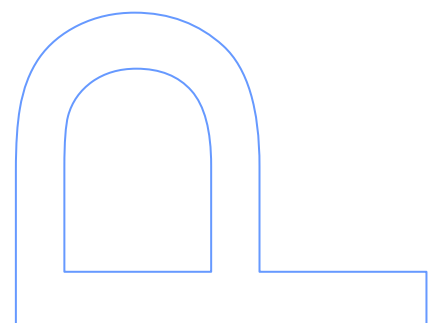
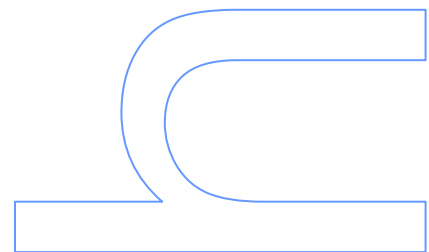
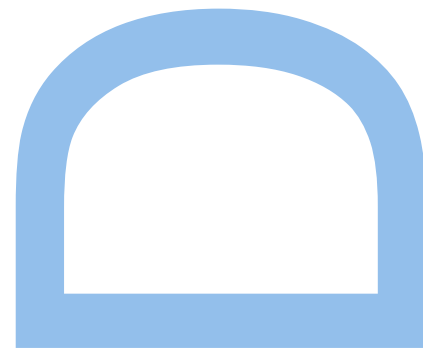
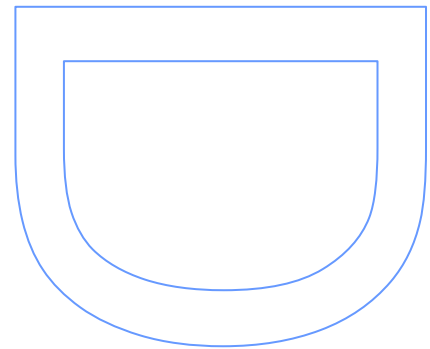
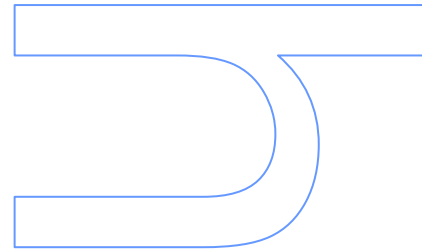
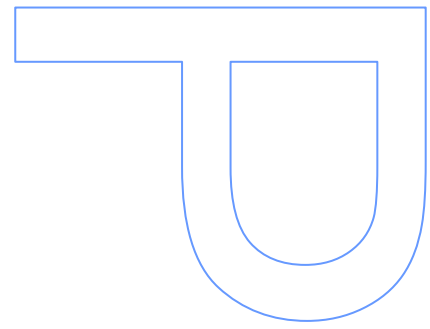


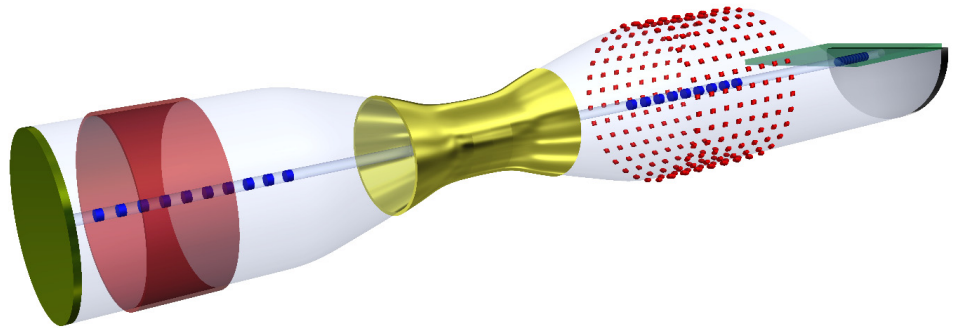
Research and Development of Optical Fibre Sensors Based on Thin Film Coating Technology

Luís Carlos Costa Coelho

Thesis Submitted to Faculdade de Ciências da Universidade
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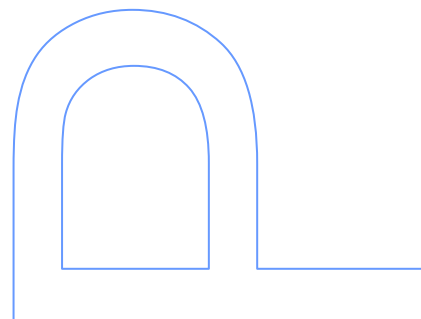
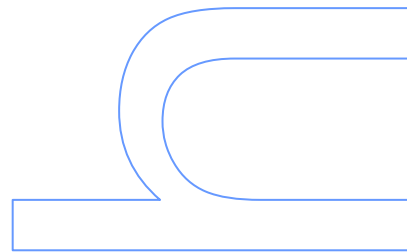
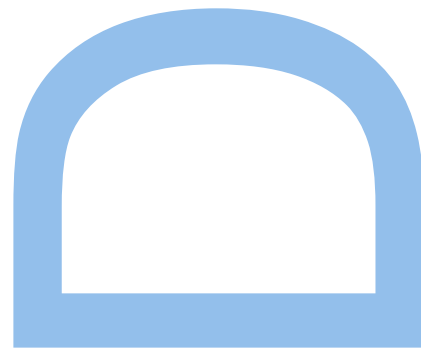
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I would like to dedicate this thesis to Sofia, Rita and Lara.

FCT

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Resumo

Nesta dissertação são expostos resultados teóricos e experimentais obtidos na investigação e desenvolvimento de estruturas específicas em fibra ótica revestida com filmes finos de metais ou óxidos para aplicação em sensores de parâmetros químicos e bioquímicos.

Apresentam-se em detalhe os sensores em fibra ótica revestidos com películas finas até aqui estudados e descrevem-se os processos físicos envolvidos na transmissão e modulação de luz. São expostas as várias técnicas utilizadas nomeadamente para fabricar as estruturas básicas e os revestimentos em torno de fibra ótica monomodo e para executar a análise morfológica e química desses revestimentos. Os estudos realizados são apresentados tendo em vista a deteção de grandezas específicas.

Os resultados experimentais obtidos incluem o estudo das propriedades espectrais de redes de período longo revestidas com óxidos tais como dióxido de titânio e óxido de zinco. A sensibilidade refratométrica intrínseca é aumentada, dependendo da espessura e do índice de refração da camada de óxido. Em particular, para valores de índice de refração do meio envolvente maiores do que o índice de refração da bainha da fibra ótica a sensibilidade pode ser superior a 12400 nm / RIU. Vários óleos alimentares têm valores de índice de refração elevado. Nesse sentido foi desenvolvido um sensor específico para monitorizar a deterioração térmica de azeite extra virgem ao longo do tempo, bem como para detetar a sua contaminação com solventes orgânicos.

As características espectrais de uma banda de atenuação das redes de período longo são também estudadas em tempo real durante o processo de oxidação de filmes finos de vários metais depositados sobre a superfície da fibra ótica na região da rede. A monitorização das mudanças que ocorrem numa das bandas de atenuação permite obter informações detalhadas sobre a transição de fase de oxidação dos filmes finos de metal.

A deteção de pequenas concentrações de gases ou vapores inflamáveis e com elevado risco de explosão é de extrema importância para a segurança de pessoas e bens. Investigou-se a possibilidade de deteção de hidrogénio e vapores, tais como etanol e hexano, usando redes de Bragg em fibra ótica revestidas com paládio e redes de período longo em fibra ótica revestidas com camadas de óxido de zinco.

O processo de ataque químico com ácido fluorídrico conduz à redução da secção da bainha da fibra ótica, permitindo que a componente evanescente do campo eletromagnético interaja com a interface de um revestimento de metal que originando a geração de plasmões de superfície. Estruturas cónicas revestidas com ouro e dióxido de titânio, operadas em modo de reflexão e transmissão a 1550 nm, foram fabricadas e caracterizadas tendo-se medido sensibilidades acima de 3000 e 5000 nm / RIU, respetivamente, no intervalo de índices de refração de 1.300 a 1.380.

Os dispositivos fabricados e caracterizados foram aplicados no estudo da deteção de trombina através da funcionalização da superfície da fibra com um complexo de poli-L-lisina e um aptâmero. O elevado desempenho das estruturas de deteção funcionando no modo de ressonância plasmónica de superfície permitiu detetar 10 nM de trombina com resoluções até 0.54 nM.

Abstract

This thesis presents theoretical and experimental results obtained in the research and development of specific structures in optical fibres coated with metal or oxide thin films oriented for applications in the sensors for chemical and biochemical parameters.

A detailed overview of optical fibre sensors with thin film coatings on the surface is presented, followed by a description of the fundamental physical processes involved on the light transmission and modulation. Moreover, are addressed all the techniques used to fabricate the bare structures, to perform the coatings around the cylindrical single mode fibres and to perform the morphological and chemical analysis of the thin film coatings. Different applications and studies were performed considering specific sensing parameters.

The experimental results achieved includes the study of the spectral properties of long period fibre gratings coated with oxide layers such as titanium dioxide and zinc oxide. The intrinsic refractometric sensitivity is enhanced depending of the thickness and the refractive index of the oxide layer. In particular, for refractive index values of the surrounding medium higher than the fibre cladding refractive index the sensitivity could be higher than 12400 nm/RIU. The majority of edible oils have high refractive index values. Accordingly it was developed a specific sensor for monitoring the thermal deterioration of extra virgin olive oil over time and to detect contamination with organic solvents.

The spectral characteristics of one attenuation band of long period fibre gratings were studied in real time during the oxidation process of thin film metals layered on the optical fibre surface in the grating region. The monitoring of the changes of the attenuation band permits to obtain detailed information about the oxidation phase transition undertake by the metal thin films.

The detection of small concentrations of gases or vapours, which are flammable and with high explosion risk is extremely important for the safety of people and property. Looking for the detection of hydrogen and vapours, as ethanol and hexane, an investigation using fibre Bragg gratings coated with palladium and long period fibre gratings coated with layers of zinc oxide was performed.

The chemical etching process with hydrofluoric acid applied to silica based optical fibres causes a reduction in the fibre cladding diameter allowing the evanescent component of the electromagnetic

field to interact with the metal coating interface leading to the generation of surface plasmons. Taper structures coated with gold and titanium dioxide, operated in reflection and in transmission modes at 1550 nm, were fabricated and characterized for the measurement of the surrounding refractive index, resulting in sensitivities above 3000 and 5000 nm/RIU, respectively, in a refractometric range that extends from 1.300 to 1.380.

The fabricated and characterized evanescent field based devices were applied to the recognition of thrombin through the functionalization of the fibre surface with a complex of poly-L-lysine and an aptamer. The high performance of sensing structures of this type operating in the surface plasmonic resonance mode permit detections of 10 nM of thrombin with resolutions down to 0.54 nM.

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Acronyms and Abbreviations

ALD - atomic layer deposition	FBG - fibre Bragg grating
APTES - (3-aminopropyl)triethoxysilane	fcc - faced-centred cubic
ATR - attenuated total reflection	FFT - fast Fourier transform
BBS - broadband source	FP - Fabry-Perot
BPM - beam propagation method	FPI - Fabry-Perot interferometer
BSA - bovine serum albumin	FTIR - Fourier transform infrared
CEMUP - Materials Centre of the University of Porto	FWHM - full width half maximum
CRI - cladding refractive index	GIF - graded index fibre
CVD - chemical vapour deposition	HEMA - 2-hydroxyethyl methacrylate
D4 polyurethane hydrogel	HF - hydrofluoric acid
DDMA - didodecyl-dimethyl-ammonium hydroxide	HT - high tension
DMSI - dimethyl suberimide	IPA - isopropyl alcohol
DNA - deoxyribonucleic acid	LB - Langmuir-Blodgett
E. coli - <i>Escherichia coli</i>	LbL - layer-by-layer
EDS - energy dispersive X-ray spectroscopy	LDPE - low density polyethylene
EDTA - ethylenediamine tetraacetic acid	LMR - lossy mode resonance
EO - edible oil	LPFG - long period fibre grating
ESA - electrostatic self-assembly	LSPR - localized surface plasmon resonance
E-T - Everhart-Thornley	LT - low tension
EVOO - extra virgin olive oil	M - modal interference
	MI - Michelson interferometer
	MIP - molecularly imprinted polymer

MMF - multimode fibre	PVD - physical vapour deposition
MMI - multimode interferometer	RBS - Rayleigh backscattering spectra
MOF - microstructured optical fibres	RI - refractive index
MZI - Mach-Zehnder Interferometer	RIU - refractive index unit
NIR - near infra-red	SELEX - systematic evolution of ligands by exponential enrichment
OPD - optical path length difference	SEM - scanning electron microscopy
OSA - optical Spectrum analyser	SERS - surface enhanced Raman spectroscopy
PAA - poly(acrylic acid sodium salt)	SI - Sagnac interferometer
PAH - poly(allylamine hydrochloride)	SLD - super luminescent diode
PAM - poly acrylamides	SMF - single mode fibre
PAN - polyacrylonitriles	SMF28e - common single mode fibre, Corning
PBG - photonic band gap	SMS - single mode – multimode – single mode
PBS - phosphate buffered saline	SPR - surface plasmon resonance
PCF - photonics crystal fibres	SPW - surface plasmon wave
PCSC - plastic-clad silica-core	SRI - surround refractive index
PCT - prism coupling technique	SSPE - standard saline phosphate EDTA
PDDA - poly(diallyldimethylammonium chloride)	TBA - thrombin binding aptamer
PEG - mixed polyethylene glycol	UV - ultra violet
PLL - poly-L-lysine	VIS - visible
Poly - poly(2-hydroxyethyl methacrylate)	VOC - volatile organic compounds
Hema	XPS - X-ray photoelectron microscopy
PS - polystyrene	XRD - X-ray diffraction
PSS - poly(sodium 4-styrenesulfonate)	
PTFE - polytetrafluoroethylene	
PVA - polyvinyl alcohol	
PVC - plasticized poly(vinyl chloride)	

Chapter 1

Introduction

1.1 Motivation

The outcome of optical fibres opened new perspectives and possibilities about the way of carrying information with light which capacity has been increasing exponentially along the last 20 years. In addition, a wide range of structures have been created to be used as sensing devices benefiting from the well-known advantages of optical fibres such as small size, insensitivity to electromagnetic fields, freedom of electric power, long distance covering and intrinsic multiplexing capabilities. Although optical fibre sensors are being studied and developed from several years, there is still a long path to follow to acquire the knowledge and the expertise necessary to the widespread application of this technology in the multi-sensing functionalities required by an increasingly automated world for which fibre optic sensing shows remarkable characteristics [1].

The work herein presented is grounded on the competences in optical fibre technology and optical fibre sensing of INESC TEC / Centre for Applied Photonics [2]. Therefore, the PhD programme was designed to take advantage of in-house technologies to establish know-how and technological competences in the field of thin film based optical fibre sensing. Indeed, in recent years it became apparent the addition of specific coatings onto the fibre surface could open new possibilities in fibre

optic sensing particularly at two levels, namely sensor tailoring and sensor enhancement. Within this framework, research was performed looking for the development of new guided wave sensors based on metallic, dielectric and polymeric thin deposition in common fibres, associated with the plasmonic resonance phenomena as well as when incorporating structures such as fibre gratings, considering in particular biochemical, biological and environmental sensing applications.

The research program addresses in particular deposition of different materials as sensing layers in common single mode fibres with built in long-period and Bragg fibre gratings and manipulated to support surface plasmons. The interrogation and multiplexing of these structures following different approaches and techniques proved to allow high performance sensing in the C-band of telecommunications (optical wavelengths in the range 1530-1565 nm) of a variety of mensurands relevant for chemical and biochemical applications.

This dissertation is based on a set of challenges highlighted in the following:

- Theoretical evaluation of the performance of thin film based sensing devices in standard optical fibres;
- Fabrication and characterization of dielectric/metallic thin films structures in standard optical fibres with built-in resonant devices as long period gratings and fibre Bragg gratings;
- Study of the characteristics of these structures as sensing elements when different light modulation formats are considered (intensity and wavelength) associated with diverse optical phenomena, in particular surface plasmon resonance (SPR);
- Study of the conditions to multiplex these sensing structures aiming remote and distributed sensing in field applications;
- Application of the proposed concepts, methodologies and developed structures and techniques for measurement of some target parameters, namely hydrogen, thrombin or contamination of edible oils.

It was the comprehension of the relevance optical sensing will have on the build-up of the highly technological society of the future, and of the peculiar role the optical fibre will have in this field as one of the core elements that shall turn possible the development of bio-inspired large-scale sensing networks, which motivated me to outline the PhD programme along the optical fibre sensing domain. With this background, the perception of the broad and most unexplored field of sensing with coated

optical fibres, combined with my interests in thin-films devices, naturally led to the decision to tackle the challenge of studying optical sensing based in fibres with thin-film coatings of different materials. The outcome of this endeavour is exposed in the chapters of this thesis.

1.2 Scientific Contributions

The research performed on sensing structures based on standard optical fibres incorporating thin films originated a number of novel scientific contributions here summarized.

- The performance of long period fibre gratings (LPFG) produced by the electric arc technique incorporating thin coating layers of titanium dioxide (TiO_2) and zinc oxide (ZnO) has been studied, revealing an increased sensitivity to the refractive index (RI) of the external medium (liquid), in particular for index values higher than that of the fibre cladding, which is an important RI region when analysing the characteristics of mineral and edible oils.
- Moreover, LPFGs have been used to monitor the oxidation of thin films of metals into specific states. The results obtained with this technique compares well with those registered with standard chemical and morphological techniques, with the advantages of real time monitoring, which can be remote, as well as the benefits which result from a more amenable measurement system, including the cost factor.
- The thermal deterioration of edible oils was monitored with the enhanced TiO_2 coated LPFG at 180 and 225°C up to 57 hours, being able to detect changes in the oil optical properties (refractive index) after cooling. In addition, the same sensing structure was useful to detect contaminations of edible oils with hexane, a solvent usually used to perform the extraction of some oils.
- Coated fibres with built in structures as LPFGs and fibre Bragg gratings (FBG) were also an element of study for gas detection. The usage of palladium (Pd) and ZnO thin film coatings combined with FBG or LPFG devices allow the detection of hydrogen and organic vapours such as ethanol or hexane, with compensation of the thermal cross sensitivity effects. It was also investigated the deleterious impact of humidity on the Pd surfaces over silica fibres while in presence of H_2 , as well as on LPFGs coated with high surface area and thick ZnO films, and was proposed a technique to attenuate this problem which proved to be effective.

- Surface plasmon resonance sensing structures based on chemical etched tapered standard optical fibres were researched. They evidenced high sensitivity to external RI, reaching values over 5000 nm/RIU, an indication of their adequacy for the detection of very small analyte concentrations (where RIU is refractive index unit).
- Sensing devices based on coated LPFGs and SPR fibre structures were applied to biosensing, in particular for the detection of thrombin. The higher sensitivity of SPR allows better results for small analyte concentrations (below 10 nM) in the refractive index range from 1.300 to 1.350, a region where coated LPFG does not have the highest sensitivity. On the other hand, the research performed showed sensing devices based on coated LPFGs have their sensitivity greatly enhanced when external medium with higher refractive indexes are present, in such cases turning out to be one of the most effective optical sensing approaches.

1.3 Structure of the Thesis

This thesis addresses the study of coated optical fibres for sensing. It is organized in such a way each chapter contains the state-of-the-art of the subject dealt with in the chapter, nevertheless incorporating cross links with the topics developed in the other chapters looking for the build-up of a coherent document.

The thesis is divided in 10 chapters. Chapter 1 outlines the motivation that led me to carry out research on optical sensing with coated fibres, elaborates on the potential associated with this sensing approach and summarizes the main scientific contributions derived from the research performed.

Chapter 2 presents an overview about optical fibre devices using coating layers as sensing elements or to enhance optical features of fibre structures. The description of the most used coating techniques and of the different types of principles and configurations employed in this field are presented.

The fabrication processes used to obtain the proposed sensing devices are common to several chapters, therefore chapter 3 presents the description of each of them, as well as of the most common characterization techniques. The calibration of the deposition system and of the refractive index measurement system is achieved through the characterization of titanium dioxide thin films.

The working principles of the most common fibre gratings are described in chapter 4. Long period fibre gratings coated with titanium dioxide and zinc oxide are used in a systematic study on the effect

of the coating thickness in the optical transmission spectra. The enhanced characteristics of coated long period gratings operating as refractometers are also analysed.

In chapter 5, a set of experimental studies aiming the detection of gases is presented. Some gases could work as standard targets to assess the performance of fibre optic sensing devices for gas detection, such as those based on Fabry-Perot interferometers. Specific coatings as palladium or zinc oxide over fibre Bragg gratings and long period fibre gratings are studied aiming the detection of hydrogen and vapours.

Real time monitoring of the oxidation process in metals thin films using long period fibre gratings is discussed in chapter 6. A set of metals deposited around long period fibre gratings and oxide by thermal annealing in air atmospheric pressure is studied using surface analysis techniques and by mapping the optical transmission response of the gratings during the oxidation process.

In chapter 7 it is reported the experimental results obtained with long period fibre gratings coated with titanium dioxide when targeting the detection of extra virgin olive oil thermal deterioration, as well as the monitoring of organic solvents as hexane in edible oils.

Chapter 8 deals with the phenomenon of plasmonic resonance in optical fibres. Experimental results on the fabrication and characterization of SPR based fibre optic sensing devices operating in the 1500 nm wavelength region are presented considering a sensing structure produced by chemically etching single mode optical fibres. The multiplexing of these devices is demonstrated based on wavelength addressing supported by fibre Bragg gratings.

Chapter 9 reports the results obtained when applying the sensing devices described in previous chapters for the detection of biological parameters. For this purpose the detection of thrombin using an aptamer based probe is used as a model system for protein detection. Experimental results involving the detection of Thrombin are delivered when considering optical biosensors based on long period fibre gratings coated with titanium dioxide and on SPR in optical fibre platforms.

The main conclusions derived from the R&D activity undertook along the PhD path are presented in chapter 10, where the main scientific achievements are highlighted, being also delivered suggestions for future work.

1.4 List of Publications

1.4.1 Book chapters

1. L. Coelho, J.L. Santos and D. Viegas, "Thin film application for sensors in optical fibers", CRC Press. (in press)

1.4.2 Papers Published in International Journals

1. L. Coelho, J. L. Santos, J. M. M. M. de Almeida, D. Viegas, and R. B. Queirós, "Aptamer-Based Fibre Sensor for Thrombin Detection" (submitted for publication)
2. L. Coelho, J. L. Santos, D. Viegas, and J. M. M. M. de Almeida "Monitoring oxidation phases of copper thin films using long period fiber gratings", (submitted for publication)
3. L. Coelho, J. L. Santos, D. Viegas, and J. M. M. M. de Almeida "Fabrication and Characterization of Metal Oxide Coated Long Period Fiber Gratings", Journal of Lightwave Technology (in press)
4. L. Coelho, J. M. M. M. de Almeida, J. L. Santos, and D. Viegas, "Fiber Optic Hydrogen Sensor Based on an Etched Bragg Grating Coated with Palladium", Appl. Opt. **54**, 10342-10348 (2015). DOI: 10.1364/AO.54.010342.
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7. L. Coelho, J. M. M. M. de Almeida, H. Moayyed, J. L. Santos, and D. Viegas, "Multiplexing of Surface Plasmon Resonance Sensing Devices on Etched Single-Mode Fiber," Journal of Lightwave Technology **33**, 432-438 (2015). DOI: 10.1109/JLT.2014.2386141.
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11. L. Coelho, P. A. R. Tafulo, P. A. S. Jorge, J. L. Santos, D. Viegas, K. Schuster, J. Kobelke, and O. Frazão, "Simultaneous measurement of partial pressure of O₂ and CO₂ with a hybrid interferometer," *Optics Letters* **37**, 3063-3065 (2012). DOI: 10.1364/OL.37.003063.
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2. L. Coelho, D. Viegas, J. Santos, and J. de Almeida, "Real time monitoring oxidation of transition metals with long period fiber gratings," in International Conference on Optical Fibre Sensors (OFS24), (International Society for Optics and Photonics, 2015), 96340N-96340N-96344. DOI: 10.1117/12.2195199.
3. L. Coelho, D. Viegas, J. L. Santos, and J. M. M. de Almeida, "Monitoring of high refractive index edible oils using coated long period fiber grating sensors," in *SPIE Optics+ Optoelectronics*, (International Society for Optics and Photonics, 2015), 95061A-95061A-95067. DOI:10.1117/12.2178811.
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5. J. L. Santos, H. Moayyed, I. Leite, L. Coelho, D. Viegas, and A. Guerreiro, "Optical Sensing Based in Plasmonics and the Metamaterials Enhancement Factor," in *Latin America Optics and Photonics Conference*, (Optical Society of America, 2014), LTh3C.3. DOI: 10.1364/LAOP.2014.LTh3C.3.
6. L. Coelho, J. M. Almeida, J. L. Santos, R. A. S. Ferreira, P. S. Andre, D. Viegas, "Sensing Structure Based on Surface Plasmonic Resonance in Single Mode Optical Fibers Chemically Etched," Fifth European Workshop on Optical Fibre Sensors **87940E** (May 20, 2013). DOI: 10.1117/12.2026809.

7. L.Coelho, O. Frazão. F.X. Malcata, J.L. Santos, "Water Vapor Effect on the Palladium Film Surface for Hydrogen Sensing", Europtrode XI (XI Conference on Optical Chemical sensors and Biosensors), April 1st-4th, Barcelona, Spain 2012.
8. P. A. R. Tafulo, L. Coelho, P. A. S. Jorge, J. L. Santos, K. Schuster, J. Kobelke, O. Frazao "Simultaneous Measurement of Partial Pressure of O₂ and CO₂ using Hybrid interferometer," 22nd International Conference on Optical Fiber Sensors, Pts 1-3 **8421**(2012). DOI: 10.1117/12.970474.
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10. L. Coelho, S. F. O. Silva, P. A. R. Tafulo, J. L. Santos, O. Frazao, F. X. Malcata, and M. Costa, "Optical Fibre Hydrogen Sensors Based on Palladium Coatings," International Conference on Applications of Optics and Photonics **8001**(2011).

I was also co-author of a set of other publications in international journal (16) and of presentations in international conferences (20), reporting R&D results (not included in this thesis) which appear in the PhD thesis of Colleagues of the research Group. The list of these works appear in my CV.

Chapter 2

Optical Fibre Sensors Based on Thin Films

An overview about the state of the art of optical fibre sensors based on thin films is presented. The basic concepts of the physical processes involved on each configuration along with the type of coatings and the emerging applications are briefly explored.

2.1 Introduction

One of the most important revolutions in the technology of the 20th Century was the optical transmission over glass fibres. This development, combined with the parallel progresses in microelectronics and informatics, drastically changed the way information is spread all around the World. Optical fibres consist in a cylindrical core and a surrounding cladding made of glass or plastic. The refractive index (RI) of the core is slightly higher than the cladding one allowing light propagation based on the phenomenon of total internal reflection.

The first low-loss optical fibre was produced by Corning Glass at the Bell laboratories in 1970, showing a loss of 17 dB/km by doping the silica glass with titanium (Ti). Few years later using germanium oxide instead titanium they have reached a loss value of 4 dB/km, therefore opening the possibility to be used in communications. Since then telecommunications and networking have been

engaged in a dramatic development period. Before this phase it is relevant to state plastic optical fibres have already been considered for sensing, in particular addressing temperature measurement [3, 4]. Optical fibres sensors appeared only a decade after the introduction of optical fibres in communications systems.

This sensing functionality of optical fibres has continuously expanded along the years, at a first stage mostly directed to the measurement of physical parameters such as temperature, mechanical strain, pressure, current, voltage, acceleration, rotation, vibration, acceleration, bending, torsion, displacement and others, but soon this sensing platform has been considered for the detection of chemical and biochemical species. The general basis of this process is that the light is coupled to an optical fibre and during its path can, at a single point or at a multipoint series, suffer a perturbation that can be detected with an adequate arrangement.

When compared with other type of sensors, like electric-based, fibre-optic sensors exhibit some disadvantages as the robustness and the cost of optical components, however a high number of advantages can be found to support its development. In particular: they can be used over a wide operating temperature range; they are made of electrically insulating materials which opens the possibility to be used e.g. in high-voltage environments; immunity to electromagnetic interference without disturbing the nearby devices; they can be used in explosive environments once there is no risk of electrical sparks; materials can be chemically passive without being affected by corrosion and without risk of sample contamination; and, at the top of these favourable characteristics, multiplexing capabilities allow the interrogation of a single optical fibre with multipoint sensing for one or more parameters [1].

