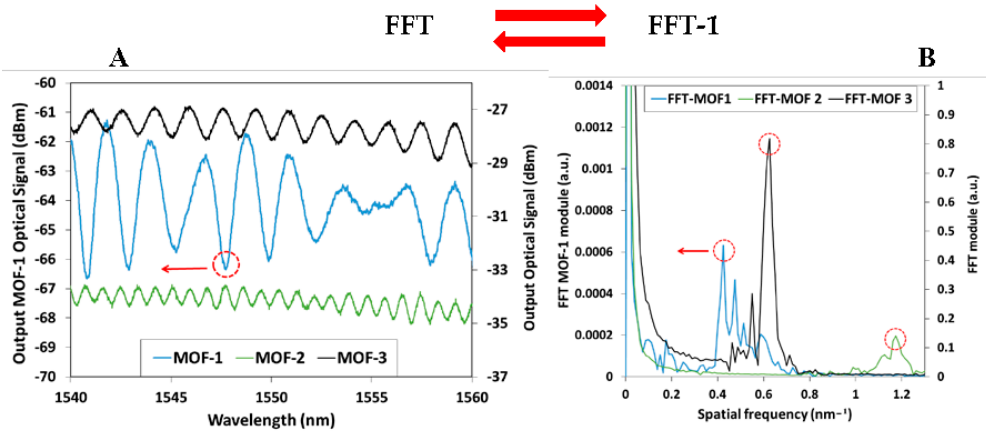

Figure 3. (**A**) Optical spectrum of MOFs and their FFTs (**B**); in both figures, the vertical left axel is applied for MOF-1 and the right axel for MOF-2 and MOF-3.

3. Results and Conclusions

As it can be observed in Figure 4, the three sensors showed different phase shift responses when they were exposed to saturated atmospheres of ethanol. In the first case, MOF-1 showed a maxima phase shift of 0.685 radians, which implies the lowest sensitivity among the sensors. As it was previously mentioned, it is a consequence to the dimensions of the core, which make difficult to couple light into the sensing section of the structure, and consequently, the sensitivity of the sensor is reduced. Sensors fabricated with MOF-2 and MOF-3, with bigger cores, showed higher sensitivities. Although the external dimensions of the cores of these last fibers are similar, the maxima phase shift obtained for MOF-3 (5 radians) is five times greater than the maxima phase shift obtained for MOF-2 (1 radian). This increment in the sensitivity is produced by the effect of the MOF-3′s core hole. This hole causes that the light travels less confined along the core (in comparison with MOF-2). Thanks to this fact, the penetration depth of the evanescent components of the fields is increased and consequently, its interaction with the ITO thin film and the sensor sensitivity. Furthermore, the sensors' response was repetitive and the sensors reached the baseline in a short period of time (below 100 s) after every exposure to VOC.

Finally, we can infer that the geometry of the core and its dimensions play an important role in the sensitivity of the MOF-sensors, so it is crucial its correct design and optimization.

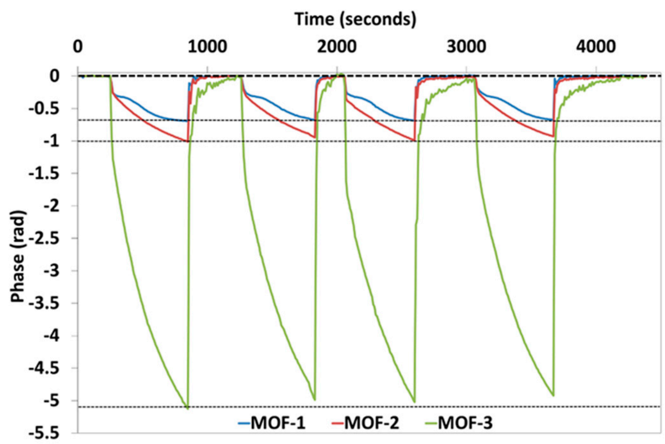

Figure 4. Phase responses of the three sensors for saturated atmospheres of ethanol.

Acknowledgments: This work was supported by the research grant TEC2016-79367-C2-2-R and TEC 2016-76021-C2-1-R (AEI/FEDER, UE) as well as Public University of Navarre program PhD grants.

Conflicts of Interest: The founding sponsors had no role in the design of the study; in the collection, analyses or interpretation of data; in the writing of the manuscript and in the decision to publish the results.

References

1. Zubiate, P.; Zamarreño, C.R.; del Villar, I.; Matias, I.R.; Arregui, F.J. High sensitive refractometers based on lossy mode resonances (LMRs) supported by ITO coated D-shaped optical fibers. *Opt. Express* **2015**, *23*, 8045.
2. Socorro, A.B.; Santamaria, E.; Fernandez-Irigoyen, J.; del Villar, I.; Corres, J.M.; Arregui, F.J.; Matias, I.R. Fiber-Optic Immunosensor Based on an Etched SMS Structure. *IEEE J. Sel. Top. Quantum Electron.* **2017**, *23*, doi:10.1109/JSTQE.2016.2633819.
3. Elosua, C.; Arregui, F.J.; Zamarreño, C.R.; Bariain, C.; Luquin, A.; Laguna, M.; Matias, I.R. Volatile organic compounds optical fiber sensor based on lossy mode resonances. *Sens. Actuators B Chem.* **2012**, *173*, 523–529.
4. Bryant-Genevier, J.; Zellers, E.T. Toward a microfabricated preconcentrator-focuser for a wearable micro-scale gas chromatograph. *J. Chromatogr. A* **2015**, *1422*, 299–309.
5. Scholten, K.; Collin, W.R.; Fan, X.; Zellers, E.T. Nanoparticle-coated micro-optofluidic ring resonator as a detector for microscale gas chromatographic vapor analysis. *Nanoscale* **2015**, *7*, 9282–9289.
6. Lopez-Torres, D.; Elosua, C.; Villatoro, J.; Zubia, J.; Rothhardt, M.; Schuster, K.; Arregui, F.J. Enhancing sensitivity of photonic crystal fiber interferometric humidity sensor by the thickness of SnO_2 thin films. *Sens. Actuators B Chem.* **2017**, *251*, 1059–1067.
7. Lopez-Aldaba, A.; Pinto, A.; Lopez-Amo, M.; Frazão, O.; Santos, J.; Baptista, J.; Baierl, H.; Auguste, J.-L.; Jamier, R.; Roy, P. Experimental and Numerical Characterization of a Hybrid Fabry-Pérot Cavity for Temperature Sensing. *Sensors* **2015**, *15*, 8042–8053.
8. Lopez-Torres, D.; Elosua, C.; Villatoro, J.; Zubia, J.; Rothhardt, M.; Schuster, K.; Arregui, F.J. Photonic crystal fiber interferometer coated with a PAH/PAA nanolayer as humidity sensor. *Sens. Actuators B Chem.* **2016**, *242*, 1065–1072.