A particularly useful feature of intrinsic fibre optic sensors is that they can provide distributed sensing over very large distances using the same signal acquisition setup.

In the early 80s optical fibre sensors with thin film coatings started to be discussed in the scientific community to analyse the possibility of detecting weak magnetic fields by using magnetostrictive perturbation of optical fibres [5]. The inclusion of these films adds additional flexibility for the tailoring of the optical fibre sensing platform, therefore is not surprising the steadily increase over the years of such combination, with a rather steep growing in recent years accompanying the fast progresses in Nanosciences and Nanotechnologies.

The evolution of the number of papers published in the field of optical fibre sensing in general and with thin film coatings is depicted in Figure 2.1.

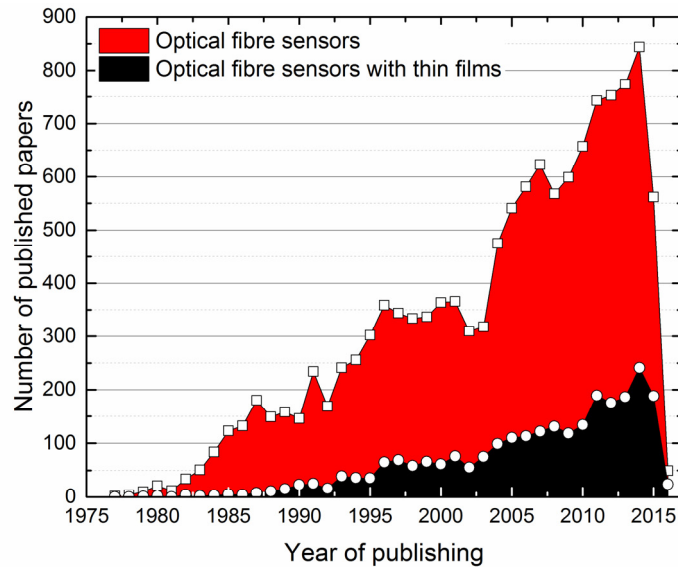


Figure 2.1 – Time evolution of the published scientific papers in international journals related to optical fibre sensors compared to the ones using thin film coating. Source: SCOPUS (Keywords: fibre optic sensor and film or coated or coating).

The interest on this subject is growing every year and more than 10% of the total papers published in this field use thin film coatings, in particular applied to the detection of chemical and biological entities.

2.2 Principles and Configurations for Optical Sensing

In the past twenty years, much effort was focused on miniaturizing fibre optic sensors by the application of different techniques. Some examples include different coating techniques, different layouts or different types of fibres that could be plastic, silica, hybrid, or microstructured fibres or retro-reflected fibres, side polished, D-type, tapered, decladded, U-bent fibres, using in-fibre gratings, nanoparticle coatings, or interferometric configurations, among many others [6-8].

Over the years tens of different optical fibre configurations for sensing were studied in order to measure physical parameters as strain, temperature, pressure and other quantities by modifying a fibre so that the quantity to be measured modulates the intensity, phase, polarization, and the wavelength of light in the fibre [8].

Some important principles and configurations are presented briefly based on the modulation approaches *evanescent field* and *plasmonics*.

2.2.1 Modulation Approaches

The optical field propagating in the fibre can be manipulated by several optical mechanisms triggered in the sensing region by the targeted measurand, inducing different field modulation fingerprints, such as intensity, wavelength or phase modulation.

– *Intensity Modulation*

The simplest type of fibre optic sensors is probably provided by intensity measurements based on the modulation of the losses in a certain light path creating an optical intensity modulation signal [1]. The light could interact with the measurand through several configurations changing the intensity. For example, two inline fibres separated by some microns proposed by Udd where the amount of light that reaches the second fibre depends on the alignment between the fibres which is modulated by the measurand [9].

One of the most used phenomenon in intensity measurements is the total internal reflection. Light is propagated along the core and reaches the fibre end at an angle that allows the total internal reflection and through a mirror that forces the light to be collected. When the external refractive index starts to approach that of the core some light propagates out of the fibre core and is lost which results in an intensity modulation.

– *Wavelength Modulation*

Optical fibre gratings are usually inscribed in single mode fibres by introducing a small modulation in the effective refractive index of the core with a certain periodicity. This modulation creates unique spectral characteristics in the transmission spectrum. Depending on the period and the modulation two main types of gratings could be created, e.g., short period fibre Bragg grating (FBG) and long period fibre grating (LPFG). The Figure 2.2 presents a scheme with both types in the same fibre section [10].

FBGs are commonly used as sensors to monitor changes in the measurand (e.g., strain or temperature) by follow the wavelength shift of the reflected Bragg band. The resonance condition of a Bragg grating is given by the equation (2.1) [11].

$$\lambda_B = 2n_{\text{eff}}\Lambda \quad (2.1)$$

Where Λ is the grating period and n_{eff} is the effective refractive index of the core. With this device a narrow spectral band centred at λ_B is reflected while the rest of the broadband light signal is transmitted. The bandwidth of the reflected signal depends on several parameters, as the grating length and the induced refractive index, with typical values around 0.05 to 0.5 nm.

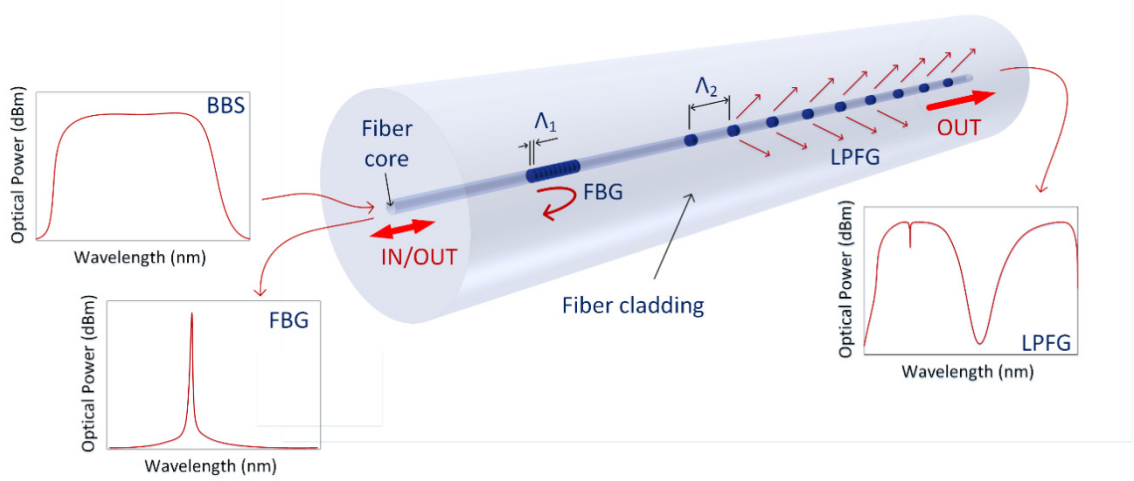


Figure 2.2 – Scheme of two in-line fibre gratings: a fibre Bragg grating and a long period fibre grating. On the left, typical curve of a broadband source as light input and the reflection signal with the Bragg narrow band. On the right, the transmission signal containing both bands.

LPFGs are a different type of devices and started to be used as lossy filters. They are very attractive as refractometers since they present high sensitivity to the external medium without any special treatment.

In a single mode fibre the light is propagated in the fundamental mode LP_{01} with a propagation constant β_{01} , while the propagation constants of the cladding modes are noted as $\beta_{cl}^{(n)}$. The phase matching condition between the guided mode and the forward propagating cladding modes is given by equation (2.2) [12].

$$\beta_{01} - \beta_{cl}^{(n)} = \frac{2\pi}{\Lambda} \quad (2.2)$$

Where Λ is the periodicity of the grating that satisfies the coupling condition from the fundamental mode to the n^{th} -cladding mode. The phase matching vector is short resulting in a grating period of hundreds of microns. As a result several attenuation bands are generated in the transmission spectrum of the fibre with a bandwidth of several tens of nm [13]. As the surrounding refractive index changes

from the unit to near cladding refractive index, the principal effect is a shift of the attenuation bands to shorter wavelengths [14, 15].

More details considering the theoretical aspects are presented in section 4.2.2.

– Phase Modulation (Interferometric Layouts)

Critical parameters for the evaluation of sensor performance are the sensitivity and resolution with which the measurement is performed. With respect to these, interferometric sensing is a rather appellative approach. Fibre optic interferometers can be categorized into four types: Fabry-Perot, Mach-Zehnder, Michelson, and Sagnac, with some of the basic layouts shown in Figure 2.3.

The Fabry-Perot interferometer (FPI) is in general formed by two parallel mirrors, separated by a medium, at a certain distance [Figure 2.3-(a)]. The superposition of both reflected and transmitted beams at the two parallel surfaces results in an interference which depends on the distance and the medium between the mirrors.

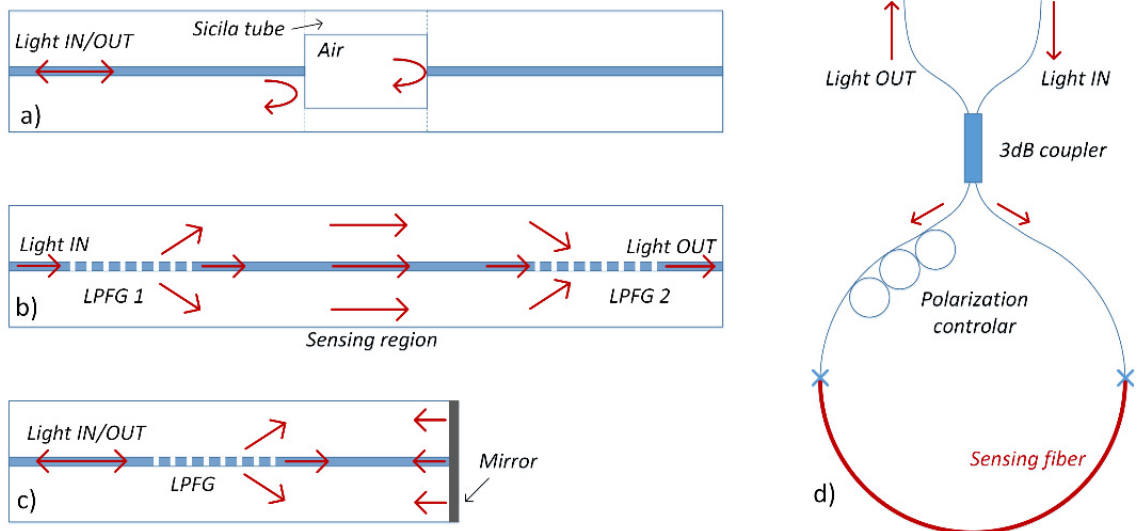


Figure 2.3 – Scheme of different types of fibre interferometers: a) Fabry-Perot, b) Mach-Zehnder, c) Michelson and d) Sagnac.

The input light spectrum reflected or transmitted in the cavity is modulated mainly by the optical phase difference between the two reflected or transmitted beams. The phase difference of the FPI is given by

$$\delta_{\text{FPI}} = \frac{2\pi}{\lambda} n 2L \quad (2.3)$$

where λ is the wavelength of incident light, n is the RI of cavity material or cavity mode, and L is the physical length of the cavity [16].

Mach-Zehnder interferometers (MZI) can be applied to optical fibres by considering two fibre arms where the incident light propagates after splitting, with the further recombination creating an interference pattern according to the optical path length difference (OPD) between the two arms. The LPFG is in charge to couple part of the light from the core to the cladding of the fibre. In sensing applications one arm is used for reference and is kept free of perturbations while the other one is exposed to the external medium and used for sensing. In a single fibre, illustrated in Figure 2.3-(b), the light is split between the core (reference) and cladding (sensing arm) and then after recombination interference occurs. In the situation illustrated in Figure 2.3 -(b) the light split/recombination is performed with a pair of LPFGs, although proved alternatives have been used based on a core mismatch fusion splice, on a multimode fibre length section, on a smaller core fibre, on a fibre taper or others [17]. This type of MZIs has the same physical length in both arms, but the optical path lengths are different due to the lower effective refractive index of the cladding mode when compared with the one associated to the core mode.

A similar operation principle applies to the Michelson interferometers (MI) where the incident light is split into two fibre arms, but instead being recombined again the fibre ends are cleaved and coated with mirrors forcing the light to be reflected back to the same split device and then recombined [Figure 2.3-(c)].

Sagnac interferometers (SI) consist of an optical fibre loop, along which two beams from a beam splitter are propagating in counter directions with different polarization states [Figure 2.3-(d)].

If the loop is rotated the light propagates in both directions at different speeds (c_+ and c_-), originating a difference in the propagation times, therefore a phase shift, $\Delta\phi$, is introduced given by equation (2.4) [18]:

$$\Delta\phi = \frac{8\pi^2 R^2 \omega}{\lambda_0 c}; c_{\pm} = \frac{c}{n} \pm \omega R \left(1 - \left(\frac{1}{n_{\text{eff}}^2} \right) \right) \quad (2.4)$$

The phase shift is proportional to the enclosed area by the loop, A , and to the angular velocity, ω , with n_{eff} the effective RI of the fibre.

Other type of devices used in optical fibres is the multimode interferometers (MMI) [19] which can be produced by concatenating a section of a multimode fibre with large core between two single mode fibres in a single mode – multimode – single mode configuration (SMS). The multimode interference in the multimode section leads to the formation of a single or multiple images of the input excitation profile at periodic intervals along the propagation direction, a phenomenon called self-imaging. At the specific periodic position in the multimode fibre section length the spectrum shows a pattern of very well defined resonance loss peaks with their wavelength position sensitive to a set of parameters such as refractive index, curvature, temperature or strain [20].

2.2.2 The Evanescent Field Concept

The guide of light in an optical waveguide has associated the presence of an evanescent field at the interface between the waveguide core and the surrounding, phenomenon that can be used as a sensing mechanism for parameters which modulate the refractive index of the waveguide external medium, which is translated to a modulation of the evanescent optical field, therefore to a modulation of the optical field that propagates down the waveguide.

Considering the propagation of light in a fibre core with refractive index n_1 surrounded by the external medium with lower refractive index n_2 , the electromagnetic field decreases exponentially with the radial distance z to the fibre axis, as given by equation (2.5) [1]:

$$E(z) = E_0 \exp\left(\frac{-z}{d_p}\right) \quad (2.5)$$

where d_p is the penetration depth, which is greater when the difference between n_1 and n_2 is smaller. When the cladding is removed and the evanescent field is high enough to interact with the external medium the optical response can be used as sensor. Some of the above mentioned configurations use that concept, although there are other possibilities which can be explored. One way to reach the core of an optical fibre is by side polishing. Usually the fibre is glued into a silica block and is polished in one side [21]. When the cladding in the polished region is close to zero a thin film material layer is deposited interacting with the evanescent field and creating a sensing surface. This kind of procedure tends to increase the sensing device dimensions.

The scheme of the evanescent field concept using a single mode fibre core with a lower refractive index cladding is shown in Figure 2.4.

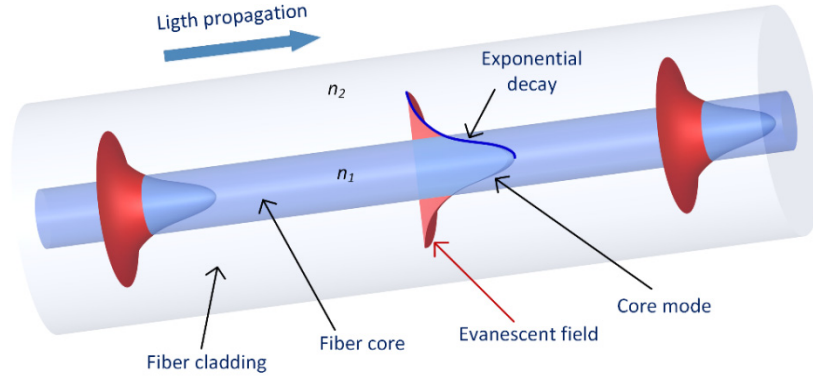


Figure 2.4 – Scheme of the evanescent field concept using a single mode fibre core with a lower refractive index cladding.

The tapered fibres are an alternative to side-polished fibres by reducing the thickness of the fibre in a symmetric way. The taper is produced by heating (with a gas burner [22], scanning focused CO₂ lasers [23] or electric arc [24]) and stretching the fibre with minimum loss. In this process, longitudinal tension is applied to the optical fibre, elongating the fused region until the desired length and waist are obtained. Since cladding modes are generated in the taper region, their propagation characteristics will be strongly influenced by parameters such as fibre bending or the external medium refractive index. Optically, at the beginning of the taper the fundamental mode propagates as a core mode. As the fundamental mode enters the taper transition section, it starts to spread out into the cladding region until the core-cladding waveguide structure vanishes. From this point, the mode enters the taper waist as a cladding mode. Here, the cladding and the surrounding medium act as the waveguide structure. The most sensitive region is the taper waist in which the overall diameter is a minimum and hence the evanescent field intensity is most pronounced. The diameter of the tapered fibre is controlled by the local heating energy and the pulling force applied. If the geometry of the taper is perfectly symmetric which is possible with uniform heating distribution typically using the travelling-burner technique, the intensity of the input light is equal to the one at the output and the taper is called as adiabatic.

Another way to reduce the fibre diameter is using chemical etching by submersing the silica fibre in a bath of hydrofluoric acid (HF) [25]. After ~36 minutes of exposure to liquid HF solution at a concentration of 49.5% the diameter of the fibre is typically reduced from 125 µm down to 9 µm, and almost all the cladding were removed. Other procedures can be optimized depending on the

concentration of the HF solution and if it is used vapour or liquid phase. In these type of structures the core dimensions does not change, but the shape of the mode field exposing the evanescent field to the outer medium is dependent on the refractive index of this medium.

Fibres with a removed cladding in a small section is probably the most studied configuration due to the easy way to expose the core of the fibre. Usually the optical fibre used is a multimode plastic-clad silica-core (PCSC) fibre and the plastic cladding can be easily removed with a chemical solvent. In a small region without the cladding the evanescent wave is free to interact with the external medium changing the optical properties of the guided mode.

Another type of optical fibre that can be used for evanescent field devices are the microstructured optical fibres (MOFs). Some examples are shown in Figure 2.5. The usual optical fibres are made from two materials with different RI, being the fibre formed by the core and the cladding. Microstructured optical fibres are designed to have air holes architecture inside and along the entire length becoming a potential configuration for chemical and biological sensing. With a specific architecture this type of fibres are also known as photonic crystal fibres (PCFs).

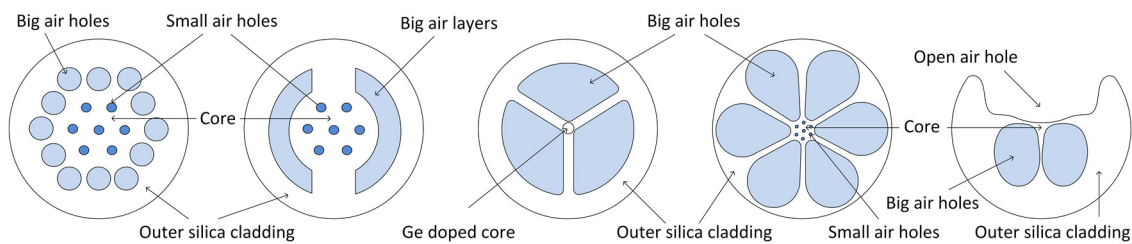


Figure 2.5 – Examples of microstructured optical fibre design configurations from [26, 27].

The PCFs can be classified as the spectral characteristics of the light guided in a solid core or in a hollow core relying on the modified effective RI distribution or on the existence of photonic band gaps (PBGs). These characteristics depend of the shape, the size and the position of the holes being controlled during the fabrication process [28]. In the case of a solid core MOF the modal field is less confined to the core and more located in the air-holes of the cladding via evanescent field effects. The direct interaction of the evanescent field with the filling medium gas or liquid opens the possibility to new sensor designs with long interaction lengths and with small sample quantity. If the holes are coated with a thin film of a metal, dielectric or a sensitive coating the interaction of these coatings with the strong evanescent field provides high variation in the modulation signal at the output, therefore high sensitivity to the measurand [29]. Different kind of geometries can be achieved with this type of optical fibres [26, 27].

2.2.3 Plasmonic Effect

The importance of surface plasmon resonance (SPR) fibre optic sensors in the field of chemical, biological and environmental sensing has notably increased in the last years, and many different configurations and analyte have been studied in the literature [30]. However, the demanding requirements of SPR systems impose the necessity of improving the performance beyond that of the bulk configurations in order to fully exploit the advantages of optical fibres. The optical fibre can be an almost ideal platform for SPR, which has been proved to be an outstanding basis for chemical and biological sensors [31]. Optical fibre configurations already demonstrated advantages when compared with other surface plasmon resonance configurations due to their mechanical stability, flexibility, and the possibility to transmit optical signals at remote distances.

– *Surface Plasmon Resonance*

Many optical systems based on SPR have been developed to work as refractometers, chemical sensors or even to measure the thickness of metal and dielectric thin films. These systems are usually large, expensive and cannot be used for remote sensing. Optical fibre sensors based on SPR have been studied with different configurations and applying different geometries to excite the surface plasmon waves (SPW) at the interface metal/dielectric [32]. The surface plasmon effect will be explored with more detail in section 8.1.

In optical fibres the angle of light oscillation is usually maintained along the full optical path and the output signal is measured as a function of the wavelength. When the evanescent field of the guided mode reaches a suitable metal interface the result is a sharp dip at a resonance wavelength due to the transferred energy from the incident photons to the surface plasmons which reduces the energy of the reflected light [33].

When considering nanoparticles instead of a continuous metal thin film this plasmonic effect is known as localized surface plasmon resonance (LSPR) [34]. It occurs when the frequency of the incident light matches the one of the conduction electrons of the metal nanoparticles. Depending on their size and shape, the nanoparticles start to oscillate like a dipole, a quadrupole or higher order multipole. In the process, absorption of the incident light takes place, originating the typical signatures of a plasmonic interaction. For a specific nanoparticle, the wavelength corresponding to the maximum extinction of the incident light (resonance wavelength) is highly dependent on the surrounding medium refractive index [35].

Recently, the lossy mode resonance phenomenon (LMR) is being studied by several authors [36-38] presenting very similar properties to SPR. In optical fibres LMR occurs when the real part of the thin film permittivity, in opposite to SPR, is positive and higher in magnitude than both its own imaginary part and that of the material surrounding the thin film. LMRs have been observed with indium tin oxide, titanium dioxide and indium oxide.

– *Surface Enhanced Raman Spectroscopy*

The Raman spectroscopy is a well-known phenomenon that can provide information about the molecular vibrational frequencies and molecular structure unique for each sample, creating a kind of fingerprint of the molecular structure, therefore becoming very attractive for analytical spectroscopy [39]. Unfortunately, the inherent low Raman scattering cross section and the high fluorescence signal limits its applicability. These drawbacks are overcome with surface enhanced Raman spectroscopy (SERS), discovered in 1974, where the Raman scattering signal from molecules is enhanced by metal nanostructures due to a plasmonic effect of enhancement of the electrical field [40]. The Raman scattering intensity from molecules close to the surface of certain finely divided metals is enhanced by a factor of about 10^6 . This results from the excitation of localized surface plasmons at rough metal surfaces, creating an enhanced electric field (E). The incident and the scattered light are influenced by this field enhancement, resulting in a total enhanced Raman signal proportional to E^4 . A smaller contribution to SERS enhancement comes from a charge transfer process for adsorbed molecules with appropriate acceptor or donor orbitals that interact with the metal substrate. The metals that exhibit the largest SERS enhancements are silver, gold and copper [41].

The development of optical fibre probes for SERS measurements was firstly demonstrated in 1991 with a multimode fibre [42]. Different configurations were studied later using cleaved [43], angled [44] or tapered fibres [45], but only with side-polished fibres [46], photonic crystal fibres [47] and polished or etched fibre tips the sensitivity can be increased due to higher area of contact.

2.3 Coatings for Guided Optics Sensing Structures

2.3.1 Coating techniques

Numerous coating techniques are usually adopted with optical fibres depending on the type of coating target. The production of metallic, dielectric or polymeric thin films can be achieved through a wide range of techniques from physical to chemical [48]. Some physical vapour deposition (PVD) techniques could be used to produce thin films on optical fibre surfaces like sputtering, thermal evaporation and electron beam evaporation. The sputtering technique deposition is usually made in an ionized Argon (Ar) atmosphere, where the Ar^+ ions are accelerated with enough energy to collide with the target ejecting few atoms from it. These atoms travel to the direction of the substrate surface producing the desired film layer by layer at a relative low temperature. In the thermal evaporation technique the coating element is heated until the temperature reaches the melting point. Then the material starts to evaporate in high vacuum environment condensing in the substrate, producing a thin film. In an electron beam evaporator a high-energy electron beam is focused into a small spot of the coating element. The element is heated then evaporate and condensate in the substrate. [49, 50]

Chemical deposition techniques are also used in thin films production and are mainly divided in two main groups. The first incorporates the chemical vapour deposition (CVD) and the atomic layer deposition (ALD) using a gas phase to transport volatile molecules to the substrate [51]. The second group is based on the Sol-Gel processing [52] using the liquid phase as the mass transfer media which can be complemented with physical processes like drop, spin and dip coating.

CVD is a technique used to deposit layers of a metal through chemical reactions with a mixture of gases at high temperature. The interactions with the surface of a substrate, resulting in the decomposition of some constituents of the gas mixture, allow the formation of a solid film on the substrate [53]. The ALD is based on the saturation of an individual and sequentially performed surface reaction between the substrate and precursor molecules. The saturation mechanism makes the film thickness directly proportional to the number of reaction cycles executed instead of the reactant concentration or time of growth as in CVD and PVD [54]. Thus, the thin film is grown in a layer-by-layer process allowing sub-nanometre thickness control with good uniformity.

The Sol-Gel process is a very good process of producing high quality glasses and ceramics. It is prepared from hydrolysis and condensation polymerization of the alkoxide solution followed by a

thermal treatment for densification process. The preparation can be adjusted to be used by dip coating, spin coating or even spray coating [55]. One old process is electroplating which consists on plating one material onto another by hydrolysis using two electrodes, cathode and anode, and an external source of current. Electroless plating involves several simultaneous reactions in an aqueous solution between the reducing agent present in the solution and the metal ions without the use of external electrical power. The metallic phase appears in the bulk of the solution or as a precipitate in the form of a thin film around the solid surface [56]. Another useful way to produce thin films is with the Langmuir-Blodgett (LB) technique [57], which is based on the transference of a monolayer previously formed in an air-liquid interface to the substrate surface. An inexpensive process for multilayer production is the layer-by-layer (LbL) assembly, also called as electrostatic self-assembly (ESA). Here the substrate is cleaned to negative charge the surface and is exposed to a polyanion solution of opposite charge for a short time, producing by adsorption a monolayer of polyons on the surface. The substrate is then alternately dipped into cationic and anionic polymers creating a multilayer polyanion-polycation thin film [58, 59]. Ion exchange process can be applied to these coating techniques mostly for doping materials changing its optical properties in which ions of one substance are replaced by similarly charged ions of another substance [60]. This process is widely used for doping materials.

The above deposition techniques are the most used to fabricate fibre sensors involving thin film coatings. Figure 2.6 represents some of the different type of coatings for sensing combined with configurations using a single mode fibre optic.

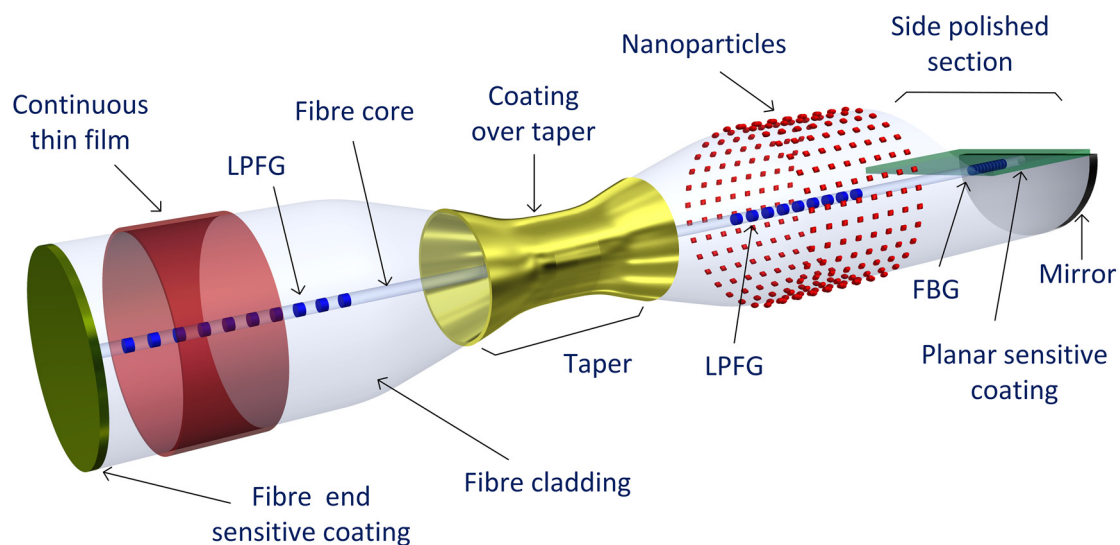


Figure 2.6 – Schematic example of an optical fibre coated with thin film coatings in different sensing configurations.

Different materials can be used for coating optical fibre devices. The coatings for optical fibre sensing can be used for enhancement of the physical properties inherent to the sensor, or can be used to detect a specific target, changing then the optical properties of the film that can be traceable by the in-fibre optical device. A brief explanation of different coatings with specific deposition techniques will be performed based on their nature.

2.3.2 Coating Materials

– *Polymeric Coatings*

Polymers are probably the most used coatings for fibre optic sensing because they are easy to produce and support wide applications, with the possibility to trap different particles permitting therefore to be chemically modified to target a specific measurand. Due to these characteristics this type of materials is widely used for sensing pH, humidity, oxygen and can act as a linker for biological and chemical applications.

Most of the polymers used for sensing with fibres are polyelectrolytes. They are polymers carrying ionic charge along the polymer chain. Depending upon the charge, these polymers are anionic or cationic and can be used in single layers or in combinations with both varying the charge of the coating surface [37, 61, 62].

Cationic polyelectrolytes allows to selectively attract negatively charged functional groups to the coated surface to be detected. Some examples are poly(diallyldimethylammonium chloride) (PDDA) [58, 61, 63] and poly(allylamine hydrochloride) (PAH) [37] which, if used in combination with an anionic polyelectrolyte, can be utilized to form a layer by layer absorbed film of negatively and positively charged polymers for biomedical applications, for example cell encapsulation.

Anionic polyelectrolytes selectively attract positively charged functional groups and some examples are polyvinylamine sulfonated backbone with anthrapyridone chromophore (Poly R-478) [58], poly(acrylic acid sodium salt) (PAA) [37, 61] and poly(sodium 4-styrenesulfonate) (PSS) [63, 64], both with the property to absorb water more than 200 times his own volume, therefore changing their optical properties.

Other natural or synthetic polymers currently used for sensing are for example polyvinyl alcohol (PVA) [65], poly(2-hydroxyethyl methacrylate) (Poly-HEMA) [66], poly acrylamides (PAM) [67],

polyacrylonitriles (PAN), plasticized poly(vinyl chloride) (PVC) and ethyl cellulose, polystyrene (PS) [67], poly(1-trimethylsilyl-1-propyne), PS-co-fluoroacrylate and phenyl-trimethoxysilane-co-tetramethoxysilane ("ormosil"), Damival E 13650 and Araldite DBF [68].

Some polymeric coatings allow the selective ion-exchange between two electrolytes or between an electrolyte solution and a complex. Typical ion exchangers are resins (polymers), porous structures providing high surface area. They can be anion or cation exchangers depending if they exchange negatively or positively charged ions. They can be selective for certain ions or classes of ions, or be unselective depending on their chemical structure. Ion exchange is a reversible process and the ion exchanger can be regenerated with the original ions by washing any excess of these ions.

Other types of polymeric coatings are in the form of gel structure which can be defined as a system containing molecules, chains, particles, etc., partially connected to each other in a fluid and depending of their properties can be distinguished by aerogel, xerogel, cryogel, organogel or hydrogels [69].

– *Metallic and Oxides Coatings*

Metals and oxides can be classified according to the physical properties as dielectric constants, thermal expansion coefficients, magnetic properties and vulnerability to oxidations or oxidation stability. Metals useful to induce plasmonic effects are aluminium (Al), gold (Au) or silver (Ag), the latter although being chemically instable, it is the one which presents better sensitivity. Metals could be used for strain applications due to the high expansion coefficients either due to thermal effects as copper (Cu) or Al or due to absorption affinity of specific elements as palladium (Pd).

Some metals are ferromagnetic at room temperature as iron (Fe), nickel (Ni) and cobalt (Co) presenting magnetostriction coefficients of 14, 33 and 50, respectively. This property of ferromagnetic materials is defined as the change of the length in the direction of the applied field [70]. In addition, rare earths with $64 \leq Z \leq 69$, alloys of ferromagnetic elements, some alloys of manganese (Mn), presents ferromagnetism properties [71]. New materials as TbDyFe alloys are becoming very attractive presenting magnetostriction coefficient over 2000 and have been applied to magnetic field fibre sensors [72].

Metal oxides are widely used in photovoltaic devices, solar cells, biomedical fields, laser optics as micro mirrors, anti-reflection coatings, band-pass filters, etc [73]. The most commonly used materials are silicon dioxide (SiO₂) and titanium dioxide (TiO₂) both electrically insulating which,

in some applications, is a drawback. Some other materials as zinc oxide (ZnO) or copper oxide (CuO), both semiconductors, are attracting attention due to their intrinsic properties. Indium tin oxide (ITO) has unique combined properties of transparency to visible light and electrical conductivity.

2.3.3 Nanoparticles

A nanoparticle is a microscopic particle with at least one dimension less than 100 nm. Typically, metallic, ceramic or polymer nanoparticles [74-76] of about few nanometres diameter can be synthesized in colloids by laser ablation or with chemical techniques in a variety of solvents. Colloids stabilize nanoparticles in solution in order to prevent aggregation by the absorption of electrical charges on the surfaces leading to a repulsion of the nanoparticles. The intrinsic properties of a nanoparticle are mainly determined by the size, shape, composition, crystallinity, and structure. Changing one of these parameters enables, in principle, fine-tune optical, electrical, and catalytic properties of this nanoparticle.

Nanoparticles can be used to improve the efficiency of photodetectors [77], to induce SPR [78, 79] or to increase the interaction surface of the sensing device for gas sensing [80].

2.4 Applications

The applicability of fibre optic sensors with thin film coatings is very wide and is growing because of the development of new materials, of fibre structures and of coating processes. The coatings can be used not only to help the detection of specific target, but also to increase the sensitivity of a specific sensor. The applications herein presented will be separated in measurement of physical parameters, measurement of chemical and biological entities and others like gases.

2.4.1 Measurement of Physical Parameters

Since the beginning of optical fibre sensors they have been used to measure physical parameters as strain, temperature, pressure or magnetic field. The FBG are known to have optimal characteristics to be used as a strain sensor due to the change of the spectral position with this parameter. In fact, the majority of the studied configurations uses this capacity to measure other parameters indirectly. Temperature affects the silica fibre due to the thermal expansion coefficient of silica changing the

period of the FBG and the spectral position of the narrow grating peak. The same effect is obtained with LPFGs and in-line Fabry-Perot (FP) cavities. The thermal expansion of the silica changes the length cavity so the spectral fringes of the optical interference changes according to it. For example, the typical sensitivity to thermal variations of an FBG inscribed in a common single mode fibre SMF28e is $\sim 11 \text{ pm}/^\circ\text{C}$ at room temperature level. This sensitivity can be changed by switching the material of the silica fibre to one with higher thermal expansion coefficient or by coating the FBG region. Metals are the materials with higher thermal expansion coefficients so they are commonly chosen. While the metal expands it will apply an extra strain to the fibre increasing the sensitivity to thermal variations. This is valid for cryogenic temperatures [81] and to high temperatures [82] depending on the coating the material. This effect is more pronounced if the fibre cladding is reduced from the 125 microns standard size. By this way the effect of the metal expansion becomes dominant over silica.

The silica thermal expansion coefficient becomes negative around 120 K and for cryogenic temperatures down to 4.2 K (for the liquid helium) the bare FBG is insensitive to thermal variations. One way to overcome this drawback is by coating it with a thick layer of a metal with thermal expansion coefficient higher than zero at that temperature range which is still capable to expand or shrink and transmitting this effect to the silica fibre. Indium was found to be the appropriate metal to be used, achieving sensitivities around 15 pm/K [81].

On the other extreme, high temperature sensors have been developed with a single crystal sapphire fibre at the end of a conventional fibre where a thin layer of a blackbody is sputtered to build up a cavity. The blackbody cavity is created by a thin metallic film coated with aluminium oxide to reduce oxidation or an opaque oxide film. The radiance emitted from the cavity is detected through the fibre and is used to measure temperatures up to 2000°C [82].

Another physical quantity important to be measured is pressure. Pressure sensors have been studied in particular using mechanical devices coupled to FBGs benefiting from its strain sensitivity or using FP cavities. One example is a FP cavity at the end of a commercial fibre with a capillary tube and a multilayer polymer-metal diaphragm to measure in vitro intradiscal pressure in the range of 0-70 kPa, achieving sensitivities of $0.0206 \text{ } \mu\text{m/kPa}$ [68]. The thin film coatings will be deformed by the applied pressure, changing the properties of the reflected optical signal. Pressure can be measured to sense indirectly other properties as acoustic waves. Hydrophones for underwater acoustic detection were reported by using FBGs coated with ring shaped polymers like Damival E 13650 and Araldite DBF with different size and mechanical properties, therefore providing signal amplification due to the

excited free vibration modes at specific frequencies. In this way, the sensitivity was improved up to three orders of magnitude when compared with a bare FBG within the range 4–35 kHz [83].

Low loss optical fibres commercially available can be used as magnetic or current sensors by magnetization or by magnetostriction. The coating of the magnetostrictive material induces perturbation in the optical signal when a magnetic field is applied either in a bare optical fibre or following a special configuration as the one referred in section 4.4.2. The optical fibre made of silica is an insulator immune to electromagnetic interference and does not conduct current, so it can be used in hazardous conditions as high voltage power stations or fuel tanks. As discussed before, the detection of weak magnetic fields by considering the magnetostrictive phenomenon in optical fibres started in the 80's with a theoretical work by Yariv et al. [5] using a commercial fibre and a Ni jacket which forced the elongation of the fibre. Experimental work was reported later by Sedlar et al. [84] using a single mode fibre Mach-Zehnder interferometer with one arm coated with a ceramic thin film using a modified Sol–Gel method with 2 μm thickness incorporating spinel type ferrites. The coating was used to transmit strain to the fibre when the magnetic field was applied changing the properties of the interference signal. A detection limit of 2.5×10^{-3} A/m was achieved.

More recently new materials are being applied to measure magnetic fields with fibre optics. Yang et al. [72] presented a sensing device based on an FBG coated with 1 μm of TbDyFe. The FBG was chemically etched by emersion on liquid HF to reduce the cladding diameter down to 85 μm and in a 15 mm section the thin film was sputtered. The thin film of TbDyFe has very high magnetostriction coefficient which can be resumed in a higher strain transmission to the fibre when the magnetic field is applied; combined with the cladding reduction it was possible to obtain sensitivities of 1.08 pm/mT. The same kind of sensing devices are used to provide an indirect measurement of electric currents by measuring the magnetic field that is created in the vicinity of the conducting wire which is the case of the work presented by Ding et al. [85]. Here, the electric current applies strain in magnetostrictive Fe-Co-V alloy thin film coating on top of standard optical fibres. Random refractive index fluctuations along the fibre gives place into long FBGs with random periods in the reflected spectra usually called as Rayleigh backscattering spectra (RBS). When the magnetic field is applied, strain is transmitted to the fibre and a RBS shift is measured with a minimum current variation of 0.3 A.

2.4.2 Measurement of Chemical and Biological Entities

Sensing devices can be grouped in chemical and biosensors. Chemical sensors does not use a biological component. Biosensors are a combination of transducers (depending on the sensing configuration) with bio-recognition elements which typically are in or attached to a thin layer linked to the transducer and sensing the species of interest providing quantitative information. Some applications with distinct fibre configurations are presented here.

Starting with chemical entities we can find coated optical fibre sensors to measure, for example, humidity [58], glucose [34, 86], urea [86] or pH sensors [37].

Humidity sensors have been studied based on deposition of sensitive coatings like a combination of layers of poly R-478 (anthrapyridone chromophore), as proposed by Matias et al. [58], or LUDOX SM-30 SiO₂ water colloidal discussed by Viegas et al. [87]. The first with a comparison between tapers and hollow core fibres while the second produces LPFGs with the same kind of coatings adding silicon nanospheres. As the anionic electrolyte exhibiting a hydrophilic nature and poly(allylamine hydrochloride) (PAH) or poly diallyldimethyl ammonium chloride (PDMA) as the cationic solution with a hydrophobic behaviour, the water molecules are trapped at the surface and not absorbed by the coating. These kind of sensitive coatings deposited on the surface of fibre structures, with the evanescent field exposed due to the presence of fibre tapers or LPFGs, generates a modulation in the transmitted optical signal in the presence of humidity. The two coatings were used with different purposes by the authors, one was used to detect moisture levels and other was used to increase the sensitivity.

Rivero et al. [88] proposed a new humidity sensor based on surface plasmon resonance by using silver nanoparticles embedded in a polymeric coating of cationic polyelectrolyte poly(allylamine hydrochloride) (PAH) and anionic polyelectrolyte poly(acrylic acid sodium salt) on the multimode optical fibre core surface built up by using the LbL deposition technique. The variation in the external humidity originates changes in the thickness and refractive index of the functional polymeric coating which affects the resonance spectrum as a function of the numbers of bilayers added. The result is a wavelength shift of the plasmonic resonance in the range of humidity from 20 to 80%

Srivastava et al. [34] presented a blood glucose sensor using LSPR of metal nanoparticles around a U-shaped fibre optic probe. The probe was prepared by attaching Au nanoparticles to the optical fibre core with the help of aminosilane self-assembled monolayer giving origin to the LSPR following the immobilization of functionalized glucose oxidase which will bind to the target. The

glucose in the vicinity of the sensing region lead to chemical reactions with glucose oxidase, changing the effective refractive index of the coating proportional to the concentration, therefore working in an intensity modulation scheme. These changes are reflected in the absorbance of the LSPR.

A multianalyte sensor using gel entrapment technique in a fluid for biomedical applications was proposed by Verma and Gupta [86]. By using two different SPR regions in a plastic optical fibre is possible to proceed to urea and glucose detection simultaneously. The sensing surfaces were prepared by coating the two small and separated regions with different metals and dielectric over-layers (silver/silicon and copper/SnO₂). The result is a transmission spectrum with two resonances separated by 200nm. Enzymes urease and glucose oxidase are immobilized over respective surfaces using gel entrapment method for the sensing of urea and glucose, respectively. The immobilized enzymes cause changes in the refractive index around the SPR and a blue shift of both resonances is observed with sensitivities in average of about 47.28 pm/mM and 50.15 nm/mg dl⁻¹ for urea and glucose concentrations, respectively.

The measurement of pH solutions have been described by Zamarreno et al. [37] using lossy-mode resonances in optical fibre sensors. These resonances were excited by removing the cladding of a portion of a silica optical fibre with 200 µm diameter and coating with ITO with layer by layer technique. On top of this coating multiple polymeric layers of PAH and PAA were deposited up to 1.2 µm. The pH of the solution is capable to change the thickness of this polymeric coating, therefore the refractive index. The wavelength position of the resonances in the optical spectrum varies as a function of the coating thickness and a refractive index sensitivity of 0.027 nm⁻¹ was achieved within the range of pH 3 to pH 6.

The effective control of bio interactions is the key to many biomedical applications, such as cell culture tools, biosensors and implantable medical devices. The biggest challenges of this type of coatings are related to their function and transferability between different substrate materials leading to highly effective control of biomolecule- and cell-surface interactions.

The preparation of optical fibre biosensors, a part of the optical design, requires the immobilization of bio-receptors on the surface through specific methods including adsorption, ionic bonding by layer-by-layer methods or other chemical methods [89]. The specificity of a biosensor depends on the bioreceptor molecule used. The bioreceptor is a biomolecule that recognizes the target analyte, as enzymes [90], antibodies [91] or DNA chains [92].

To perform the immobilization of such molecules in the surface of the fibre, usually it is required the deposition of a bio-compatible coating prior the immobilization of the bioreceptor. These coatings are named as linkers and can be proteins (poly-L-lysine - PLL) [63] synthetic molecules (such as (3-aminopropyl) triethoxysilane - APTES) [93] or polymers (such molecularly imprinted polymers - MIPs) [94] among others. The deposition of these coatings in the fibre is typically made with drop-coating and dip-coating.

The optical transduction of these biosensors relies on the change of the optical properties (usually refractive index) when the target connects to the bioreceptor. The optical configuration of the sensor must be designed in order to detect changes in the effective refractive index of the propagating light.

Examples of this type of coatings applied to optical fibre sensors are the detection of Thrombin [63], DNA hybridization and DNA–protein interactions [92] and *Escherichia coli* (*E. coli*) [95].

Thrombin is a key protein involved in the blood coagulation cascade. This enzyme facilitates blood clotting by cleaving the soluble fibrinogen into the insoluble fibrin strands and plays an important role in thrombosis and haemostasis. The detection can be made by coating the waveguide with PLL that could support an aptamer capable to bind to the target. A fibre optic sensor with ITO and PDDA/PSS polymeric coatings to detect Thrombin was reported [63]. The ITO was sputtered onto the uncladded fibre core surface creating an LMR-based optical fibre refractometer. The attachment of Thrombin to the aptamer changes the external RI enabling the detection of concentrations down to 100 nM of thrombin.

A SPR sensor for measuring DNA hybridization and DNA–protein interactions was proposed by Pollet et al. [92]. To excite the plasmon waves, multimode optical fibre sections with 3 cm length and 400 μm diameter were sputtered with a 50 nm Au layer on the core surface being then covered with a protein repulsive self-assembled monolayer of mixed polyethylene glycol (PEG). Streptavidin was attached to the PEG's carboxyl groups to serve as a versatile binding element for biotinylated ssDNA. A similar SPR fibre was functionalized with ssDNA aptamers against human immunoglobulin E following the same procedure. The attachment of such DNA and proteins on the Au layer caused a shift on plasmonic resonance due to the RI changes with a limit of detection of 2 ± 1 nM (~ 0.5 $\mu\text{g/ml}$).

An evanescent wave fibre optical sensor for the detection of *E. coli* outer membrane proteins (ErOMP) discussed by Queirós et al. [95] uses an LPFG as refractometric platform. The LPFG silica surface was functionalized electrostatic assembly using PLL as cationic polymer and covalent

binding using (3-aminopropyl)triethoxysilane 97% (APTES) acting as linkers and being activated by immersion in dimethyl suberimidate (DMSI). The achieved sensitivity for the last one was around $-0.1597 \text{ nm/log(concentration) [EcOMP, M]}$ in the range of 0.1 nM to 10 nM EcOMPs. The possibility of regeneration was attained under low pH conditions.

2.4.3 Other Type of Sensing Applications

One of the most interesting developments has been in the gas detection field. Some of those gases are inflammable and with a high explosion risk, therefore not compatible with the traditional electric sensors. Optical fibres are suitable to overlap this constrain due to its intrinsic immunity to electric discharges; in addition, remote operation and sensor multiplexing became readily accessible with the fibre optic approach. Considering this, several gases have been detected with optical fibres namely ethanol, hydrogen, carbon dioxide or ammonia. Some of the coated fibre optic sensing structures are briefly presented in Table 2.1 along with their main properties as the configuration, the coating, the physical effect and the sensitivity to the correspondent target. Ethanol vapour detection was proposed by Konstantaki et al. [96] based on a LPFG coated with ZnO nanorods by two-step procedure involving a pulsed laser deposition of a zinc (Zn) layer onto the optical fibre, followed by aqueous chemical growth of ZnO nanostructures. A notch extinction ratio of more than 4dB was recorded for the LPFG with 6.67 kPa of ethanol vapour concentration. The adsorption of the ethanol vapour causes a variation in the ZnO coating properties as refractive index and density which is reflected in the LPFG transmission spectrum.

Hydrogen detection at low concentrations with optical fibre sensors usually uses palladium as active medium [97]. Palladium is capable to absorb hydrogen up to 900 times its own volume due to the high and selective affinity. Because of this property the thin films of Pd can be used to detect H_2 by changing the coating reflectivity or by applying strain into the fibre. A very simple design of an hydrogen sensor is a micro mirror of palladium at the end of a fibre [98]. In this case the end of a multimode fibre was coated with 10 nm of Pd by thermal evaporation. The reflectivity changes with the conversion of the pure Pd into Pd hydride due to the hydrogen adsorption. The optical power detected with a single photodetector can measure the hydrogen concentration in the medium. The same concept was studied by Villatoro et al. [99] but using a taper instead.

Chapter 2 - Optical Fibre Sensors Based on Thin Films

Table 2.1 – A brief compilation of sensing structures associated with coated optical fibres and their main properties.

Measurand	Ref.	Config.	Coating material	Purpose / Physical effect	Coating type	Sensitivity / detection limit
CO ₂	[100]	FPI / LPFG	D4 / 4-Nitrophenol DDMA	Sensing / RI changes	Dip-coating	-
E. coli	[95]	LPFG	PLL, APTES	Act as linkers / sensing / RI changes	ESA Polymer	-0.1597+/-0.004 nm/log(concentration)
Magnetic field	[84]	FBG	spinel type ferrites	Sensing / Strain,	Sol-gel	2.5x10 ⁻³ A/m
	[72]	MZI	TbDyFe	Sensing / Strain,	Sputtering	1.08 pm/mT
Current	[85]	RBS	Fe-Co-V alloy	Sensing / Strain	Bulk material with Epoxy	0.3 A
Acoustic waves	[83]	FBG	Damival E 13650 Araldite DBF	Mechanical amplification / Vibration	Homemade mold / Melting	10 mPa/Hz ^{1/2}
Intradiscal pressure	[68]	FPI	Polymide Ni/Ti	Mechanical deformation / Length changes	Chemical Sputtering	0.0206 µm/kPa
High temperatures	[82]	FPI	Blackbody	Sensing / Emission of radiance	Sputtering	-
Cryogenic temperatures	[81]	FBG	Al, Cu, Pb, In	Mechanical amplification / Strain	Vaporization Electro-Deposition	15 pm/K
Humidity	[58]	Taper / Hollow core fibre	PDDA/Poly R-478	Sensing / RI changes	ESA	0.885 dB/%RH
	[87]	LPFG	PDDA/Poly R-478/LUDOC SM-30 SiO ₂ nanospheres	Amplification, sensing / RI changes	ESA	451.78 pm/%RH
	[88]	SPR	PAH/PAA-Ag nanoparticles	Sensing / RI changes	LbL	20 to 80%
Glucose	[34]	LSPR	Au Npt / with glucose oxidase	Sensing / RI changes	Self-assembled	-
	[86]	SPR	Cu/SnO ₂ /Glucose oxidase	Sensing / RI changes	Thermal evaporation	47.28 pm/mM
Urea	[86]	SPR / PCSC	Ag/Silicon/Urease	Sensing / RI changes	Thermal evaporation	50.15 nm/mg dl ⁻¹
H ₂	[97]	Taper / FBG	Cr, Pd	Adhesion, Sensing / Strain	Thermal evaporation (E-Beam)	80 pm/%v/v H ₂ at (53 kPa)
	[99]	Taper	Pd	Sensing / RI changes	Thermal evaporation (E-Beam)	-
	[98]	Fibre end	Ni, Pd	Adhesion, sensing / Reflectivity	Thermal evaporation (E-Beam)	-
NH ₃	[61]	LPFG	PDDA / PAA	Sensing / RI changes	ESA	0.35 nm/ppm
pH	[37]	LMR	PAH / PAA	Sensing / RI changes	LbL ESA	0.027 pH units/nm
DNA protein interactions	[92]	SPR	Au / PEG	Sensing / Amplification	Sputtering	2±1 nM (~0.5 µg/ml)
Thrombin	[63]	LMR	ITO PDDA/PSS	Amplification, Sensing / RI changes	Sputtering LbL	~ 100 nM
Ethanol vapor	[96]	LPFG	ZnO nanorods	Sensing / RI changes	PLD (Zn) Chemical growth of ZnO nanostructures.	-0.08 dB/torr

In a transmission configuration, the evanescent wave of a multimode tapered fibre interacts with the Pd coating which is converted into Pd hydride in the presence of hydrogen concentrations up to 4%. The guided light suffers attenuation changes with time response of about 30s which are monitored at the end. The Pd expansion property have been also exploited by using an optical fibre with an FBG [101]. The FBG is intrinsically sensitive to strain but in this case it was inscribed in a taper region with 50 μm of diameter in order to improve the sensitivity. The sensitive region was coated with 150 nm of Pd by an electron beam evaporator and was capable to detect hydrogen up to 1% with high sensitivity.

To detect CO_2 a sensitive polymer membrane was produced by Sol-Gel technique with a solution of polyurethane hydrogel (D4), p-nitrophenol and didodecyl-dimethyl-ammonium hydroxide (DDMA) and reported by Gouveia et al. [100]. The membrane was produced at the end of a fibre creating a FP cavity and around an LPFG. In the presence of CO_2 the refractive index of the membrane changes leading to variations in the optical response.

An ammonia gas sensor was demonstrated by Wang et al. [61] using an LPFG coated with a thin film of PDDA/PAA by the electrostatic self-assembly technique. PAA acts as a selective receptor for ammonia binding, inducing changes in the optical properties of the film which alters the effective refractive index through the thickness and the density and the wavelength position of the attenuation band with sensitivities up to 0.35 nm/ppm.

2.5 Conclusions

In the sensing field, the use of coatings in fibre optics, either continuous or incorporating nanoparticles, is nowadays an active research domain following two decades of progresses which have been translated into an increasingly number of applications associated with high measurement performance. From the simple configurations for monitoring some physical parameters as temperature or pressure, to more complex structures using new coating materials and fabrication techniques for chemical and biosensing, this type of sensing devices are becoming increasingly important.

Small variations in the optical properties of a medium derived from the changes of a specific measurand can be detected with advanced sensing structures, such as those associated with SPR and interferometric phenomenology. Plasmonic devices are widely used in bulk systems but, when

combined, the number of applications is increasing with a high variety of fibre configurations and the possibility to fine tuning the sensing device to a specific analyte by using the appropriate coating, all converging to turn out this sensing approach rather appellative.

In general, the substantial improvement of sensing performance of devices, such as fibre Bragg gratings and long period gratings, when coated compared with the bare option is a strong factor towards the research and development of this fibre optic sensing approach, particularly when chemical and biochemical entities are targeted. As such, it is foreseeable a continuous progress of this field, with the consideration of new types of coatings and of better processes to incorporate them into fibre structures, all pointing out to a consistently increase of the relevance of this optical sensing path with optical fibres, enabling substantial advantages, particularly at the level of achievable performance.

Chapter 3

Fabrication and Characterization Techniques

This chapter describes the materials and methods that were used along the work, starting with the fabrication of sensing structures such as optical fibre gratings and fibre etching or thin films deposition with physical vapour deposition system (PVD). The structure analysis of the thin films produced is also considered by using different methods namely, optical microscopy, ellipsometry, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), X-ray photoelectron microscopy (XPS) and X-ray diffraction (XRD).

3.1 Fabrication Processes

One of the objectives of this work is to take advantage of the background acquired during the years by the research group in optic devices and sensors in optical fibres and join that with the outstanding facilities for micro and nanofabrication that in time have emerged. From this synergy the production of devices in optical fibre for sensing using coatings has grown, in special by using specific equipment for the production of gratings, for etching and for metallic based coatings.

3.1.1 Optical Fibre Gratings

In this work optical fibre gratings were used as sensing devices with and without coatings. Fibre gratings can be easily described as a periodic modulation of the effective refractive index (RI) of the fibre core with low periods (hundreds of nm) which corresponds to the fibre Bragg gratings (FBGs) [102] or with long periods (from tens to hundreds of μm) corresponding to long period fibre gratings (LPFG) [13]. In this chapter the main properties, the fabrication processes and the theoretical aspects of this type of fibre gratings are presented.

– *Fibre Bragg gratings*

Several techniques are used to the FBGs fabrication using ultraviolet laser sources and are described in literature [102, 103]. The three main approaches used are interference, phase mask and direct write. Taking advantage of the background and the existent facilities at INESC TEC and in collaboration with HBM FiberSensing, SA, all the FBGs were produced using the phase mask technique whose details are described below.

The technique is based on RI modifications at the single mode fibre core by using a phase mask and an ultraviolet KrF excimer laser emitting at 248 nm with energy of 400 mJ cm^{-2} at 20 Hz. Those modifications were inscribed in standard telecommunications single mode fibres with germanium doped core (SMF28e, Corning, Inc.) which are not sensitive to the UV radiation. One way to overcome this issue is by using the hydrogen (H_2) loading technique [104]. In this process the silica fibres are placed in high pressure chambers with pure H_2 (over 10 MPa) at room temperature for several days or weeks. This leads to a diffusion of the H_2 molecules into the fibre until an equilibrium state is achieved. In H_2 loaded fibres the exposure to UV radiation causes the dissociation of the molecule and the formation of Si-OH or Ge-OH bonds at the core. The formation of Ge oxygen deficient centres leads to a RI change. The remaining H_2 molecules can be removed from the fibre by applying heat while the exposed regions with UV keep the same structure and the inscription of the Bragg grating is completed.

The scheme of the setup used to the production of the FBGs by using the phase mask technique is presented in Figure 3.1. First, the polymer protective jacket of the fibre is removed with a stripper and fixed between two clamps in a configuration aligned and parallel to the phase mask. The laser beam is then expanded through a cylindrical lens and directed through a slit in a perpendicular direction to the mask where it is diffracted. The radiation is split into $m = -1, 0, +1$ orders and the

interference pattern of two beams with orders ± 1 at the fibre has a period Λ_g which is half of the mask period Λ_{pm} [102]. This interference pattern reaches the H_2 loaded core causing RI changes at the constructive interference spots. The expected reflectivity of the FBG is determined by the RI change which depends on the number of laser pulses, while the size of the slit gives the length of the modulated region which defines the full width half maximum (FWHM) of the grating spectral signature. The production process is monitored and controlled in real time performing measurements of the transmission spectrum in an optical spectrum analyser (OSA) (ANDO AQ 6315B) and controlled with Labview™ software.

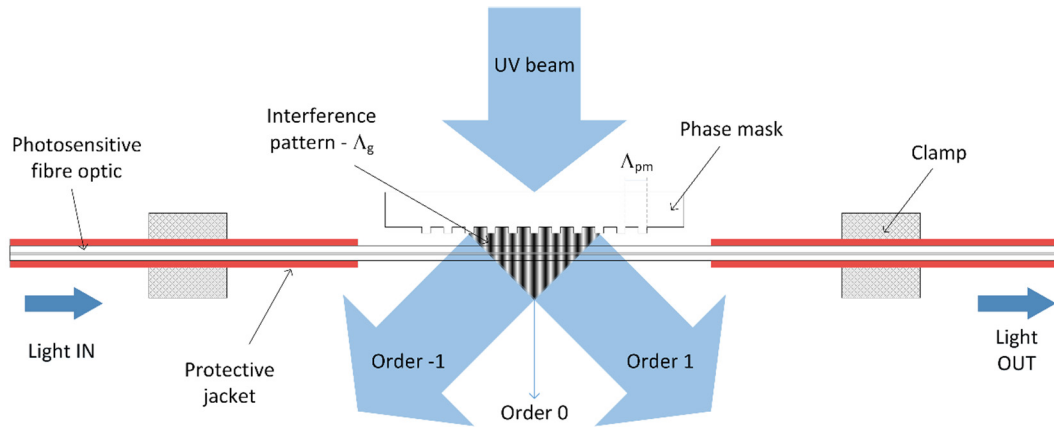


Figure 3.1 – Scheme of the top view of the setup to produce fibre Bragg gratings using the phase mask technique.

This technique applied to the fabrication of FBGs has several advantages, it is fast, reliable and reproducible. The main disadvantages are related to the need of use photosensitive or H_2 loaded optical fibres and the limitation of a mask to a specific period. The masks are usually expensive and to produce gratings with different periods different mask design is needed. Although, a single mask can be used to inscribe FBGs with periods slightly lower than the mask by stretching the fibre while the exposure takes place, this process produces a modulation which corresponds to the mask phase but, when the fibre relaxes, the modulation period is reduced affecting the wavelength position of the peak resonance in the order of few nm.

– Long Period Fibre Gratings

As the FBGs, the LPFGs can also be produced with different types of techniques described in literature [13, 105]. The RI modulation can be achieved by mechanical deformation [106], electric arc discharges [107] or with laser radiation (UV [108], CO_2 [109] or femtosecond lasers [110]).

The fabrication of the LPFGs along this work was performed at INESC TEC and is based on the induced electric arc technique [111] which consists on point-to-point short time discharges in uncoated common telecommunications single mode fibres (SMF28e Corning). This procedure is intended to increase the temperature of the silica high enough to become soft in order to produce the wanted modulation by, simultaneously, changing the local effective RI of the core and producing a micro taper at each discharge. In order to fabricate the LPFGs with this technique the procedure follows the scheme in Figure 3.2. The polymer protective jacket of the fibre is removed in a 10 to 15 cm length, depending on the grating type, and is cleaned with acetone to remove any remaining polymer. This is important because any impurity at the fibre surface will interact with the electric discharge changing its properties and contaminating the electrodes. The clean fibre is positioned between two electrodes within a space around 1 mm, clamped in one end on top of a motorized linear translational stage and stretched in the other end with a mass of about 5 g to keep the same tension and produce similar tapering regions. The electric arc is produced with a modified fusion splicer machine by applying to the electrodes a current of 9 mA with a time duration of 1 s.

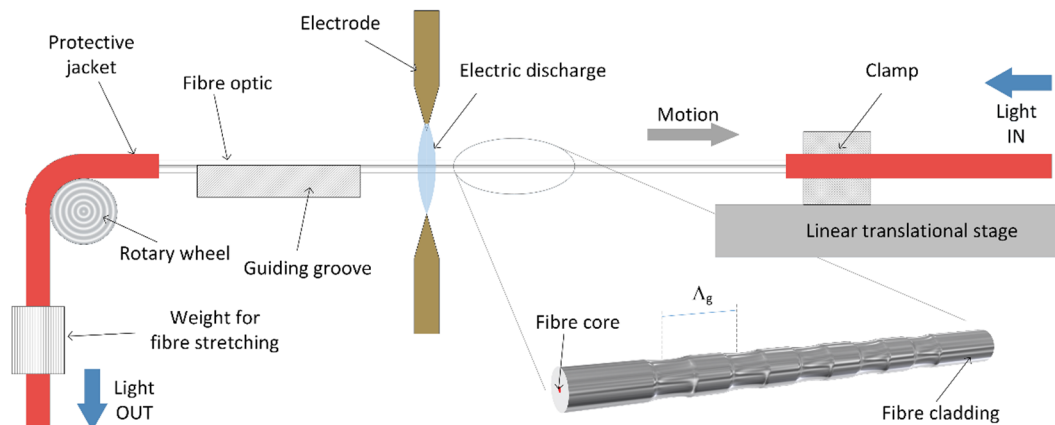


Figure 3.2 – Scheme of the electric arc technique used to produce the long period fibre gratings with periods from 345 to 540 μm .

These parameters were optimized by Rego et al. [111] for this type of fibre. The translational stage and the fusion splicer is controlled by a computer within the LabView™ software and is programmed to apply a discharge and move the fibre 387 μm with a precision of 0.1 μm . The process is repeated until the attenuation band of the LPFG reaches the maximum value (>20 dB).

The heat transfer along the fibre limits the grating period and to overcome this drawback new type of fibres are being used to reduce the grating period as single mode fibre doped with boron and

germanium [112]. Although, the work herein presented uses only standard Ge-doped single mode optical fibre.

3.1.2 Fibre Optic Etching Process

The cladding of the glass optical fibres are typically made of pure silica and for several sensing configurations the evanescent field of the core modes have to be reached. To accomplish this usually the cladding is reduced. There are two ways that stand out from others to reduce the diameter, by mechanical polishing [113] or by chemical etching [114]. The mechanical polishing technique, when applied to the fragile silica fibres tend to be a hard and time consuming process due to the difficulty in controlling the cladding reduction. The fibres are usually glued to a silica block and the entire block is polished with a small grain size. The chemical etching is a straightforward process with more controlled steps. Generally, it is implemented using a solution of hydrogen fluoride in water as etchant (Hydrofluoric Acid - HF). The chemical etching using HF can be performed in liquid phase, obtaining a fast reaction, or in the gaseous phase where the speed of the chemical reaction is much slower.

In this work the etching process was adopted to reach the evanescent field located at a few microns from the core. After removing a 10 mm section of the protection coating a solution of 48% w/w HF (from Panreac Química S.L.U., Spain) in water was used to react with the silica reducing the cladding diameter at a rate that is dependent of the liquid quantity, the temperature and humidity. During this process the HF reacts with the silica according to the following chemical reactions [25]:



In the present work the first dominates the reaction while the second is dominating for the high acid concentration situations.

The reaction of the HF with the silica fibre is limited by the surface area of contact with a slow diffusion into the lattice. The dissolution of the silica structure can be determined mathematically in equation (3.3) by considering a dissolution constant k , the surface area and the concentration of the acid [25].

$$\frac{d}{dt} \left[\frac{\pi D_w^2 L_w \rho}{4} \right] = -k (\pi D_w L_w) C_{HF} \quad (3.3)$$

Where D_w is the diameter of the fibre waist, L_w is the length of the fibre exposed to the etchant, ρ is the silica density, t is the reaction time, and C_{HF} is the HF concentration.

The equation (3.3) can be simplified in the form

$$\frac{d}{dt} \left(\frac{D_w}{D_i} \right) = -K \quad (3.4)$$

where D_i is the initial fibre waist and the constant K is equal to $2kC_{HF} / D_i \rho$.

The etching process can occurs when the HF molecule react directly with the SiO_2 surface to cause Si-O bond breaking by association of F with Si and H with O [115] However, the first step in the etching process may occurs when the H reacts with the O in SiO_2 forming hydroxyl groups and causing the Si-O bond breakage though two possible ways.

The results reported by Knotter [114] indicate that the reaction of HF with SiO_2 is not concluded with a single substitution reaction. There are more than one equilibrium reaction with a proton on the surface as can be seen in Figure 3.3. At the surface a SiOH group is bound to three oxygen atoms from the SiO_2 matrix.

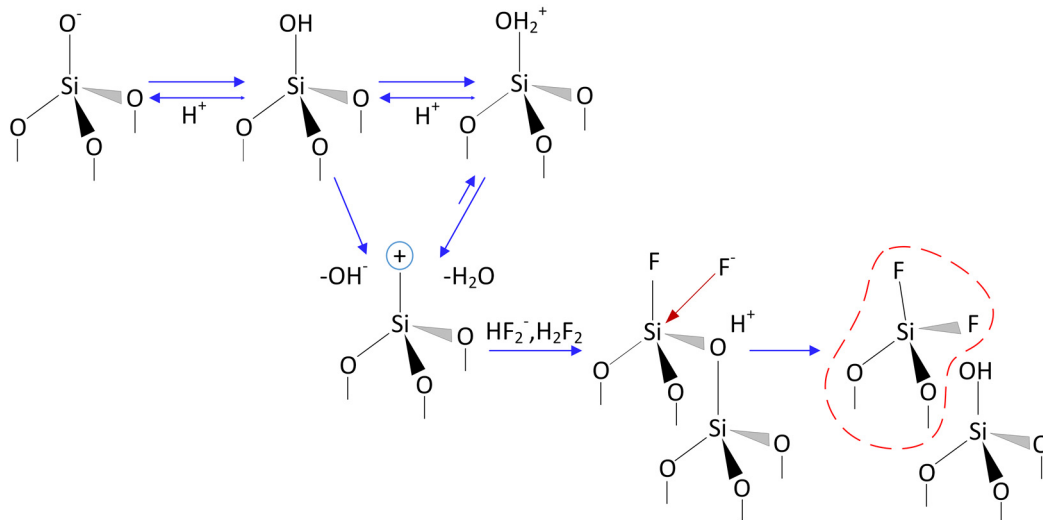


Figure 3.3 – Scheme of the reaction mechanism with the replacement of the SiOH by the SiF and the post removal from the SiO_2 matrix (adapted from [114]).

The first reaction is the elimination of the OH^- or H_2O from the surface giving place to a reactive intermediate group that can react mostly with two different nucleophiles, H_2F_2 and HF_2^- resulting the SiF bound. Other nucleophilic substitution reactions cause the removing of the SiF group out of the SiO_2 matrix exposing the new surface and restarting the reaction to sequentially until the etching process is completed. The HF reacts with the SiO_2 by breaking the bounding between Si and oxygen atoms giving rise to the SiF_4 molecule either in liquid or gas phase.

Due to the surface tension of the solution the meniscus height around the silica changes with the etching time. However, due to the acid in the vapour phase, the transition from the thicker region to the thinner region is not abrupt so the core guided mode can adjust to the new situation. The new surface created has enough roughness to improve the stability of the deposits and the general performance of the sensors [116]. The surface was analysed using an electron microscope (SEM) as described in in section 3.2.2. Figure 3.4 shows the very smooth surface of the optical fibre before (a) and after (b) chemical etching with a liquid solution of HF at 48 % concentration during 20 min. An increase of the roughness due to the etching reactions is clearly visible.

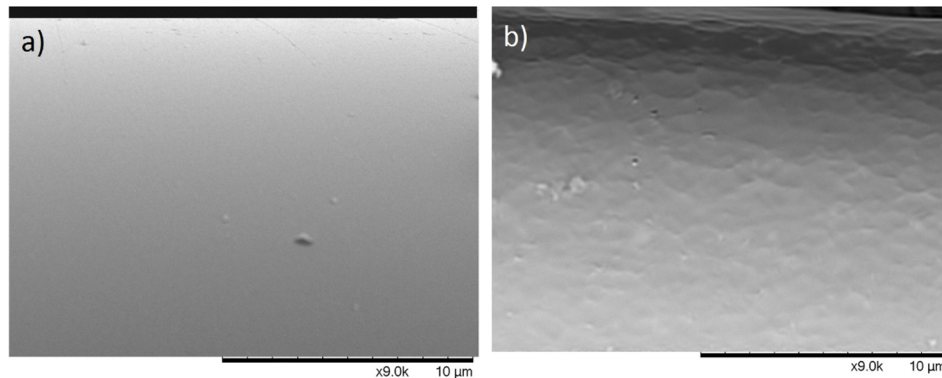


Figure 3.4 – SEM pictures of the fibre surface as fabricated (a) and after etching with a liquid solution of HF at 48 % concentration (b).

The etching rate depends on the temperature and on the humidity but most important depends on the acid concentration. The quantity of acid used plays an important role in the process. When using a large volume of acid (>20 mL) the total HF consumed in the reaction according to Haddock [25] is less than 0.5%. Therefore, a constant concentration and a linear etching rate can be assumed. Although the evaporation phenomena, the squared symbols in Figure 3.5 were fitted to a linear curve ($R^2 = 0.9976$) and an etching rate of $\sim 2.97 \mu\text{m}/\text{min}$ was measured. When the volume is low the percentage of HF consumed by the dissolution reaction increases and plays an important role in the process, reducing its concentration and increasing the reaction products in the solution. Hence the

etching rate is affected and the linear behaviour is lost. The circular symbols show the nonlinear curve of the etching rate when using few μL of acid. When the fibre diameter approaches low values the rate becomes smaller which allows a better control of the final thickness.

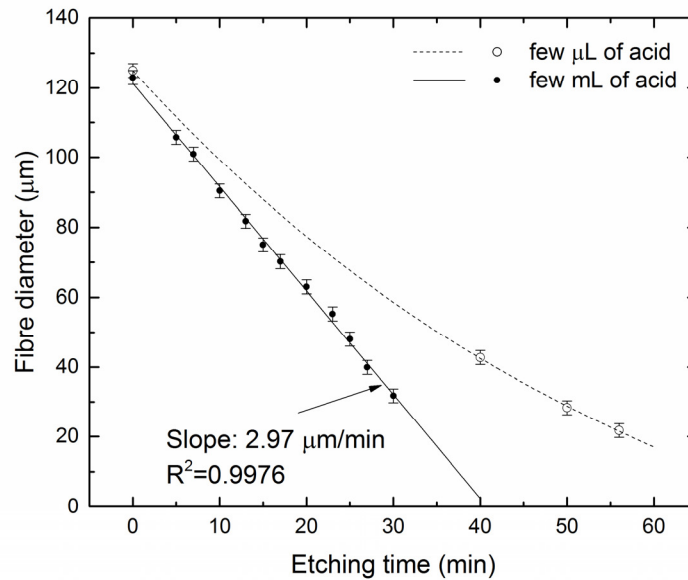


Figure 3.5 – Etching rate characterization for a silica optical fibre immersed in a liquid solution of HF at 48 % concentration with different quantities of acid. The solid line corresponds to few mL of HF solution while the dashed line translates the behaviour with smaller quantities etching solution.

All the etching processes were conducted at room temperature with humidity between 60 to 65% and a pH from 1.5 and 2.

When the fibre diameter achieved the desire value the etching process was stopped by pipetting out the etchant as quickly as possible and wash the fibre several times with water to stop the reaction. The fibre surface is now ready to be coated.

3.1.3 Deposition System

In the previous chapter several types of techniques to deposit thin films were presented depending on the final goal. The PVD method has in general good chemical stability, it is compatible with optical fibres and is easy to handle being the chosen method to fabricate the fibre coatings. All the depositions were completed with a thermal evaporation system model Auto 306 e-beam source (Edwards, UK) from INESC TEC and CEMUP. It is a versatile high vacuum electron beam evaporation system giving the possibility to produce a wide range of metals and dielectrics. The

system shown in Figure 3.4 gathers a high vacuum chamber, an electron beam source and a thickness monitor crystal.

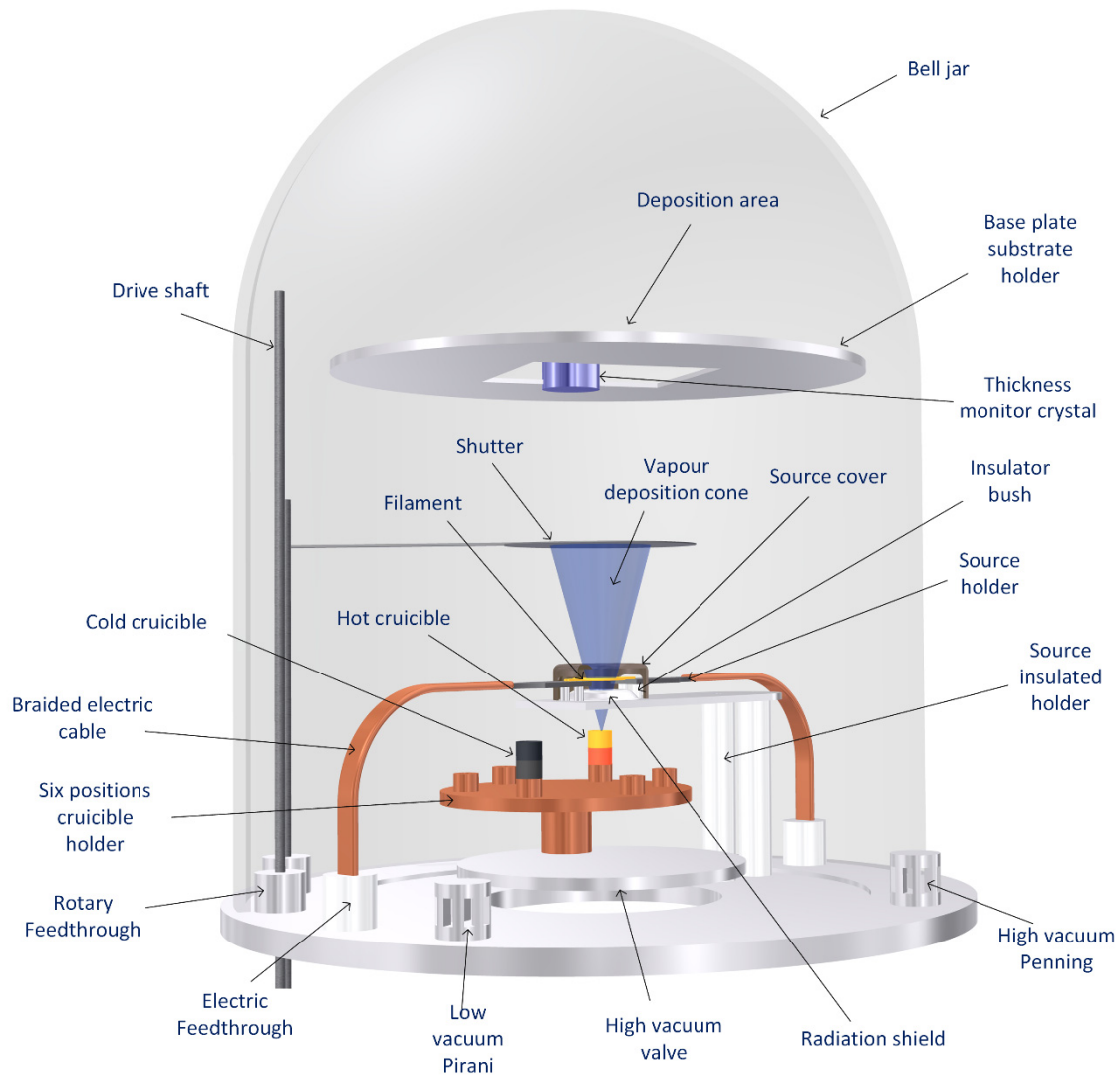


Figure 3.6 – Scheme of the deposition system comprising all the components of the electron beam evaporator Auto 360 from Edwards.

The vacuum chamber is connected to a mechanical rotary pump (model E2M5, Edwards, UK) for rough pumping down to 10^{-3} mbar and the high vacuum is achieved with one diffusion pump (model EO4/160K) with a pumping speed of 600 ls^{-1} . The vacuum pressure is measured by one pirani gauge (model PRL10K, Edwards, UK) capable to measure down to 10^{-4} mbar and with a penning gauge (model CP25EK, Edwards, UK) capable of down to 10^{-7} mbar. This system is equipped with an

automatic pumping mode being possible to switch to a manual mode for specific operations as depositions of metals in gaseous atmosphere.

A low tension (LT) power supply is connected to a circular shape filament which is heated due to the Joule effect to the point where thermionic emission takes place giving rise to an electron beam [117]. This concept follows the Richardson's law that gives the current density $J_x \left[\text{A} / \text{m}^2 \right]$ of the escaped electrons in the perpendicular direction of the heated metal given by equation (3.5):

$$J = A_R \lambda_R T^2 \exp\left(-\frac{W_F}{kT}\right) \quad (3.5)$$

where $A_R = 1.2 \times 10^6 \text{ A} / \text{m}^2 \text{K}^2$ is the Richardson's constant, λ_R is the correction factor from the material and W_F is the minimum amount of energy necessary for each electron leave the metal.

When the filament is heated the free electrons at the metal surface gain enough thermal energy to overcome the energy barrier. This is a property of all metals but only few survive very long time at temperatures high enough to fulfil the requirements. Tungsten (W) is a material with high melting temperature (3414 °C) [118] and usually used to electron beam sources.

When a high tension (HT) of more than 4 kV is applied to the filament the potential difference between it and the crucible is high enough to accelerate the electrons towards to the crucible transferring its energy directly to the target material. This beam of electrons have a conic shape and the target material should be moved to reach the highest energetic point where the concentration of electrons is maximum. These electrons creates a leakage current that is measured at the power source.

The target material will be negatively charged and needs to discharge by the crucible holder through the crucible which must be conductive. Depending on the target to be deposited the crucible material could be changed. Graphite can be used for the majority of the target materials due to the high melting point (3650 °C) [118]. However the graphite is very brittle and it could release some carbon powder that will contaminate the target material being evaporated together with it. This type of crucibles were used to produce thin films of metals like chromium (Cr), titanium (Ti), nickel (Ni) and titanium dioxide (TiO₂), which are hard materials with high melting points, while intermetallic and alumina crucibles will be used for soft materials like silver (Ag), gold (Au), aluminium (Al) and copper (Cu). Both are very clean and very hard but in the case of alumina, because it is an insulator gives rise to charge build up and electrons generated at the filament do not acquire enough energy to hit the crucible. A small cut on the side of the crucible by a diamond coated saw was enough to connect a

thin tungsten wire from the bottom of the crucible to the graphite holder. This way the high potential between the filament and the crucible is recovered and the emission takes place draining the current to the ground through the thin wire.

The thin film thickness was monitored in real time with an quartz crystal microbalance (Edwards, UK), constituted by water cooled crystal holders, quartz crystals and oscillator units that also enables direct read-out of the deposition rate with resolution of 0.1 nm. The oscillating frequency of the quartz crystal changes according to the mass of the thin film growing on its surface. Deposition of different materials can be monitored by simply changing the density ρ and acoustic impedance Z , unique properties of each material. The density parameter provides the film thickness while the acoustic impedance is used to accurately establish the sensor scale factor when the crystal is heavily loaded. A resume of the above mentioned properties of the materials used in this work together with the melting point (T_m) and the minimum evaporation temperature (T_{min}) is presented in Table 3.1.

Table 3.1 – Properties of the selected materials considering the melting point T_m , the minimum evaporation temperature T_{min} , the density ρ and the acoustic impedance Z .

Material		T_m (°C) [118]	T_{min} (°C) at $P=10^{-5}$ kPa [119]	ρ (g.cm ⁻³) [118]	Z ($\times 10^5$ g.cm ² .s ⁻¹) [120]
Aluminium	Al	660	1010	2.70	8.20
Chromium	Cr	1907	1157	7.15	29.00
Copper	Cu	1085	1017	8.96	20.30
Gold	Au	1064	1132	19.30	23.20
Nickel	Ni	1455	1262	8.90	26.70
Palladium	Pd	1555	-	12.00	24.70
Silver	Ag	962	*-	10.50	16.70
Titanium	Ti	1670	1453	4.50	14.10
Titanium (IV) Oxide	TiO ₂	1825*	-	4.17	22.10
Tungsten	W	3414	2757	19.30	54.30
Zinc	Zn	420	250	7.14	17.20

* [121]

The chamber can be accessed from outside either to change the distance from the filament to crucible or to rotate a six crucible turret, which allows sequential evaporations. In case of silicon dioxide

substrates and optical fibres the adhesion to a significant set of materials is very low which forces the introduction of an intermediate thin layer of Ti or Cr to avoid the coating to be peeled off from the substrate. The multilayer fabrication capability is then a very important characteristic of this setup.

– *Electron Beam Thickness Analysis Calibration*

The deposition system was initially calibrated to the thickness measured with the thickness monitor. To verify the thin film homogeneity in the entire deposition area a large area grid was produced and analysed, as shown in Figure 3.6. To accomplish this analysis, first a set of thin films of Ti was produced over silicon wafers substrate at a rate of 0.02 nm/s with thicknesses of 50, 200 and 300 nm measured by the thickness monitor. The coated substrates were then cleaved with a diamond cleaver and the cross section was analysed by a scanning electron microscope (SEM) that will be further described in section 3.2.2.

The images of this analysis are shown in Figure 3.7. For small thickness the resolution is very small and the image is not very clear but it is enough to extract thickness values to be compared with the ones achieved by the thickness monitor.

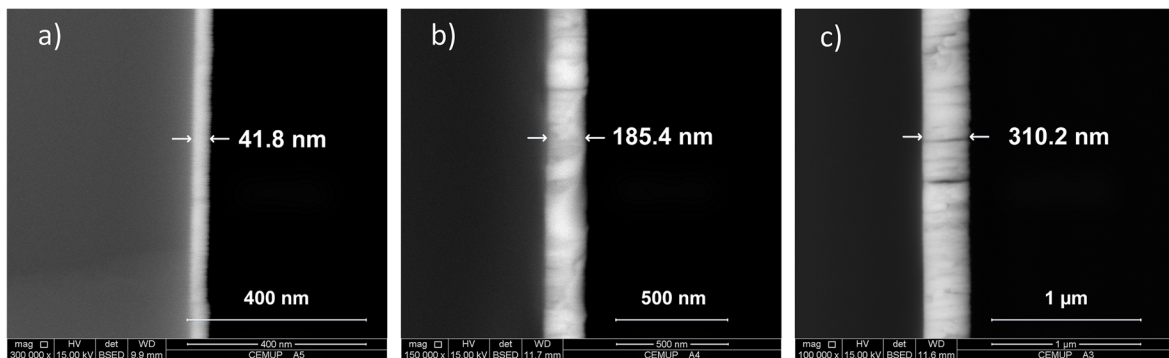


Figure 3.7 – SEM images for calibration of the thickness monitor fitted in the electron beam evaporator considering three readouts: a) 50 nm, b) 200 nm and c) 300 nm.

The calibration curve presented in Figure 3.8 shows a factor of 1.06 which proves that the thickness monitor measurements are in good agreement with the real values.

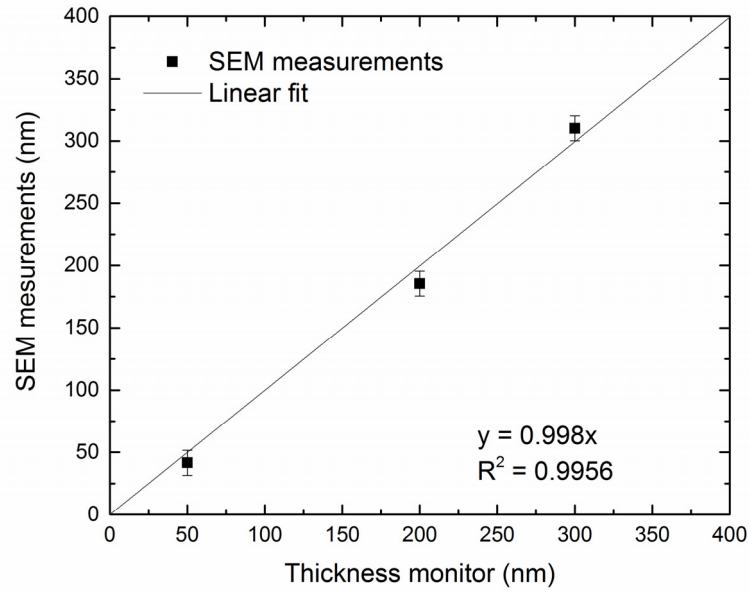


Figure 3.8 – Calibration of the thickness monitor fitted in the electron beam evaporator.

In order to estimate the homogeneity of the thermal deposition system at the working point level a 250 nm thick thin film of pure Cr metal was deposited on top of a silicon wafer with a mask of silicon stripes forming a 9x10 grid. After the deposition the mask was removed and the step profile was measured by a surface profiler model DektakXT (Bruker Co., U.S.A.). The measurements were done in the yy direction and repeated at a number of times in the xy direction until the entire area is covered. Figure 3.9 shows the aspect of the wafer after the Cr coating.

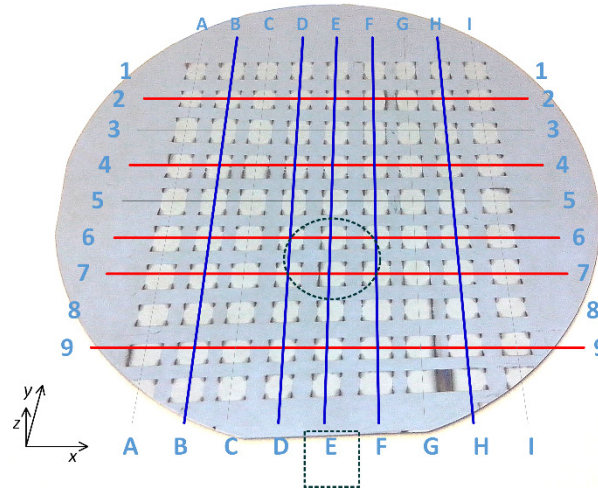


Figure 3.9 – Picture of the silicon wafer coated with a Cr matrix. The dashed circle shows the xy position of the crucible at $z = -15$ mm while the dashed square shows the xy position of the crystal thickness monitor at $z = 0$ mm.

The dashed circle shows the xy position of the crucible at $z = -15$ mm while the dashed square shows the xy position of the crystal thickness monitor at $z = 0$ mm. It is possible to observe a different colour at the square coating edges which indicates a thickness variation at the edges although it was not visible in the profile measurements. The grid was labelled in the x and y direction with lines from 1 to 9 (y axis) and the columns from A to I (x axis). The lines and columns were marked as red and blue respectively, and the Figure 3.10 shows the step profile analysis corresponding to the marked profiles of each column (left) and each line (right).

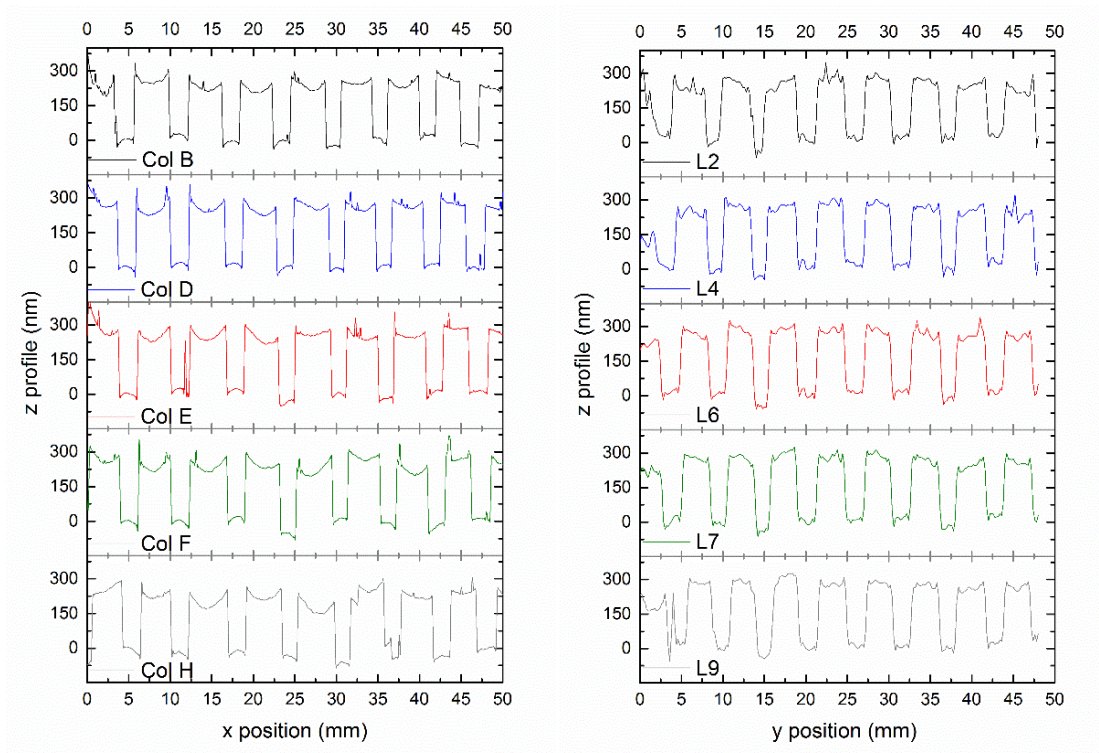


Figure 3.10 – Step profile analysis corresponding to the marked profiles of each column (left) and each line (right).

It is possible to observe that despite the large deposition area, the thickness variation is not significant being the average thickness of 254.9 nm with a standard deviation of 20.5 nm. This is important when the substrate is not at the same position in every deposition procedure which happens when more than one substrate is used or when a rotary system is used.

– Rotary System

The growth of homogeneous thin film coatings around optical fibres is difficult due to its intrinsic cylindrical shape. The most used technique is the sol-gel dip coating which is not dependent of the

substrate shape but has limitations to the type of coatings pretended. Another way to produce homogeneous coatings on a cylindrical optical devices is by forcing a constant rotation movement of the substrate during deposition. This method has been proved with the majority of coating techniques discussed in the previous chapter. For this purpose a rotation device was designed and fitted to the electron beam vacuum chamber (Figure 3.11). With this device is possible to produce coatings on optical fibres with a good homogeneity level.

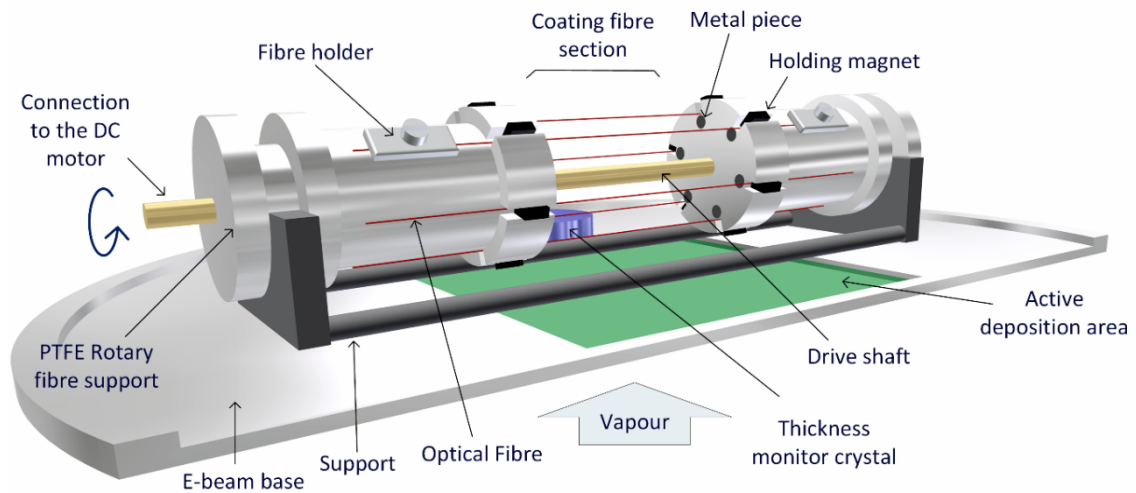


Figure 3.11 – Scheme of the home made rotary system for coating optical fibres.

The fibres are stretched and fixed at both sides with square magnets and metallic cylinders and then the spare fibre is rolled around the polytetrafluoroethylene (PTFE) rotary support and locked with the fibre holder. The system is able to support 6 fibres if those are to work in transmission mode or 12 if the deposition is focused on a tip. The drive shaft is connected to a DC motor with a gearbox located outside the chamber through a combination of angle gears and a special rotary feedthrough for high vacuum chambers.

The calibration of the system aiming to determine the film thickness in the cylindrical shape substrate was performed by using the same procedure as before. A set of thin films was produced over silica fibres substrate at a rate of 0.02 nm/s with a rotation speed of 5 rpm. Thin films of different thicknesses (380, 500 and 610 nm, measured by the thickness monitor) were produced around the optical fibres using the rotary system. After cleaving those fibres were analysed by SEM. The images of this analysis are shown in Figure 3.12. The optical fibres are mainly constituted by SiO_2 which is an insulator and prevents the correct discharge of electrons that are hitting the sample. This leads to

the formation of bright spots in the silica substrate region. Although the measurement of the thickness is possible and can be compared with the thickness monitor in the static position.

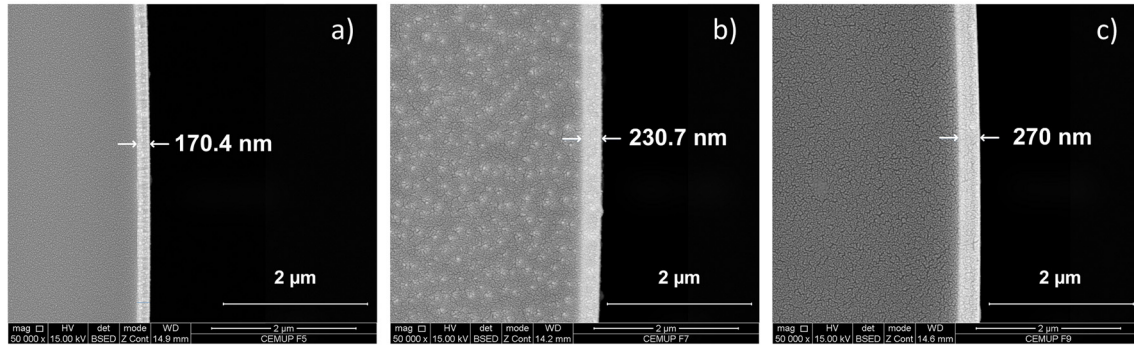


Figure 3.12 – SEM images for calibration of the rotary system to the thickness thin film considering three readouts at the static position: a) 360 nm, b) 500 nm and c) 610 nm.

The calibration curve presented in Figure 3.13 shows a ratio of 2.23 ± 0.1 between the static and dynamic measurements. This value will be used in this work to produce all the thin film coatings over optical fibres.

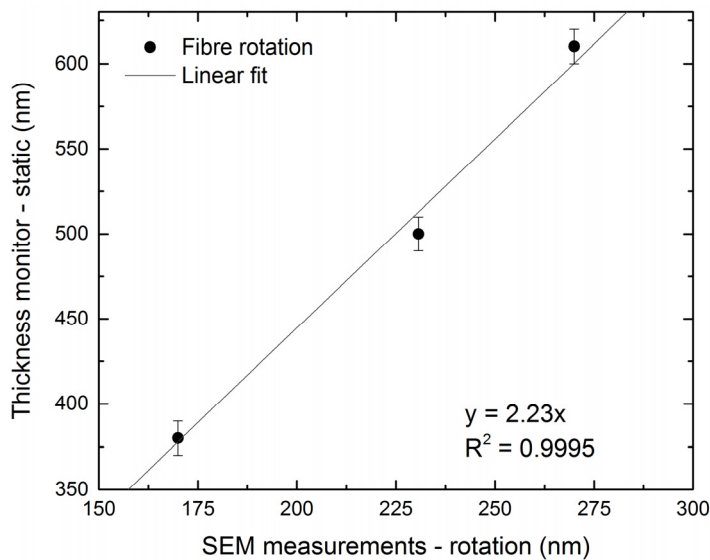


Figure 3.13 – Thin film thickness calibration in the rotation mode compared to the static mode.

The importance of using this rotary system can be found in Figure 3.14 showing an optical fibre coated with Ti in a static position close to the thickness monitor a), and in a dynamic position placed in the rotary system b). The static position produces thin films over optical fibres with high inhomogeneity while rotating the cylindrical shape substrate reduces abruptly this morphological characteristic.

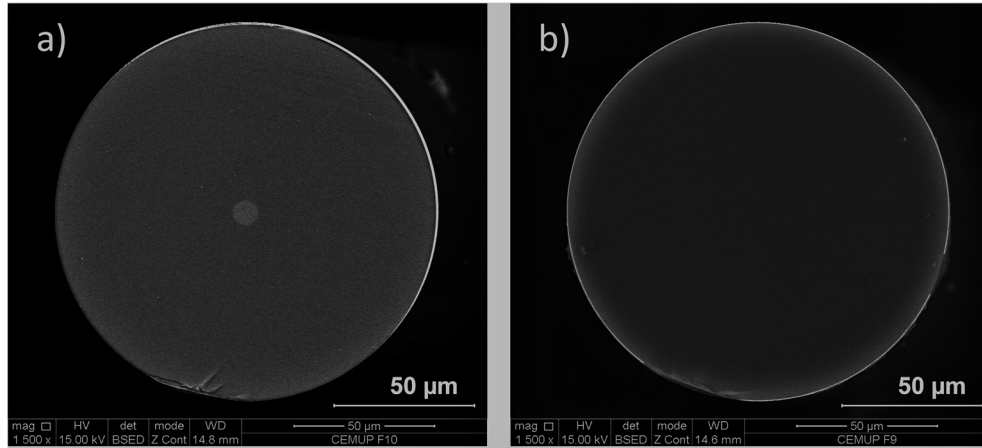


Figure 3.14 – SEM pictures of two fibres coated with pure Ti: (a) in a static position with lateral coating, (b) using the rotary system with homogeneous coating around the cylindrical fibre shape.

Another way to measure this ratio was through a narrow planar silicon substrate with a mask on top and attached to rotary system. A set of thin films of Ti was fabricated with the same rotation velocity and evaporation rate of the fibre coating. The thickness measured in the thickness monitor was 100 and 200 nm respectively. Figure 3.15 shows the step profile of the coating in rotation obtained with the profilometer.

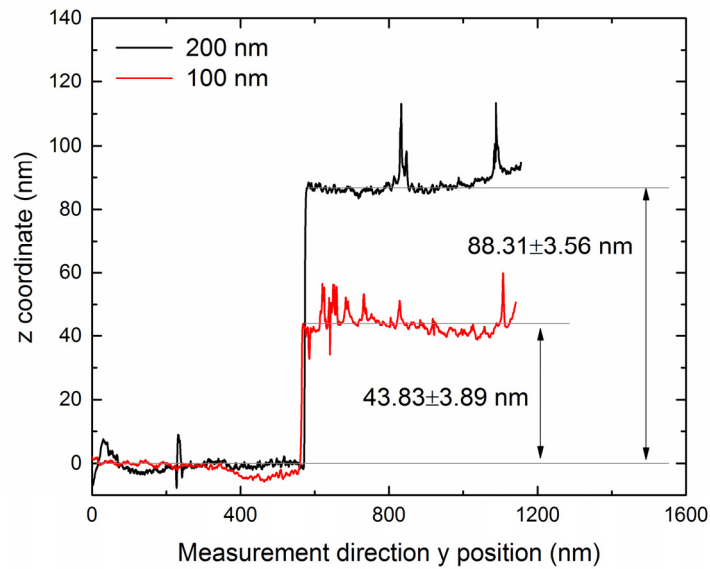


Figure 3.15 – Step profile of a planar substrate while in rotation for two Ti films. The thickness measured in the static position was 100 nm and 200 nm.

The results show high roughness but even though they are in good agreement with the SEM measurements, with a rate between static and dynamic measurements of 2.02 ± 0.1 .

– *Titanium Dioxide Deposition and Characterization*

The melting point of Ti is $\sim 1650^\circ\text{C}$ [118] at 101.325 kPa and evaporates at 1300°C with a vapour pressure around 10^{-5} kPa [119] which makes it an excellent element to be evaporated with e-beam technique. In spite of the good results with Ti evaporation, the TiO_2 thin film fabrication is not so trivial. The deposition of TiO_2 through e-beam evaporator has been tried using several forms of the starting material from single crystal to powder or sheets, although without success. When those forms are heated in vacuum with the electron beam two main processes occur. First, the reduction reaction by releasing oxygen atoms. The rutile crystal decomposes at 1870°C [122] and becomes metallic due to the excess of Ti atoms in the crystal composition. When in powder or even in small pieces other process takes place. Each light weight particle receives negative charge from the highly energetic electron beam with low draining efficiency. Before the energy transferred to the particle is high enough to rise the temperature until melting point the repulsive electric forces due to charge build up causes a *snowing* effect inside the vacuum chamber. This second process depends on the material density and it occurs also with metals when in small pieces or powder. When the size is increased this effect is not an issue for higher dense materials.

To avoid these problems the evaporation of a single rutile crystal in the same e-beam chamber was attempted by adding a pure oxygen atmosphere. Although the pressure was maintained in low levels, below the limit of the working point of the diffusion pump ($\sim 10^{-2}$ mbar) and to avoid electric arc discharges to the nearby metal pieces. Even though the quantity of oxygen inside the chamber was not enough to compensate the reduction reaction of the rutile crystal.

The process of growing TiO_2 thin films was achieved through thermal oxidation of Ti while the evaporation of pure metal takes place. Pure Ti metal wire with 1.5 mm diameter and a purity of 99.6% (Goodfellow Cambridge Ltd. UK) was used, and a controlled flux of oxygen with 99.999% purity (Linde Portugal, Lda., Portugal) was maintained at a constant pressure of $\sim 1.1 \times 10^{-3}$ mbar inside the vacuum chamber. This pressure was found to be high enough to oxidize the metal and low enough to maintain the high vacuum pump working properly. After the Ti metal reaches a temperature in the order of 1000°C [123] it starts to react with the oxygen molecules and in few minutes the top layer of the target is oxidized and the evaporation process takes place producing a thin film in the form of TiO_2 at the substrate. The low deposition rate (~ 0.01 nm/s) and the continuous oxygen pressure allow the formation of a thin oxide film at the substrate.

Two different sets of coatings were produced on top of silicon wafers, one of pure Ti metal and the other with TiO_2 both with 100 nm of thickness. The result can be observed in the SEM images on Figure 3.16. It shows pure Ti (a) and TiO_2 (b) thin film samples when produced inside the vacuum chamber with 200 000x magnification. It's visible high uniformity in both samples with a smoother surface in the oxide film sample. It suggests the existence of a high homogeneous thin film without chunks of material.

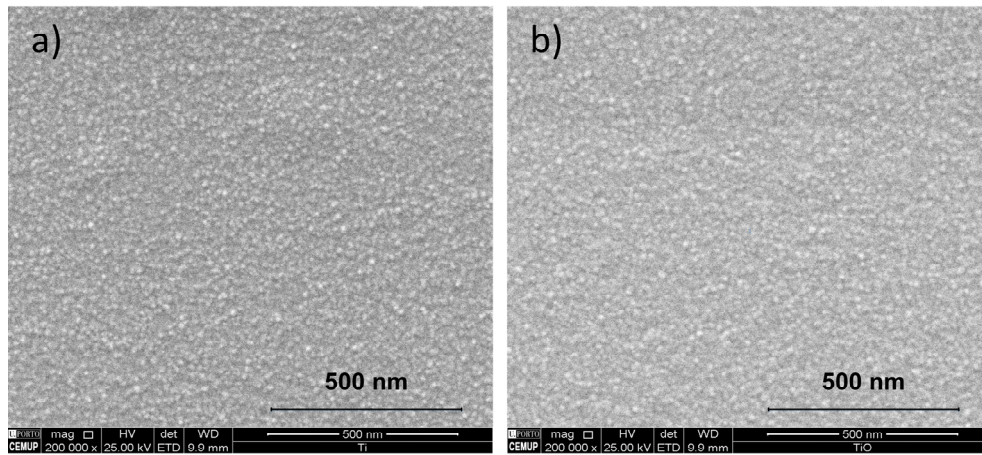


Figure 3.16 – SEM pictures of the surface silicon wafers coated with pure Ti metal (a) and with TiO_2 (b).

After the morphological analysis was accomplished by the SEM images the TiO_2 sample was object of chemical analysis with the energy dispersive X-ray spectroscopy module described in section 3.2.2 (Figure 3.17).

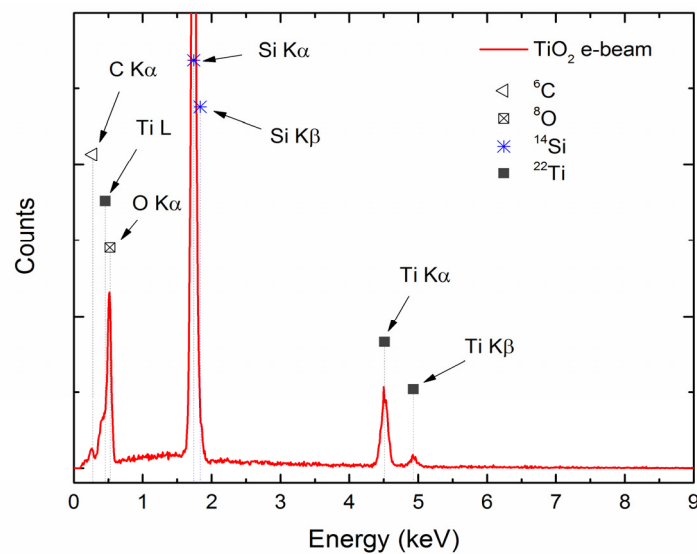


Figure 3.17 – EDS for the TiO_2 coating produced with the electron beam evaporator.

From the Figure 3.17 can be observed the very clean coating layer for energies up to 9 keV where only a carbon contamination (line C K α) and the substrate (band Si K) are present. The Ti L band is convoluted with the O K α line. The spectral position of the lines are in good agreement with the literature [124].

3.2 Structure Analysis

The coatings produced along this work were analysed with some techniques, namely ellipsometry, scanning electron microscopy, energy dispersive X-ray spectroscopy, X-ray photo electron microscopy and X-ray diffraction. A brief description of each technique is described next.

3.2.1 Spectroscopic Ellipsometry

Spectroscopic ellipsometry is a surface sensitive, non-destructive, non-intrusive optical technique used to measure the thickness and the optical constants of thin films. It was used in this work to estimate the RI profile of several samples of TiO₂ coatings.

Ellipsometry [125, 126] is based on the measurement of the change of the light polarization state upon reflection on a sample. The fundamental equation is given by equation (3.6)

$$e^{i\Delta} \tan \psi = \frac{r_p}{r_s} = \rho \quad (3.6)$$

which relates the signal phase shift, $\Delta = \delta_p - \delta_s$, with δ being the phase angle, and the change in the relative amplitude of the parallel (p) and perpendicular (s) components of the reflected electric field, $\tan \psi = |r_p|/|r_s|$, where r_p and r_s are the complex Fresnel reflection coefficients. Modern phase-modulated ellipsometers measure the parameter values designated as I_s and I_c , being ψ and Δ calculated using the appropriate formulation:

$$I_s = \sin(2\psi) \sin(\Delta) \quad (3.7)$$

$$I_c = \sin(2\psi) \cos(\Delta) \quad (3.8)$$

The characterization involved an initial measurement on the substrate region, not covered by the film, in order to determine the native silica thickness covering the silicon substrate, assuming a two

layers structure model. The obtained values for the silica layer thickness were used in the models for the TiO₂. The optical constants for the TiO₂ films were calculated using the Lorentz model.

$$\varepsilon = \varepsilon_{\infty} + \frac{(\varepsilon_s - \varepsilon_{\infty}) \times \omega_0^2}{(\omega_0^2 - \omega^2) + i\Gamma\omega} \quad (3.9)$$

The spectroscopic ellipsometry measurements were made using an AutoSE ellipsometer (HORIBA Scientific) with a total of 218 points in the wavelength interval 500-800 nm, an incidence angle (θ_0) of 69.8 °, an acquisition time of 40 ms per point and an average of 20 measurements per point, resulting in a signal to noise ratio of 20. A measurement spot area of 250×250 μm² was used. The surface of the samples was mapped, in order to select a region with a low relative amount of defects.

The RI values of the films were calculated in collaboration with CICECO and Instituto de Telecomunicações (IT) from University of Aveiro assuming a four layers structure model as illustrated in Figure 3.18. The data were minimised using the *simplex* algorithm [127] for three different samples.

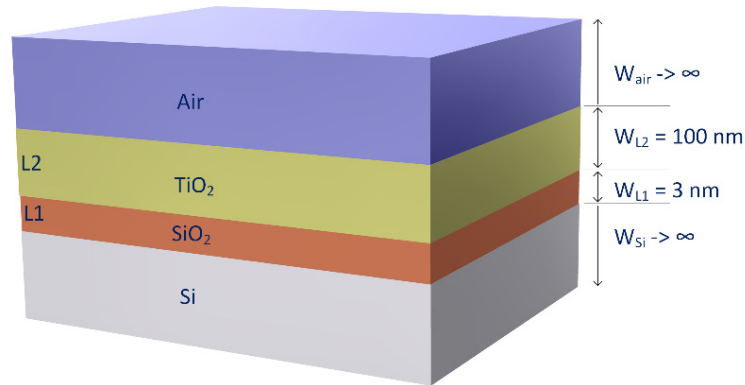


Figure 3.18 – Structure model used to interpret the ellipsometry data. On the right side the thickness of each layer is indicated.

Figure 3.19 exemplifies the behaviour of the ellipsometric parameters and the data best fit for the measurements acquired for sample 1. The thickness of the three samples was estimated by the method with 100.53 ± 0.61 nm, 129.87 ± 1.38 nm and 132.10 ± 0.13 nm respectively

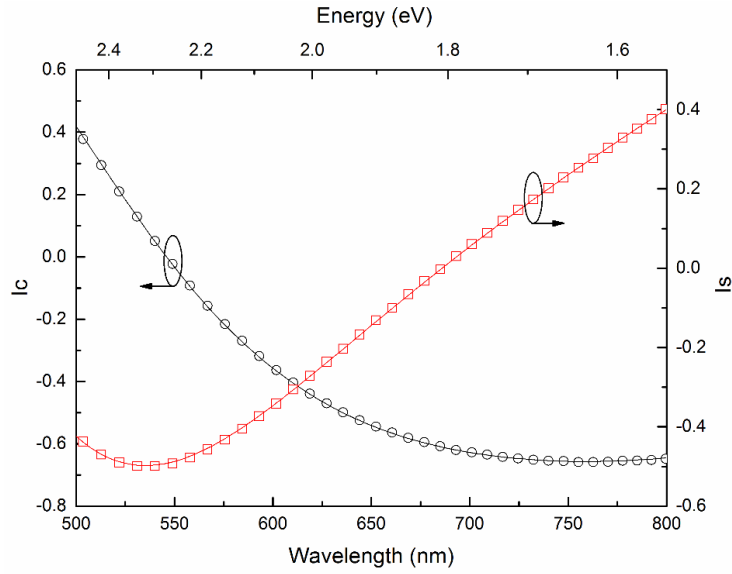


Figure 3.19 – Ellipsometric parameters I_C (circles) and I_S (squares). The solid lines represent the data best fit ($\chi^2=0.0473$) within 500-800 nm. Thickness= 132.103 ± 0.128 nm with negligible roughness

From the fit described in the previous section, the material dispersion curves were estimated for the three samples, as shown in Figure 3.20.

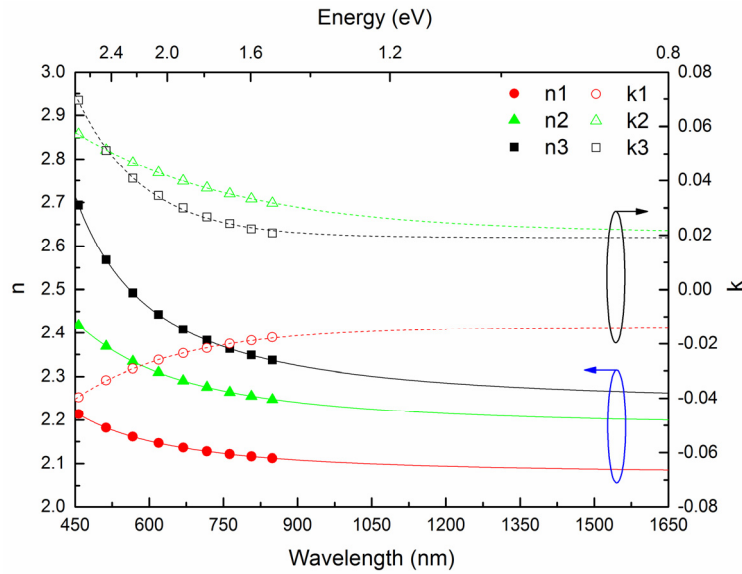


Figure 3.20 – Dispersion curves for all samples extrapolated to higher wavelengths (lines). The RI was obtained experimentally with the real part (close symbols) and the imaginary part (open symbols).

The ellipsometer is limited to the 500 to 800 nm range and the extrapolation to higher wavelengths of the real part of RI was provided by the implementation of the *Sellmeier* equation:

$$n^2(\lambda) = 1 + \frac{B_1\lambda^2}{\lambda^2 - C_1} + \frac{B_2\lambda^2}{\lambda^2 - C_2} + \frac{B_3\lambda^2}{\lambda^2 - C_3} \quad (3.10)$$

where n is the RI, λ is the wavelength, B_i and C_i for $i=1,2,3$ are the *Sellmeier* coefficients.

From these data is possible to assume that the material is oxidized with a real RI component around 2.2 ± 0.1 . From the literature the Ti metal RI real and imaginary components are $n = 3.6799$ and $k = 4.5327$ respectively at 1550 nm [128]. Given that the imaginary component of the RI is less than ± 0.02 it may be assumed that these thin films are not metal.

Each sample was measured in three different locations with low RI variations, suggesting high homogeneity.

3.2.2 Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy

Scanning electron microscopy is a very useful technique to obtain high resolution and focus images of coating surfaces or micro and nanostructures. It consist on focusing accelerate electrons onto the sample with high energy and collect the diffracted electrons, due to the electron sample interaction, on a detector and construct the image that corresponds to the sample profile. Typically a SEM system have an electron gun to produce electrons and accelerate them in the sample direction with energies in the range 1-40 keV being focused in a spot that can be less than 10 nm with a set of electron lenses. The interaction between the incident electrons with the sample originate several effects as emission of secondary electrons, backscattered electrons, diffracted backscattered electrons, transmitted electrons, bremsstrahlung X-rays, visible light (cathodluminescence) and heat [129].

In this work, besides the secondary electrons that produce the SEM images, the backscattered electrons that were used to detect contrast between areas with different chemical compositions and the X-rays were used for elemental analysis.

These emissions can be detected with different type of detectors. The secondary electrons are collected by a scintillator-photomultiplier system known as the Everhart-Thornley (E-T) electron detector [130]. The secondary electrons hit a scintillator which emits photons which upon incidence on a photocathode give rise to electrons that are accelerated onto the photomultiplier by applying a positive bias voltage, increasing the collection efficiency. The backscattered electrons can also be

detected with the E-T detector however only the electrons that travel along the direct line towards the detector which reduces the efficiency. The collection efficiency of the backscattered electrons is improved by increasing the number of detectors, either scintillators or solid-state based with high solid angle of collection. The volume of interaction follows a drop shape and depending on the energy of the incident electrons the penetration depth can be from 1-5 μm and the spatial resolution is around 1.2 nm.

The acquisition is accomplished in high vacuum regime, $<10^{-5}$ mbar and the samples tend to become electrically charged which is an issue in the case of insulator samples. Usually the surface is sputter-coated with a thin layer of Au in order to facilitate the discharge of the sample. In the case of samples that could not be coated with a metal, the pressure inside the chamber can be slightly increased and the discharge is made through the gas, affecting the spatial resolution.

The SEM images of metals and oxides presented in this work were obtained by the model Quanta 400FEG ESEM (FEI corporate headquarters, USA) at the Materials Centre of the University of Porto (CEMUP). The FEI Quanta 400FEG ESEM equipment is fitted with the model EDAX Genesis X4M which allows detection of X-rays emission, bring the possibility to identify the chemistry of the sample (Energy dispersive X-ray spectroscopy - EDS analysis).

The thin film coatings studied along this work and analysed by SEM were the metals nickel (Ni), copper (Cu), titanium (Ti), zinc (Zn), aluminium (Al), palladium (Pd) and the oxides were silicon dioxide (SiO_2), nickel oxide (NiO), copper oxide (CuO and Cu_2O), titanium dioxide (TiO_2), aluminium oxide (Al_2O_3) and zinc oxide (Zn).

3.2.3 X-ray Photoelectron Spectroscopy

Surface analysis can be accomplished by irradiating a sample with mono-energetic soft X-rays and analysing the energy of the emitted electrons, this technique is called X-ray photoelectron spectroscopy (XPS) [131], also known electron spectroscopy for chemical analysis (ESCA) [132].

Electromagnetic radiation with energy from 200 eV to 1 MeV falls in the X-rays band and are usually produced in vacuum by bombarding a metallic anode with high energy electrons emitted by an electron gun. The energy and the intensity of the emitted X-rays depends on the electrons energy and on the anode material which typically is magnesium (Mg) or aluminium (Al). Usually is used as X-rays source the $K\alpha$ transition of Mg (1253.6 eV), Al or monochromatic Al (1486.7 eV) [131, 133].

These photons have limited penetrating depth in a solid substrate in the order of 1-10 μm . They interact with atoms in the top layer of the sample and electrons are emitted due to photoelectric effect [132]. The equation (3.11) returns the measured kinetic energies of the emitted electrons [131].

$$\text{KE} = h\nu - \text{BE} - \phi_s \quad (3.11)$$

where $h\nu$ is the energy of the incoming photon (X-ray), BE is the binding energy of the atomic orbital from which the electron originates and ϕ_s is the spectrometer work function, i.e. the energy necessary for the electron escape from the material. The chemical state of an atom changes the BE of a photoelectron. Because each element has a unique set of binding energies the XPS can be used to identify and quantify the concentration of the elements in the surface of the sample [134].

The equipment used to perform the XPS analysis was the Kratos Axis Ultra HSA (Kratos Analytical Ltd, UK) at CEMUP which operates in ultra-high vacuum regime, $<10^{-9}$ mBar. Photoelectrons generated are collected with high efficiency using combined magnetic and electrostatic lenses. They are counted by the delay line detector which provides >100 energy channels which are used to acquire high resolution spectrum or wide scan or survey spectrum.

The thin film coatings studied along this work and analysed by XPS are the oxides CuO , Cu_2O , ZnO , NiO , TiO_2 and Al_2O_3 .

3.2.4 X-ray Diffraction

The X-ray diffraction (XRD) [135] is based on the interaction of a monochromatic X-rays beam, with a target material. In this case the incident beam hit the parallel structure planes at an angle and is reflected at the same angle. The process of diffraction occurs in materials with regular structure (i.e. crystalline) and the scattered X-rays interfere constructively and destructively forming a specific diffraction pattern used to identify and characterize all the compound of the lattice. In case of a non-regular structure, e. g., polycrystalline, aggregate or powder, all possible diffraction peaks from the powder will be detected because the experimental angle is systematically changed. The scheme of the XRD process is described in

Figure 3.21.

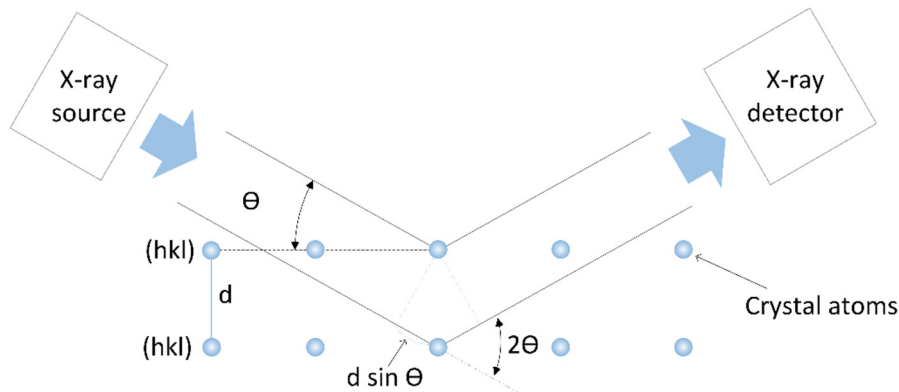


Figure 3.21 – Scheme of the X-rays diffraction process.

The blue spheres represent the atoms in the reciprocal lattice where d is the distance between the planes of the sample formed by the atoms which orientation is defined by the so-called Miller indices h , k and l [136]. The incident X-ray beam is reflected out of the sample and may go through several slits (collimator and filter) before entering into a detector which registers the intensity at an angle 2θ with respect to the sample plane. When an incident beam angle is equal to the angle of reflection, the beams reflected are in phase with each other; which means that they have path difference proportional to an integer number of wavelengths. This condition is referred to as the Bragg diffraction condition described by the Bragg's Law with the equation (3.12):

$$n\lambda = 2d \sin \theta \quad (3.12)$$

where n is a positive integer and λ is the wavelength of the incident wave, d is the distance between the lattice planes and θ is the scattering angle. For specific angles each material satisfies the Bragg diffraction condition and the interference will be detected with a peak intensity giving origin to a unique diffraction pattern intensity as a function of 2θ . Each peak position corresponds to an orientation of the planes in the lattice defined by the Miller indices.

The X-ray diffraction analysis will be presented and discussed for samples with thin films of CuO, Cu₂O, ZnO, NiO, TiO₂, Al₂O₃ and Cr₂O₃ on top of Si wafers and performed with the XRD model X'Pert Pro (PANalytical, Netherlands) at the University of Trás-os-Montes e alto Douro, Portugal. This is equipped with an X-rays source from Cu K α .

3.3 Conclusions

This chapter was focused on the identification and characterization of different techniques used to the fabrication of fibre structures as on the morphological and chemical analysis of the coating surface. The procedures here presented will be applied on the structures studied in the next chapters.

Chapter 4

Optical Spectroscopy for Sensing Using Coated Long Period Fibre Gratings

The sensitivity to the external medium and the range of operation are some of the major characteristics of the fibre optic devices when applied to the sensing field. Structures as long period gratings present intrinsically good performance which is substantially increased when specific coatings are attached to the surface. In this chapter a study about the sensing performance of the deposition of different layers of titanium oxide and zinc oxide over the gratings is presented.

4.1 Introduction

Optical fibre gratings were briefly introduced in previous sections as wavelength modulation devices with the correspondent fabrication techniques described in section 3.1.1. In this chapter the detailed properties of optical structures as fibre Bragg gratings and long period fibre gratings are presented. Optical fibre gratings, also called band-rejection filters, have a wide range of interesting properties such as, immunity to electromagnetic radiation, small dimensions and low weight, flexibility, high melting temperature, high sensitivity and bandwidth, ability to monitor several parameters

simultaneously, multiplexing (several sensors can be written in the same fibre which allows measurements spatially distributed), long-distance transmission, possibility of real-time monitoring and low reactivity of silica. In this chapter the focus is on LPFG sensing devices working as refractometers which are exploited for a wide range of refractive index (RI) samples. As discussed before, the bare LPFG has been extensively studied, however is still possible to improve the sensitivity and accuracy to external mediums either by excitation of higher order modes or by coating the LPFG surface with thin films of oxides with high RI. In this section LPFGs coated with layers of titanium dioxide (TiO₂) and zinc oxide (ZnO) were experimentally characterized to variations of the surrounding refractive index (SRI) greater and smaller than the cladding refractive index (CRI).

4.2 Gratings in Optical Fibres

A fibre grating can be defined as an optical diffraction grating and its effect upon a light wave incident on the grating at an angle θ_1 can be described with the equation:

$$n \sin \theta_2 = n \sin \theta_1 + m \frac{\lambda}{\Lambda} \quad (4.1)$$

where θ_2 is the angle of the diffracted wave, m is the integer that determines the diffraction order and n is the fibre RI. This equation predicts the directions on which the constructive interference may occur for specific angle θ_1 and wavelength λ at which a fibre couples light between two modes efficiently. Figure 4.1 represents the diffraction of a light wave by a grating with period Λ

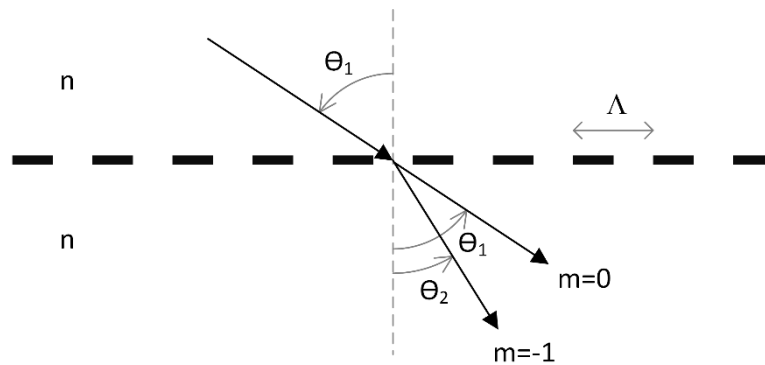


Figure 4.1 – Representation of a light wave diffraction by a grating [137].

Fibre gratings can be classified in two types, Bragg gratings or long period gratings. The former is related with the coupling between modes propagating in opposite directions while the latter corresponds to the coupling between modes propagating in the same direction.

4.2.1 Fibre Bragg Gratings

A fibre Bragg grating is produced by inducing small RI changes creating localized mirrors for a specific wavelength. By combining a set of these mirrors spaced by a period Λ a modulation is created as a sinusoidal variation along the core fibre [102]. Typically, the grating period is in the order of few hundred nanometers. The RI profile along the fibre axis z can be represented as equation (4.2):

$$n(z) = n_{\text{core}} + \delta n \left[1 + \cos\left(\frac{2\pi z}{\Lambda}\right) \right] \quad (4.2)$$

where n_{core} is the core RI, δn is the applied RI amplitude modulation due to the exposition to UV radiation and z the length along the fibre. The modulation induced is known as grating planes and corresponds to the selective mirrors above mentioned.

When light is launched into this structure, part of it is diffracted to the next grating planes and can, under specific conditions, interfere constructively in the backward direction. This phenomenon occurs when phase matching between the forward and backward propagation LP_{01} guided modes is present. From the mode coupling mechanism the forward propagating fundamental guided mode has a propagation constant given by

$$\beta_{01} = \frac{2\pi n_{\text{eff}}}{\lambda} \quad (4.3)$$

where n_{eff} is the effective RI and n_{clad} the cladding RI with $n_{\text{clad}} < n_{\text{eff}} < n_{\text{core}}$. The mode coupling mechanism in FBGs is represented in Figure 4.2. The small dark regions represents the forward and backward core propagation mode. Obviously, a large $\Delta\beta$ requires a small grating period.

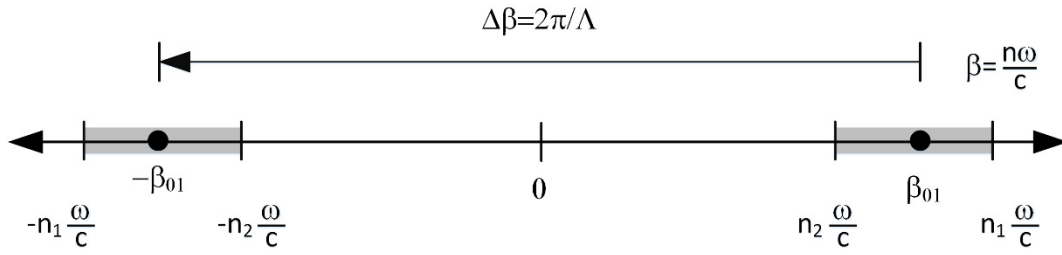


Figure 4.2 – Mode coupling mechanism in fibre Bragg gratings with the propagation constants of the forward and backward propagating guided modes [12].

Considering that $\theta_2 = -\theta_1$ and combining equations (4.1) and (4.3) the phase matching condition assume the form:

$$\Delta\beta = \beta_1 - \beta_2 = \frac{2\pi}{\Lambda} \quad (4.4)$$

where β_1 and β_2 are the propagation constants of the forward and the backward propagation modes and $\Delta\beta$ is the difference in the propagation constants of those two modes.

From equations (4.4) and considering that $\beta_1 = \beta_{01}$ and $\beta_2 = -\beta_{01}$ the phase matching condition is given by equation (4.5) which is a different way to write the Bragg's law from equation (3.12):

$$\lambda_B = 2n_{\text{eff}}\Lambda \quad (4.5)$$

where λ_B is denominated Bragg wavelength. The result is a narrow reflected peak at the reflected spectrum with a reflectivity calculated by using equation (4.6):

$$R(\lambda) = \frac{k^2 \sinh^2(SL)}{\delta\beta^2 \sinh^2(SL) + \cosh^2(SL)} \quad S = \sqrt{k^2 - \delta\beta^2} \quad (4.6)$$

where L is the length of the grating, k is the coupling constant, Λ is the grating period, $\delta\beta = \beta_{01} - \pi/\Lambda$, is the detuning parameter, $\beta_{01} = 2\pi n_{\text{eff}}/\lambda$ is the propagation constant of the guided mode with n_{eff} the effective RI of the core and λ is the radiation wavelength.

The reflectivity is maximum when $\delta\beta = 0$ is verified:

$$R_{\text{max}} = R(\lambda_B) = \tanh^2(kL) \quad (4.7)$$

The remaining broadband light signal is transmitted with a transmittance given by (considering an ideal situation):

$$T(\lambda_B) = 1 - R(\lambda_B) \quad (4.8)$$

The optical spectra of a generic FBG is shown in Figure 4.3 in both reflection (a) and transmission (b) modes.

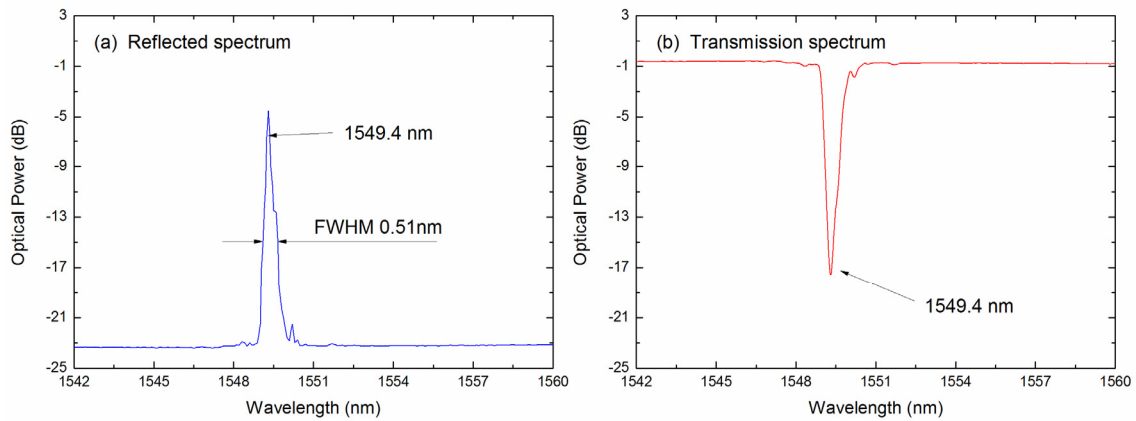


Figure 4.3 – Typical spectra of a FBG inscribed in a hydrogen loaded optical fibre through the mask technique with an UV laser: (a) reflection mode, (b) transmission mode.

The reflected signal was adjusted to a Gaussian curve showing a very narrow band with a full with half maximum (FWHM) of 0.51 nm which makes the interrogation easier and allow the possibility of implement a series of FBGs in a limited spectral window. In addition, the transmitted spectrum presents the full transmitted signal without the reflected narrow band.

The FBG modulation is applied to the core fibre and the light is not coupled to the cladding which makes it insensitive to the SRI medium. The applications in the sensing field are very wide [11, 138] but the main efforts are based on the high sensitivity of strain and temperature sensors [81]. When the section of the fibre grating is stretched the grating period Λ changes leading to a wavelength shift in the spectrum of the resonant peak. The same effect occurs with temperature, due to the thermal expansion coefficient of the silica reaching a wavelength shift higher than 10 pm/K, and with changes in the refractive index of the core/cladding materials.

The FBGs can be used also as refractometric sensing devices. As an example, the silica cladding can be replaced by the measurand medium changing the effective RI which can be achieved with some geometrical changes, as polishing or etching until the core is exposed, or even produce them in certain microstructured fibres [139]. Up to now only the RI modulations produced perpendicular to the

propagation direction were being considered but they can be produced by introduced a modulation oriented with a specific angle producing tilted FBGs [140]. With a tilt angle besides the mode coupling between forward and counter propagating modes, typical for the common FBGs, the mode coupling between forward propagating core mode and counter propagating cladding mode or the mode coupling between the forward propagation core mode and the radiation mode may also occur.

4.2.2 Long Period Fibre Gratings

Like the FBGs, LPFGs are obtained by introducing a periodic modulation in the RI of the fibre core along the z axis [12]. In general, the RI modulation period is in the range $100\ \mu\text{m}$ to $1000\ \mu\text{m}$ and has a length of a few centimetres.

This kind of structures can be considered as a different type of FBG in which the period of the RI modulation is such that a phase matching condition between the fundamental core mode and a forward propagating cladding mode of an optical fibre exists.

The mode coupling mechanism in LPGs is represented in Figure 4.4.

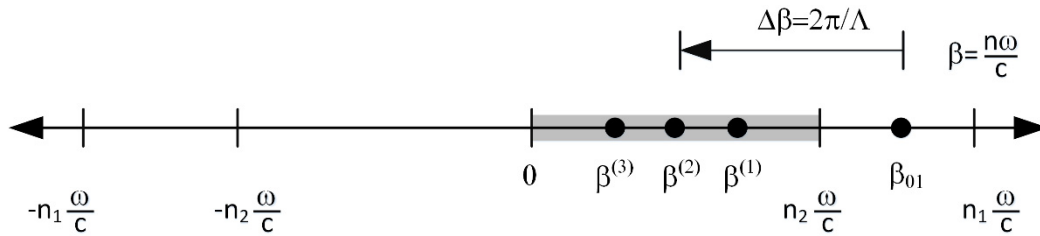


Figure 4.4 – Mode coupling mechanism in long period gratings with the propagation constants of the forward propagating guided modes [12].

The small dark region represents the forward radiation modes at the cladding and the smaller $\Delta\beta$ requires a higher grating period.

From equations (4.3) and (4.4) and considering that $\beta_1 = \beta_{01}$ and $\beta_2 = \beta^{(i)}$ the phase matching condition assumes then the resonance condition of a long period grating given by equation (4.9):

$$\lambda = [n_{\text{eff}}(\lambda) - n_{\text{clad}}^i(\lambda)]\Lambda \quad (4.9)$$

where $n_{\text{eff}}(\lambda)$ is the effective RI of the propagating core mode at wavelength λ , $n_{\text{clad}}^i(\lambda)$ is the effective RI of the i^{th} cladding mode and Λ is the period of the LPFG. As a result, several attenuation bands are generated in the transmission spectrum of the fibre [13]. Each of these attenuation bands are a result of a portion of light that is coupled from the core to a specific cladding mode which corresponds to a minimum of transmission T_i and calculated by the equation:

$$T_i = 1 - \sin^2(k_i L) \quad (4.10)$$

where L is the length of the LPFG and k_i is the coupling coefficient for the i^{th} cladding mode. An example of the LPFG transmission spectrum is shown in Figure 4.5 produced by the electric arc technique with a period of $396 \mu\text{m}$.

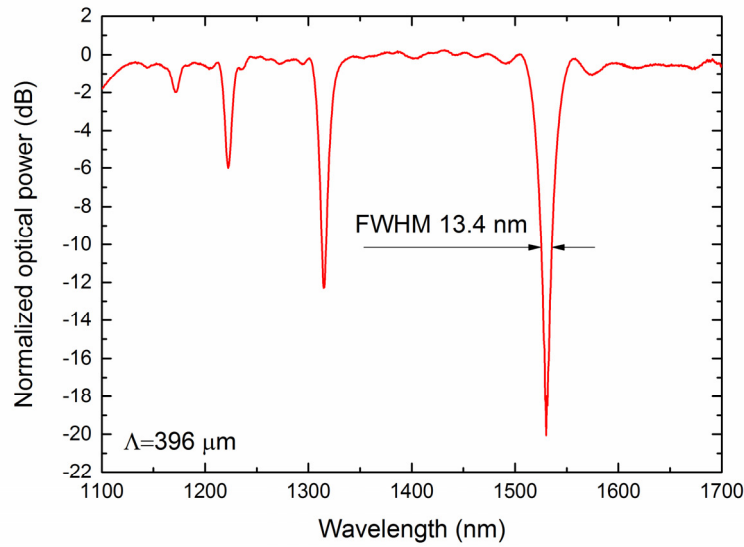


Figure 4.5 – Typical spectrum of a LPFG inscribed in a common optical fibre through the electric arc technique with $396 \mu\text{m}$ period.

Each attenuation band corresponds to a specific coupled cladding mode. Compared to the FBG the bands are much wider with FWHM around 13.4 nm . Therefore, the attenuation bands are not reflected back so they are typically used in transmission mode.

The wavelength position of this attenuation band depends on the SRI by changing the effective RI of the i^{th} cladding mode. The sensitivity to the SRI depends on which cladding mode is being considered and in general it increases with the order mode until reaches the so-called turning point where the sensitivity is maximum [141]. At this point each grating period presents two resonance wavelengths at each cladding mode where the phase matching condition is satisfied. The difference

in wavelength of those two resonances at a specific mode provides higher sensitivity than the common LPFGs. Higher order modes can be achieved with lower grating periods until the turning point is reached, which is true for periods less than 300 μm [15] at 1.5 μm .

The sensitivity to SRI at the grating region is the key feature of an LPFG enabling the use as a sensing element device in chemical and biochemical analytical measurements [16], for the detection of organic aromatic compounds [142] or as biosensor [143]. Nevertheless, this kind of structures have also been used as strain, bending and temperature sensors [107].

As the SRI changes from a RI of ~ 1 , in air, to near CRI with liquid solutions, the main effect is a shift to shorter wavelengths of the attenuation bands, which increases for higher order modes. It has been demonstrated [144] for this kind of structures, the highest wavelength and transmission sensitivity to the external medium occurs for SRI values slightly lower than the CRI, above that value the sensitivity is negligible, as can be seen in Figure 4.6, which illustrates the wavelength shift of a bare LPFG for a wide RI range [14]. A higher sensitivity for the higher order modes is expected.

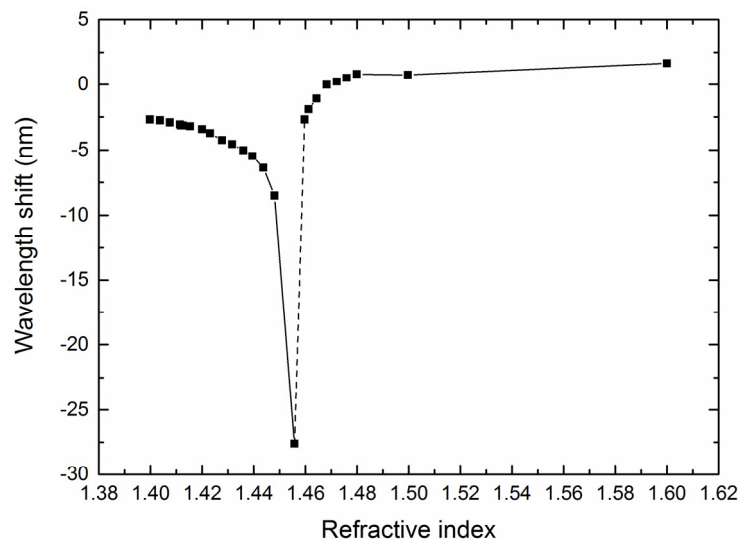


Figure 4.6 – Wavelength shift of a LPFG attenuation band with a period of 400 μm in function of the surrounding RI [145].

When the SRI is higher than the CRI all the attenuation bands show a considerable reduction in wavelength and transmission sensitivity [146]. This drawback can be overlapped by coating the LPFG with a material that has a RI higher than the CRI. The coating of LPFGs with Langmuir-Blodgett nanolayers was first proposed by Tatam et al. [147]. Comprehensive theoretical and numerical investigations with experimental demonstrations have shown that high RI layers induce

strong changes on standard LPFG spectral properties by favouring the transition between cladding guided modes to overlay guided modes, through the change of the wavelength and the minimum transmission value of the attenuation band [148-152]. According to the theory of LPFGs described previously, there is a dependence between the spectral positions of the attenuation bands with the effective refractive index of the cladding modes, which in turn, depends on the refractive index of the external medium.

For instance, the deposition of a TiO_2 or ZnO thin film on the LPFG sensor induces a re-distribution of the cladding modes that leads to a wavelength and amplitude shift of the attenuation bands. A systematic study of LPFGs coating with TiO_2 and ZnO over layers with different thicknesses and for SRI from 1.000 to 1.600 is presented next section.

4.3 Enhanced RI Sensing Characteristics of LPFGs with Over Layer Coatings

The LPFG sensing device working as refractometer is exploited in this section for a wide range of RI samples. As discussed before the bare LPFG has been extensively studied, however is still possible to improve the sensitivity and accuracy to the external mediums either by excitation of higher order modes or by coating the LPFG surface with thin films of oxides with high RI, as TiO_2 or ZnO .

Two sets of LPFGs were produced by using the electric arc technique as described in section 3.1.1, coupling the core mode to the LP_{11} cladding modes, which corresponds to an antisymmetric perturbation, according to Ivanov and Rego [153]. Well defined attenuation bands are formed with periods of $396\text{ }\mu\text{m}$ and $387\text{ }\mu\text{m}$ at 1550 nm and 1480 nm respectively, corresponding to the antisymmetric 6th order cladding mode, in standard single mode fibre (SMF28, Corning, Inc.).

In general, the grating attenuation band value was reached with a sensor length of $45\pm 5\text{ mm}$. The LPFGs were then coated with metal oxides. The first set was coated with TiO_2 and the second set with ZnO . The procedure to overcoat both sets was based on the e-beam thermal evaporation as described in section 3.1.3. While the TiO_2 was produced during the deposition from pure titanium oxygen atmosphere, the ZnO was produced from pure zinc with post thermal oxidation. The improvement of the adhesion between the silica fibre and the Zn metal coating was accomplished with a 3 nm layer of chromium (Cr).

All the LPFGs were optical characterized using the setup is illustrated in Figure 4.7 where the LPFGs were placed in a transmission configuration with a light source and an optical spectrum analyser (OSA). One end of the fibre was clamped with a magnet and the other end was fixed with a mass of 5 g in order to guarantee the fibre is stretched at a constant tension and with the same opto-mechanical characteristics.

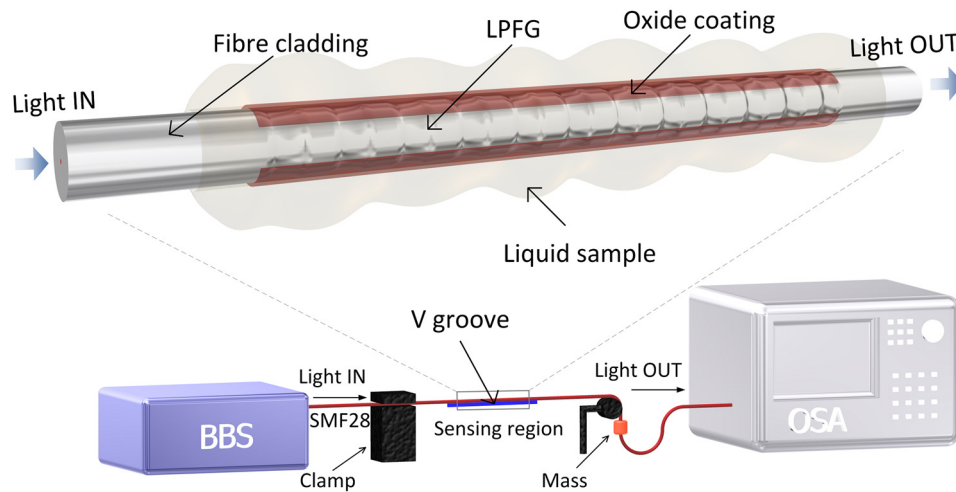


Figure 4.7 – Scheme of the measuring setup with an optical source, an optical spectrum analyser and the sensing device magnified on the top.

The studies were performed by measuring the transmission spectral characteristics of each coated LPFG when the SRI at the sensing device was changed from 1.300 to 1.640 at 589.3 nm using a set of RI calibrated oils (Cargille-Sacher Laboratories Inc., NJ, U.S.A.). The oil sample to be tested was placed in a glass V groove aligned with the sensing region in the fibre covering the entire LPFG length. After each measurement both fibre and the V groove were flushed with acetone to avoid contamination to the next oil sample.

4.3.1 LPFGs Coated with Titanium Dioxide Thin Films.

Titanium dioxide is probably the most studied material in the surface science of metal oxides [154]. TiO_2 is nontoxic, biocompatible, corrosion free and low cost material which during the past decades was applied to emerging areas as photovoltaics, photocatalysis and sensors [155].

– Materials and Methods

The first set of LPFGs was coated with TiO_2 with thicknesses of 10, 20, 30, 40, 50, 60 and 80 nm with an RI estimated to be 2.2 ± 0.1 by the ellipsometric characterization described in section 3.2.1. The sensing device was characterized using the setup shown in Figure 4.7 with a white light optical source as the input optical signal to the OSA (model ANDO AQ 6315B). The broad band source chosen is useful to work in a wide wavelength range allowing the characterization of several cladding modes in the same spectra acquisition.

– Experimental Results and Discussion

Figure 4.8 shows the transmission spectra from 1200 to 1600 nm of a bare LPFG and with a 20 nm thick TiO_2 film with air as external medium. The inset is the magnification of the LP_{16} cladding mode. A blue-shift of all bands was expected [148], and is consistent with the results presented for a LPFG coated with a Langmuir-Blodgett thin film [146]. A shift to shorter wavelengths of about 3.0 nm for the LP_{16} was measured. Also, it was observed a decrease of the amplitude of all bands, more pronounced for the higher LP_{16} cladding mode.

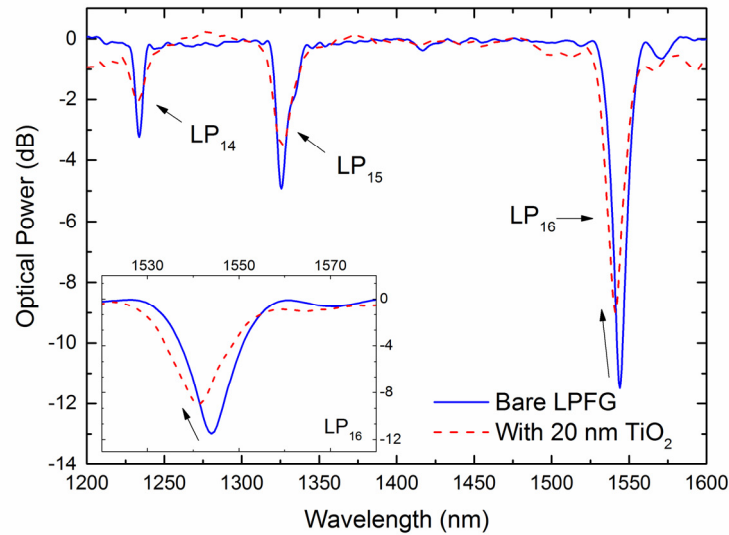


Figure 4.8 – Transmission spectra of a bare LPFG and with a 20 nm thick TiO_2 film with air as external medium.

Figure 4.9, Figure 4.10 and Figure 4.11 present the measured transmission spectra corresponding to LP_{14} , LP_{15} and LP_{16} modes, respectively, and for several SRI values between 1.300 and 1.600. The behaviour of a bare LPFG is shown in Figure 4.9-(a), Figure 4.10-(a) and Figure 4.11-(a), while the dependence of a LPFG with 40 nm of TiO_2 with RI changes is presented in Figure 4.9-(b), Figure

4.10-(b) and Figure 4.11-(b). A blue-shift of both LP_{14} , LP_{15} and LP_{16} bands is observed until the value of the SRI is comparable to the CRI (1.457) of the fibre. For SRI higher than CRI a shift for higher wavelengths is observed together with a substantial reduction in the attenuation of the bands. Although this behaviour is similar for both types of LPFG, the wavelength and attenuation shifts with variation of the SRI are more stressed for the coated LPFG due to the higher effective SRI.

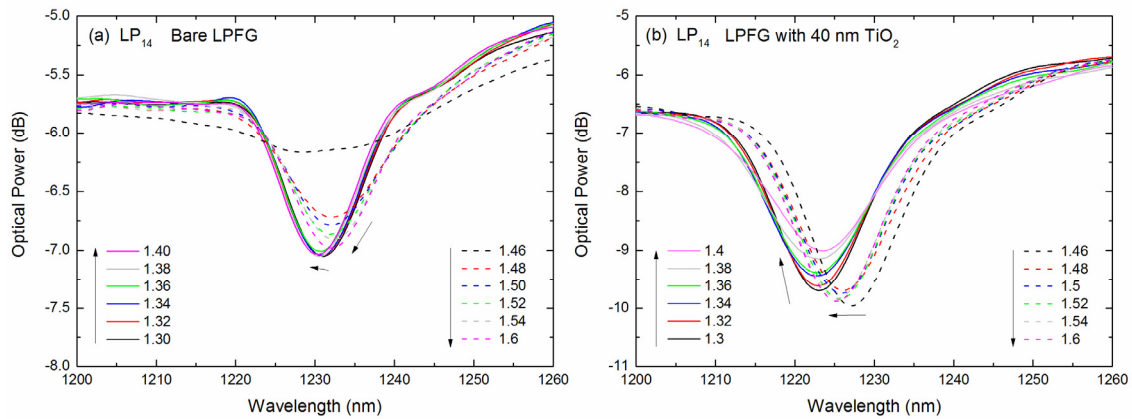


Figure 4.9 – Transmission spectra of the LP_{14} mode for several SRI values: (a) for a bare LPFG; (b) LPFG coated with 40 nm of TiO_2 .

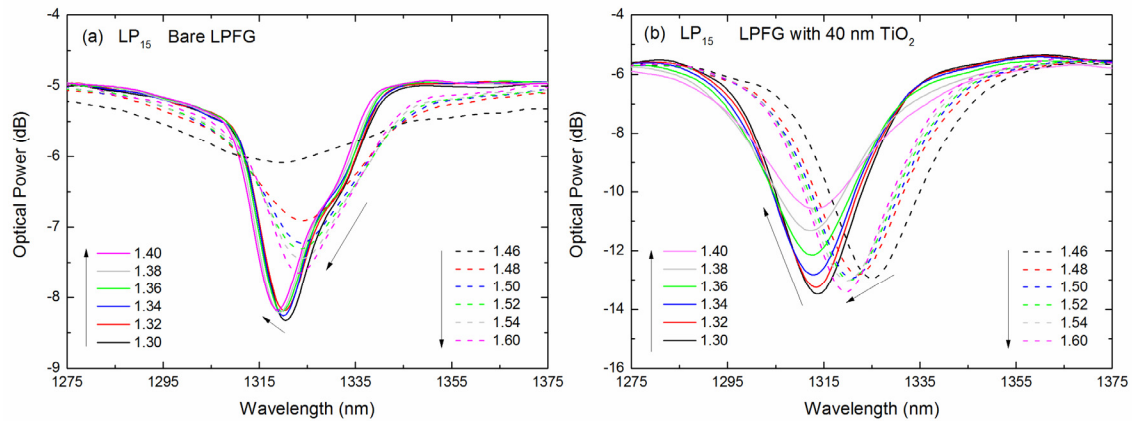


Figure 4.10 – Transmission spectra of the LP_{15} mode for several SRI values: (a) for a bare LPFG, (b) for a LPFG coated with 40 nm of TiO_2 .

Modes LP_{14} and LP_{15} of the bare LPFG have low wavelength sensitivity for the all range of SRI values, Figure 4.9-(a) and Figure 4.10-(a). On the other hand, for a coated LPFG (40 nm TiO_2), from Figure 4.9-(b) and Figure 4.10-(b) an increase in sensitivity, albeit small, can easily be noticed. The wavelength sensitivity to variations in the SRI increases with the order of the cladding modes [12], as it can be verified comparing the data here presented.

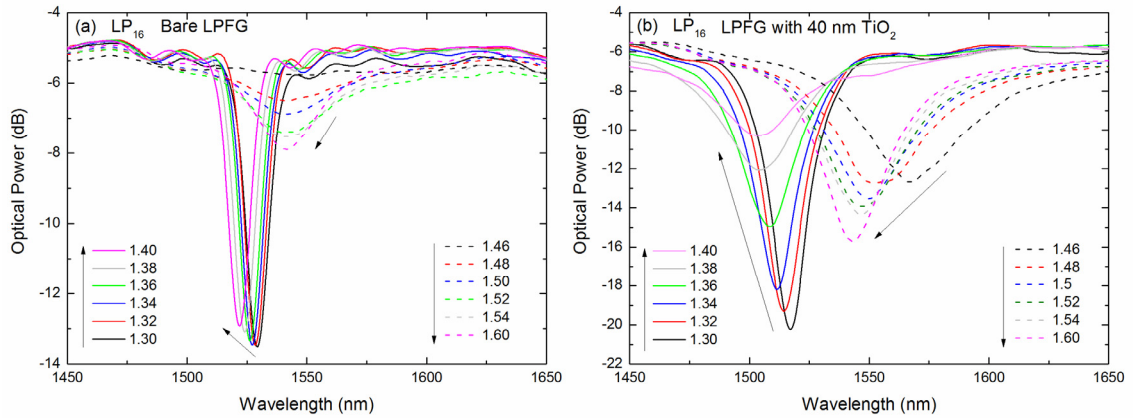


Figure 4.11 – Transmission spectra of the LP₁₆ mode for several SRI values: (a) for a bare LPFG; (b) LPFG coated with 40 nm of TiO₂.

The mode LP₁₆ presents higher wavelength shift than the LP₁₄ and LP₁₅, either for the bare or for the coated LPFG. From the Figure 4.11 (LP₁₆ mode), it is obvious an increased sensitivity of the coated (a) over the bare (b) LPFG for SRI values from 1.300 to 1.400. According to Vengsarkar et al. [12], bare LPFGs are not sensitive to wavelength and have low attenuation sensitivity for SRI above the CRI. However, for SRI higher than the CRI the coated sensor presents a large wavelength shift, while the bare LPFG sensitivity is insignificant.

The normalized wavelength shift to the initial state (at RI = 1.000) as a function of the SRI, from 1.300 to 1.640, is shown below for the LP₁₆ mode for a LPFG without thin film and for LPFGs with several values of TiO₂ film thickness between 10 and 80 nm. The Figure 4.12 shows the wavelength shift for SRI up to 1.460 where the attenuation mode is no longer visible while the Figure 4.13 shows the same for SRI higher than 1.420.

For SRI values smaller than the CRI, in particular from 1.300 to 1.400, the wavelength shift increased for all the film thicknesses considered. This region is quite interesting due to the characteristic of many biological materials, although a bare LPFG is virtually useless. For example, in the 1.340 to 1.360 RI region, the average wavelength shift indicates a sensitivity of 100 nm/RIU for the bare LPFG and 215 nm/RIU for a 40 nm TiO₂ coated LPFG. Also, the corresponding value is 330 nm/RIU for a 60 nm coated sensor.

It can be seen, in the region of SRI smaller than the CRI, the well-known LPFG high wavelength sensitivity feature moves to shorter wavelength as the thin film thickness increases. As the coating thickness increases the range of refractive indices analysed is reduced because the attenuation band corresponding to the LP₁₆ mode disappears. The introduction of an over layer changes the coupling

condition of the LPFG increasing the effective RI of the external medium leading to higher sensitivities in a wider RI range.

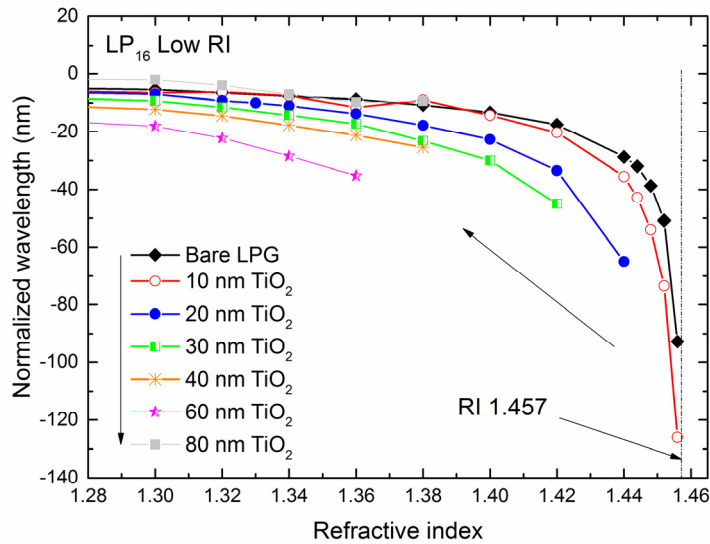


Figure 4.12 – Normalized wavelength variation with the SRI for a LPFG without thin film and for LPFGs over coated with 10 to 80 nm of TiO₂ for the RI range from 1.300 to 1.460.

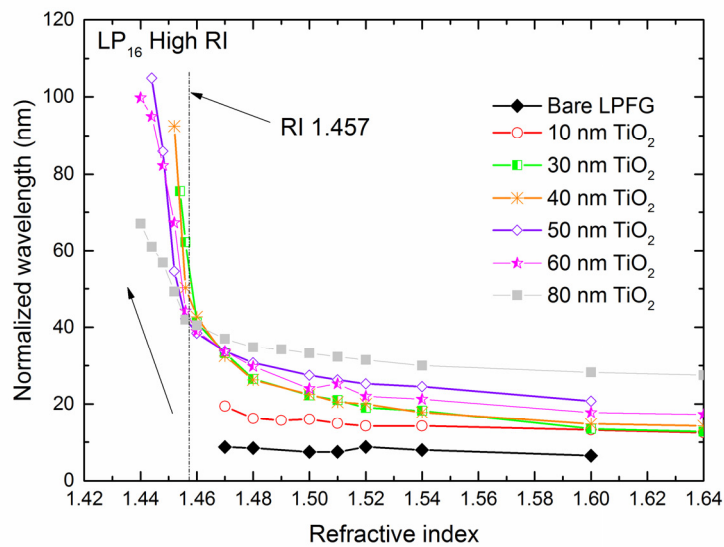


Figure 4.13 – Normalized wavelength variation with the SRI for a LPFG without thin film and for LPFGs over coated with 10 to 80 nm of TiO₂ for the RI range from 1.420 to 1.640.

For SRI higher than the CRI, a steady increase of the wavelength shift with the thin film thickness was observed, whereas the bare LPFG presents any shift in wavelength. In particular, for the LPFG

coated with 40 nm, the average sensitivity is about 825 nm/RIU in the RI region between 1.460 and 1.480.

A close observation of Figure 4.13 reveals that values of the SRI in the range 1.420 to 1.460 can lead to different positions in the wavelength spectrum (in the right or left side of the initial state) depending on the value of the thin film thickness. Assuming a linear approximation, from Figure 4.13, a negative average wavelength sensitivity above 5250 nm/RIU was calculated in the RI range from 1.444 to 1.456 for a 50 nm thick film. However, there is a small difference in the wavelength shift for different film thicknesses in the flat region of RI above 1.480 (about 20 nm for TiO₂ thicknesses from 10 to 80 nm).

The Figure 4.14 and Figure 4.15 presents the 1st derivative of the data plotted in Figure 4.13. It can be easily observed that the sensitivity increases with the TiO₂ coating being possible to choose the correct film thickness depending on the SRI that needs to be measured. When the RI approaches the CRI the sensitivity to the SRI is considerable increased up to 2000 nm/RIU. In spite of the extinction of the band occurs for lower RIs when the thickness of the TiO₂ coating is increased the sensitivity is in general improved.

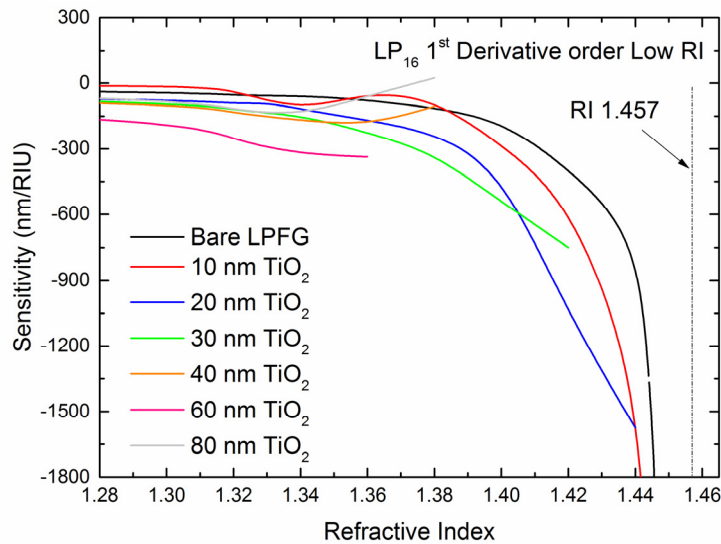


Figure 4.14 – Wavelength sensitivity as a function of the SRI for a LPG without thin film and for LPGs over coated with 10 to 80 nm of TiO₂ for the RI range from 1.28 to 1.46.

From the Figure 4.15 the sensitivity to the SRI reaches values over 10 000 nm/RIU by using a coating layer of TiO₂ with 40 nm of thickness. In addition the RI range of operation with improved sensitivity is wider allowing to be used with analytes for which bare LPFGs are useless.

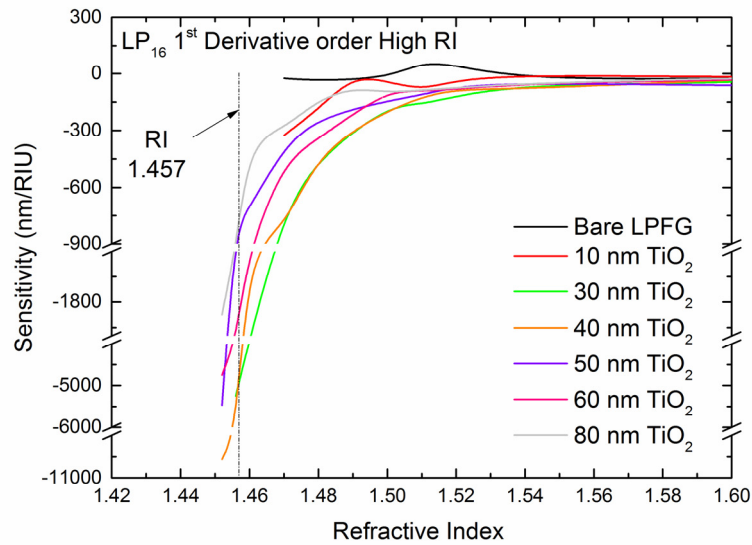


Figure 4.15 – Wavelength sensitivity as a function of the SRI for a LPG without thin film and for LPGs over coated with 10 to 80 nm of TiO_2 for the RI range from 1.420 to 1.640.

Without any coating, only the surrounding medium influences the effective index of the cladding mode. Increasing the film thickness both, film and external medium, influence the cladding mode because the external average RI increases. Above a certain thickness the average RI is equal to that of cladding and no guided modes are supported by the cladding and no attenuation bands are observed [147] For higher film thicknesses the attenuation bands can be explained by the existence of leaky modes due to the RI profile. Increasing the SRI the leaky mode becomes better confined with additional attenuation [14].

The variation in the attenuation was also studied for the mode LP_{16} when the SRI is changed from 1.300 to 1.640 and considering the same coating thicknesses as before. From Figure 4.16 the attenuation shift for SRI higher than the CRI is not relevant for sensing capabilities but for the SRI lower than the CRI the result is very interesting.

The dependence of the attenuation with the coating thickness when considering the same RI is notorious and this effect can be used to apply the highest attenuation sensitivity to the RI working range when required.

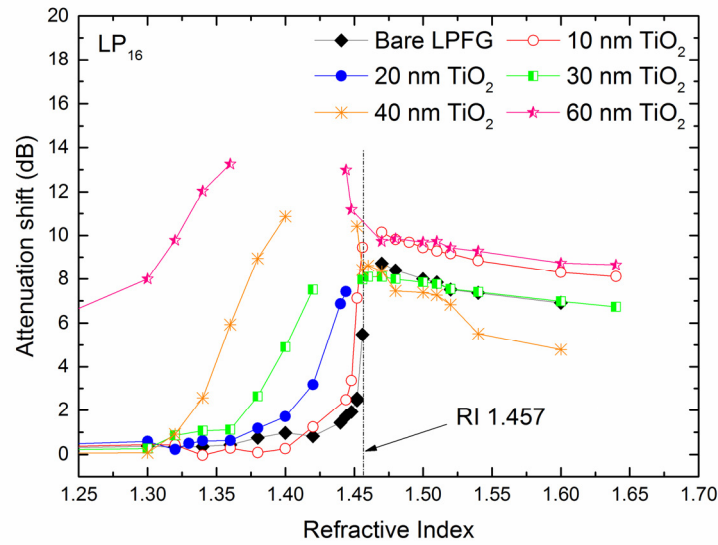


Figure 4.16 – Comparison of the LP₁₆ mode attenuation of a bare LPFG and LPFG with TiO₂ coatings, for several SRI values between 1.300 and 1.600.

4.3.2 LPFGs Coated with Zinc Oxide

ZnO is an advantageous material for the implementation of chemical sensors [156], because of its optical and electrical properties and the variety of methods available for its synthesis [157], and the multiplicity of geometries that can be produced [158].

The RI of ZnO is smaller than the TiO₂, around 1.929 at 1450 nm [159], but higher than the pure silica which would still increase the sensitivity of the LPFGs.

– Materials and Methods

A set of metal Zn thin films was deposited around the LPFGs in the range from 10 to 100 nm of thickness for optical characterization. They were then oxidized by thermal annealing in air at 400 °C for 1 hour with ZnO oxidation state. The detailed oxidation process and the morphological analysis will be discussed in detail in the Chapter 6. At this point is important to retain that the final oxide thin film is ZnO with a thickness higher with a factor of 2.9 in relation to the as deposited metal coating.

The LPFGs coated with ZnO were characterized using the same setup (Figure 4.7) although with the input light from a super luminescent diode source (SLD) model S5FC1550S-A2 (Benchtop SLD –

Throlabs, Germany) and the detection from an optical spectrum analyzer model Yokogawa AQ 6370D.

– Optical Characterization of ZnO Coated LPFG

Transmission spectra, from 1350 to 1600 nm, are presented in Figure 4.17 showing the curves corresponding to LP₁₆ mode of a LPFG with an 87 nm thick ZnO coating, for several SRI values between 1.300 and 1.600.

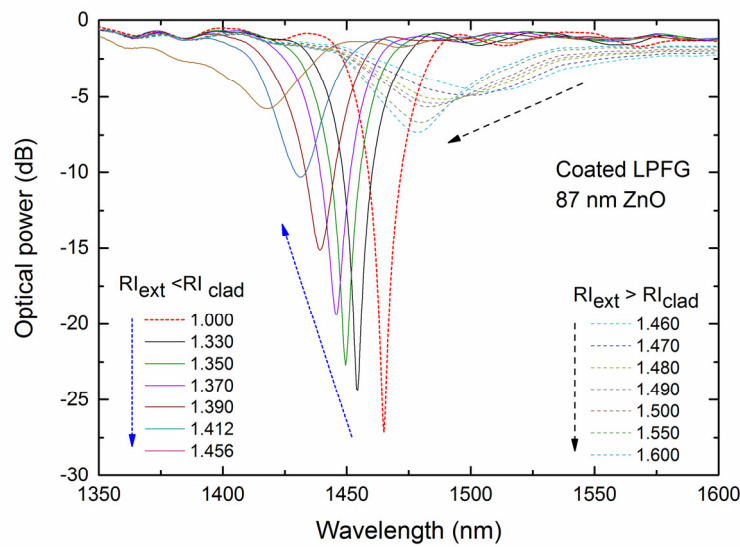


Figure 4.17 – Transmission spectra corresponding to the LP₁₆ mode of a LPFG with an 87 nm thick ZnO coating, for several SRI values between 1.300 and 1.600.

A blue-shift of the resonance band is observed until the value of the SRI is comparable to the CRI (1.457) of the fibre.

For SRI higher than the CRI a shift for higher wavelengths is observed together with a substantial reduction in the attenuation bands. In spite of this behaviour being present on both bare and coated LPFGs, the wavelength shift and the attenuation variation with the SRI are more marked for the coated LPFG due to the higher effective SRI.

The normalized wavelength shift to the initial state (corresponding to the RI=1.00) as a function of the SRI, from 1.300 to 1.600, is shown in Figure 4.18 and Figure 4.19 for a LPFG without coating and for LPFGs with several values of ZnO thickness between 58 and 145 nm. For instance, in the 1.320 to 1.360 region, the average wavelength shift indicates a sensitivity of 56.3 nm/RIU for the bare LPFG and 806.3 nm/RIU for a 145 nm thick ZnO coated LPFG. It is important to emphasise

that when the SRI is smaller than the CRI of the LPFG the high wavelength sensitivity feature moves left to smaller RI values as the ZnO thickness increases, Figure 4.18.

With the increasing of the coating thickness the range of SRI decreases since the attenuation band disappears. This can be explained by an eventual complex RI of the ZnO coatings that would give rise to vanishing of modes, as it was observed previously, experimental and theoretically [152, 160].

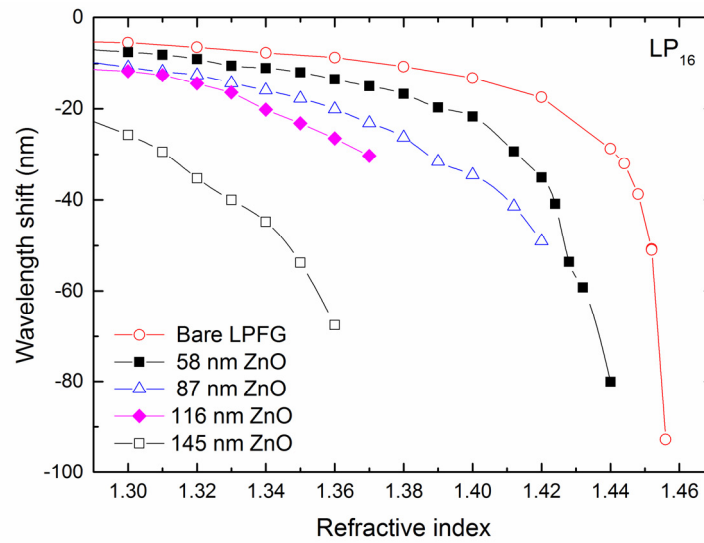


Figure 4.18 – Normalized wavelength shift as a function of the SRI for a bare LPFG and for LPFGs coated with 58 to 145 nm of ZnO in the RI range from 1.300 to 1.460.

For SRI higher than the CRI an increase of the wavelength shift with the thin film thickness was measured, while for the bare LPFG there is no wavelength shift. For instance, in the RI region between 1.450 and 1.470, characteristic of most mineral and edible oils for example, the average sensitivity is about 3433 nm/RIU, for a 58 nm thick film. Assuming a linear approximation, from Figure 4.19 an average wavelength shift sensitivity of 5925 nm/RIU was calculated in a broad range of RI values, from 1.440 to 1.460, for a 116 nm thick film.

The sensitivity level for all the ZnO coating thickness was estimated in the RI range from 1.300 to 1.600 applying the 1st derivative function to the data plotted in Figure 4.18 and Figure 4.19. The results are shown in Figure 4.20 and Figure 4.21. It can be easily observed that the sensitivity increases with the ZnO coating, as was obtained with TiO₂ coated LPFGs. The same possibility to choose the correct film thickness according to the SRI that needs to be measured was found. The sensitivity can be as high as ~1400 nm/RIU at an RI of 1.360, a region characteristic of volatile organic compounds (VOC) such as ethanol and acetone.

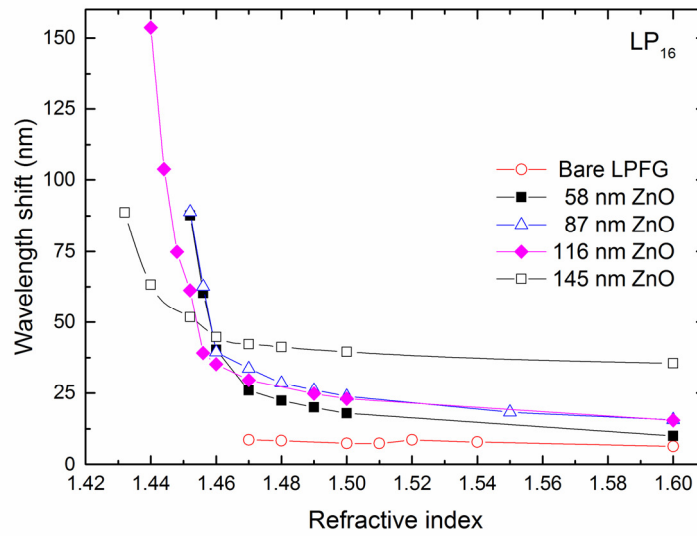


Figure 4.19 – Normalized wavelength shift as a function of the SRI for a bare LPFG and for LPFGs coated with 58 to 145 nm of ZnO in the RI range from 1.420 to 1.600.

The Figure 4.20 shows a considerable improvement in the sensitivity to the external RI and a better performance is achieved in comparison to the same obtained using the TiO_2 coated LPFGs. In the Figure 4.21 the wider range of RI with high sensitivity need to be highlighted, in particular for lower values than the CRI. Moreover, the combination of several LPFGs with different coatings can lead to cover a full RI range with high sensitivity, in particular from 1.43 to 1.48 where the bare LPFG has a discontinuity. To check the stability/repeatability of the process, several acquisitions were obtained, confirming the effectiveness of this sensing structure.

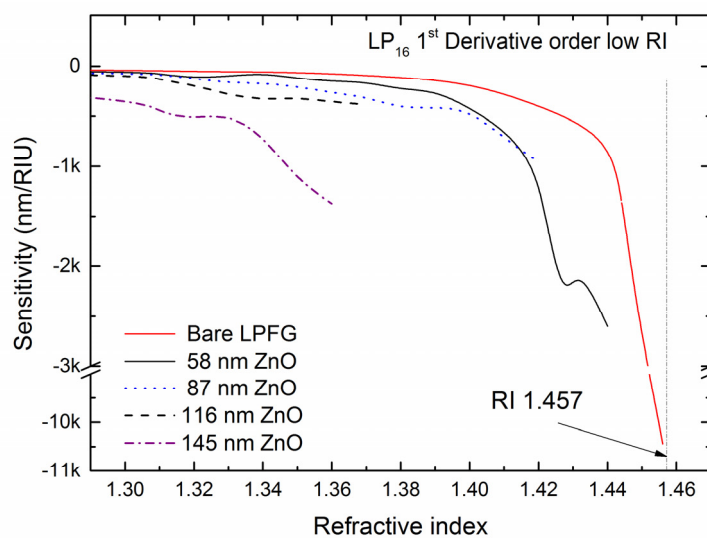


Figure 4.20 – Wavelength sensitivity as a function of the SRI for a bare LPFG and for LPFGs coated with 58 to 145 nm of ZnO in the RI range of 1.300 to 1.460.

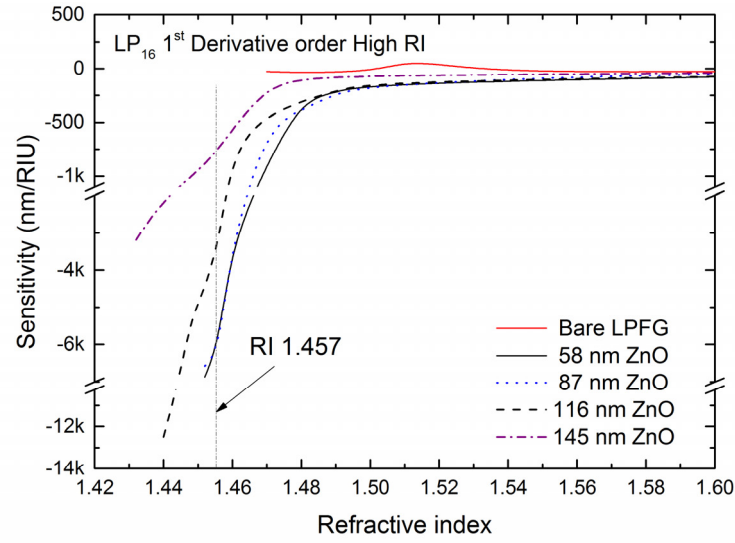


Figure 4.21 – Wavelength sensitivity as a function of the SRI for a bare LPFG and for LPFGs coated with 58 to 145 nm of ZnO in the RI range of 1.420 to 1.600.

The spectral resolution R is calculated considering the values obtained from two measurement associated with two different values of the external RI, obtained from the following expression [161]:

$$R = \frac{\sigma}{S_{RI}} = \frac{\delta n}{\delta \lambda} \sigma \quad (4.11)$$

where δn is the RI difference, S_{RI} is the sensitivity to RI variations, $\delta \lambda$ is the difference in the wavelength resonant dip and σ is the highest standard deviation of two steps.

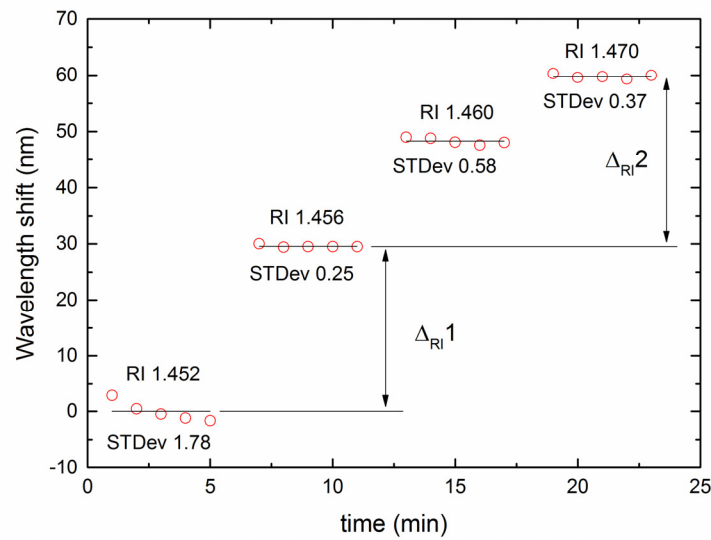


Figure 4.22 – Normalized wavelength shift of the dip of the LPFG when the SRI undertakes step variations.

From the data shown in Figure 4.22 a spectral resolution better than 2.4×10^{-4} was calculated in the RI range of 1.452 to 1.456.

The sensitivity to the SRI manifests also as a change in the minimum of the transmission value of the attenuation band, as can be seen in Figure 4.23 for ZnO films with thicknesses from 0 to 116 nm.

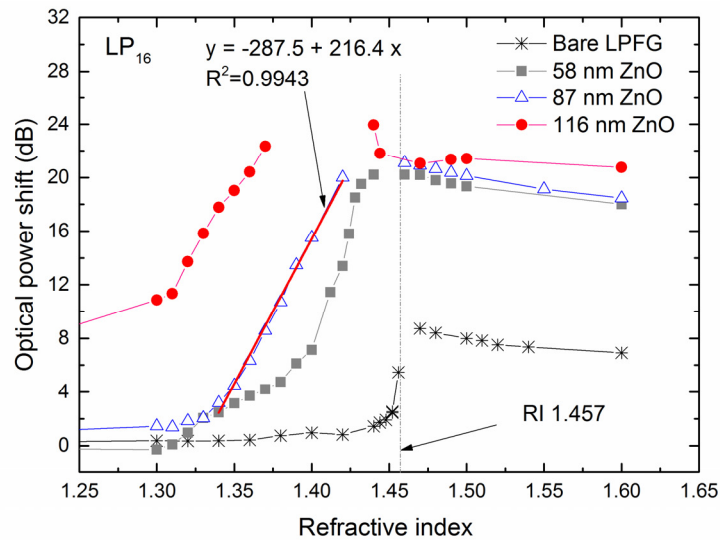


Figure 4.23 – Optical power shift of the LP_{16} mode for several surrounding RI values in the range from 1.300 to 1.600 with a comparison of the bare LPFG and LPFGs with ZnO coatings of 58, 87 and 116 nm thick. The 87 nm thick ZnO coating is with a linear fit in the RI range from 1.340 to 1.420.

The behaviour is similar to the same with TiO_2 coatings in Figure 4.16. For the particular case of 87 nm coated LPFG the attenuation variation with RI lower than the CRI presents a good linear behaviour. Therefore, this coated LPFG could be used as an intensity sensor in a wide range of RI, from 1.340 to 1.420, with high sensitivity, 216.4 dB/RIU, and linearity ($R^2=0.994$). As intensity sensor a RI resolution better than 1.55×10^{-3} was calculated.

4.4 Conclusion

Optical fibre sensors based on coated long period fibre gratings were studied and enhanced results were achieved improving the sensitivity and the range of RI operation. Two distinct metal oxides, TiO_2 and ZnO with different fabrication methods were discussed in this section with high sensitivity to the external medium covering a wide range of refractive indices.

The study to optimize the wavelength sensitivity to the external medium of TiO_2 coated LPFGs was performed by varying the thickness of the films between 10 and 80 nm. The systematic measurement

of the transmission spectrum allowed the calculation of the wavelength sensitivity as a function of the film thickness and of the SRI medium in the 1.300 to 1.600 RI range. The TiO_2 coated LPFGs presents an improved wavelength sensitivity in the 1.300 to 1.400 RI range, thus adding an extra degree of freedom to design LPFG sensors able to analyse aqueous and organic samples or to monitor biological processes. In the region above the CRI, in particular in the 1.460 to 1.480 RI region, the TiO_2 coating also enables LPFG to be used as refractometer of liquid mixtures, for example of mineral or edible oils.

Measurement of the transmission spectrum of LPFGs coated with ZnO allowed the calculation of the wavelength and attenuation sensitivity as a function of the film thickness (from 29 to 145 nm) and of the SRI medium in the 1.300 to 1.600 RI range. An improved wavelength and attenuation sensitivities in the 1.320 to 1.360 and in the 1.350 to 1.420 RI ranges, respectively, was achieved, thus adding an extra degree of freedom to design LPFG sensors able to analyse liquid organic compounds. In the region above the CRI, in particular from 1.450 to 1.470 RI, the ZnO coating enables LPFGs to be used as refractometer of liquid mixtures, for example mineral or edible oils.

These two works provide a detailed and systematic experimental results about coated LPFG with two kind of materials which opens the possibility of tuning the optical response of LPFGs to be used in a wide range of possibilities in external mediums with RI.

In both cases the sensitivity to SRI values from 1.300 to 1.400 was considerable improved, a region typical of certain chemical and biological systems where a bare LPFG is useless. This study is important for further development of new applications.

Chapter 5

Gas Sensing Spectroscopy

The detection of gases (and vapours) is a rather important topic in human health and in the safety of people and property. The typical electric sensing devices are simple and robust but in high temperature environments or where high risk of explosion exists they cannot be used. Fibre optic sensing devices could be an alternative. This chapter intends to introduce a study with a set of sensing devices to measure the concentration of different gases.

5.1 Introduction

One of the most effective ways to optically detect gases (and vapours) is by using its optical absorption characteristics. Gases and vapours have well defined optical absorption spectral bands which can be used as a fingertip for their identification. These absorption bands can be used to identify and quantify the components of the gas medium with high resolution through the direct light/analyte interaction. The need of high power lasers at specific wavelengths make these systems expensive. In addition, the length of interaction should be large enough to improve the signal-to-noise ratio to a value compatible with the desirable performance, but this approach causes alignment issues even when optical fibres are used.

Simple methods can be applied to the detection of gases and vapours, in spite of lower resolutions and in some cases, low selectivity. Some solutions are presented in this chapter using small and reliable devices in optical fibres. In following sections are presented three different configurations based on: i) a single Fabry-Perot interferometer (FPI), ii) a fibre Bragg grating (FBG) and iii) a long period fibre grating (LPFG). In single Fabry-Perot interferometers the light interacts directly with the gas medium changing the spectral characteristics. In the FBG configuration, a metal coating absorbs hydrogen, which induces strain to the fibre, therefore changing the Bragg wavelength peak position. The LPFG configuration consist on the change of the evanescent field spectral properties when the LPFG covered with a specific coating is in contact with the gas.

5.2 Fabry-Perot Based Interferometry Applied to Gas Detection

5.2.1 The Working Principle

Fabry-Perot interferometer is commonly used as a high-resolution optical spectrometer [162]. It is based on the interference of multiple Fresnel reflection of plane waves at two separated highly parallel mirrors as described in Figure 5.1. The interface between two different mediums can act as a partly transparent mirror and reflecting a small amount of the incident light at each interaction. With appropriate configurations they can be applied to optical fibre sensing devices [17]. In this case, typical FPIs can be classified in two types: extrinsic when the cavity is external to the fibre and intrinsic when the cavity is embedded within the fibre. The medium between the mirrors can be air [163], polymers [164] or water [165] depending on the application. Low finesse fibre FPI are commonly used as optical sensors for measurements of physical parameters such as strain, temperature, refractive index or pressure [166-168].

The output optical signal is given by the interference of the transmitted and reflected components, T_m and R_m , respectively.

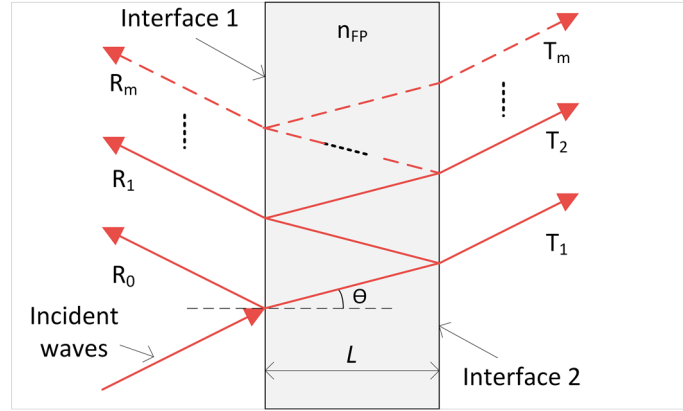


Figure 5.1 – Scheme of the Fabry-Perot interferometer principle.

The transmitted and reflected power that comes out from the FPI can be obtained by assuming that none of the incident energy is absorbed. In this case the flux density of the incoming wave I_i should be equal to the sum of the flux density reflected (I_r) and transmitted (I_t) from the cavity. So $I_i = I_r + I_t$ and the total power reflectivity R_{FP} and transmissivity T_{FP} of the FPI are given by equation (5.1) and equation (5.2), respectively [169, 170];

$$R_{FP} = \frac{I_r}{I_i} = \frac{F \sin^2(\phi/2)}{1 + F \sin^2(\phi/2)} \quad (5.1)$$

$$T_{FP} = \frac{I_t}{I_i} = \frac{1}{1 + F \sin^2(\phi/2)} \quad (5.2)$$

where $\phi = 2\pi OP / \lambda$ is the phase delay, caused by the internal reflections in the cavity, OP is the optical path length difference within the cavity given by $OP = nL \cos \theta$ and F is the finesse coefficient of the interferometric channelled spectrum:

$$F = \left(\frac{2R_{FP}}{1 - R_{FP}^2} \right)^2 \quad (5.3)$$

The length L of the FP cavity can be obtained by analysing the output spectrum when the refractive index of the medium is constant [171].

$$L = \frac{\lambda_{m1} \lambda_{m2}}{2n_{FP} |\lambda_{m1} - \lambda_{m2}|} \quad (5.4)$$

where λ_{m1} and λ_{m2} are the peak wavelengths corresponding to the maximum of the m^{th} adjacent fringes of the FPI and n_{FP} is the refractive index of the cavity.

5.2.2 Extrinsic Fabry-Perot Cavity

One simple way to illustrate the FPI with single mode optical fibres is to use a cavity between two aligned fibre connectors through a sleeve as shown in Figure 5.2.

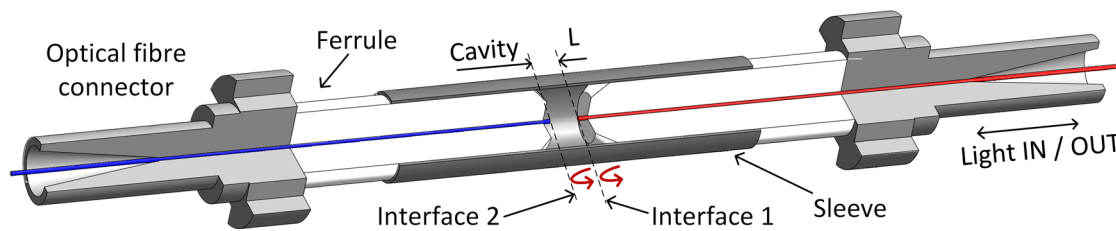


Figure 5.2 – Optical fibre Fabry-Perot cavity created using two ferrules (connectors FC/PC from a commercial patch cord) and a sleeve.

The Figure 5.3-(a) shows the reflected spectra for three low finesse FP cavities with different lengths obtained in a sealed chamber in vacuum (continuous lines) and at 100 kPa of nitrogen (N_2) (dashed lines). The number of fringes in the same wavelength interval depends on the length L which can be calculated using equation (5.4) with the values $L_1 = 68 \mu\text{m}$, $L_2 = 126 \mu\text{m}$ and $L_3 = 262 \mu\text{m}$ assuming the refractive index of 1.000. Smaller the length higher the fringe period and amplitude as expected. One fringe of each spectra was monitored while the N_2 pressure was increased up to 480 kPa and the wavelength sensitivity is shown in Figure 5.3-(b).

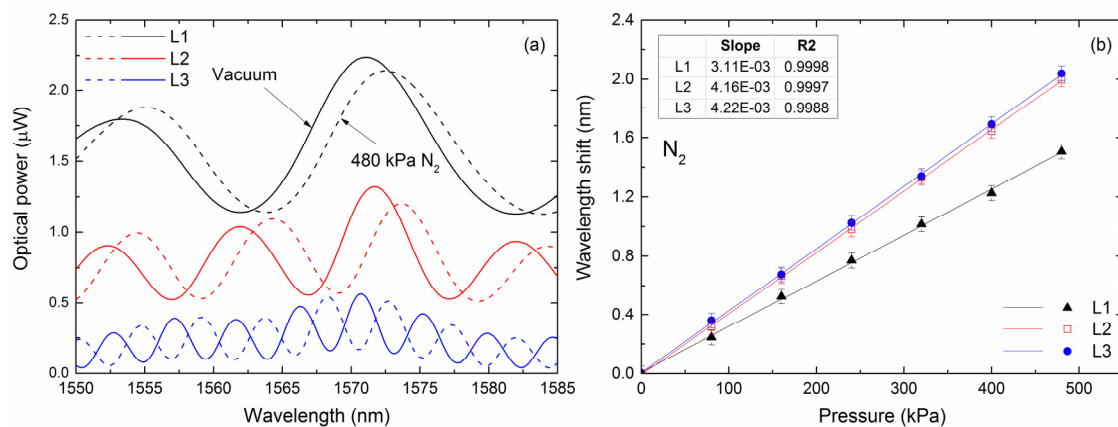


Figure 5.3 – Optical behaviour using different cavity lengths, $L_1=68.4 \mu\text{m}$, $L_2=126.7 \mu\text{m}$ and $L_3=262.0 \mu\text{m}$: (a) Spectrum variations of the cavities at 0 and 480 kPa; (b) wavelength sensitivity to N_2 for pressures up to 480 kPa.

The sensitivity depends on the optical path and for the smaller cavity length the sensitivity is lower as observed. The effect of the gas pressure on the cavity length should be very small and can be neglected. On the other side the refractive index of the cavity changes and affects the spectral response. This is one of the processes that can be used to measure the refractive index of gases [172].

The same structure was applied to different gas mixtures using a cavity with 125.8 μm length and the results are depicted in Figure 5.4.

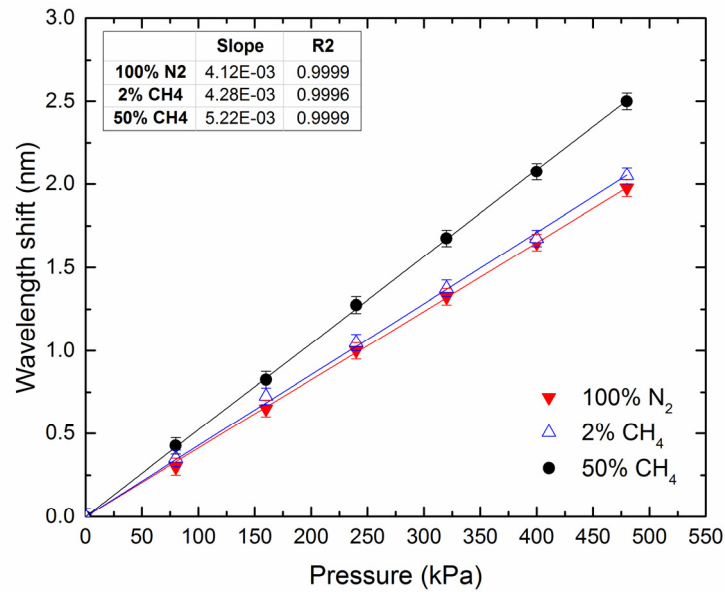


Figure 5.4 – Wavelength sensitivity to 100 % of N_2 , 2 % of CH_4 and 50% of CH_4 for pressures up to 480 kPa using a cavity with 125.8 μm length.

Despite the sensitivity of the FP to the refractive index is constant, the sensitivity to the pressure depends on the gas and, in theory, can be used to estimate the gas refractive index at each pressure value. It is known that the gaseous RI is dependent of the pressure, temperature and composition [173]. From the experimental data and for the same applied pressure the wavelength shift is slightly higher when 2% of methane (CH_4) is added to the final N_2 composition. A more evident situation is when the concentrations of CH_4 and N_2 are 50%. The sensitivity changes from 4.15 nm/MPa with N_2 atmosphere to 5.20 nm/MPa by adding 50% of CH_4 . This is in agreement with the RI values for N_2 (1.0002911 at 546 nm) and CH_4 (1.0004478 at 529 nm) [174].

5.2.3 Simultaneous Measurement of Partial Pressure of O₂ and CO₂ with a Hybrid Interferometer

Low finesse fibre FP interferometers are commonly used as optical sensors for measurements of physical parameters such as strain, temperature, refractive index, pressure, and others [166-168]. Several authors have applied the chemical etching technique to create optical fibre sensors based on FP cavities to measure refractive index in liquids with temperature displacement [167], as well as strain and temperature [168]. Simultaneous measurements of the partial pressures in a mixture of two gases, oxygen (O₂) and carbon dioxide (CO₂), is reported in this section based on hybrid interferometer which consists of a low finesse intrinsic FP cavity and a modal interferometer (M).

– Experimental Setup

The intrinsic FP cavity was created by splicing an SMF with a graded index multimode fibre (GIF) section with 62.5 µm core diameter (GIF625) that is approximately 150 µm long. The fibre tip was then chemically etched by immersion in a solution of hydrofluoric acid (HF) at 48 % during 8 min, creating a ~83 µm long concavity in the GIF section. The fibre with the concavity was then spliced to a cleaved silica tube section 125 µm in diameter and 1.3 mm in length, and a centred hole with 20 µm of diameter. This last fusion was done with the splicing machine on a manual mode by a controlled arc discharge ($I = 32$ mA, $t = 550$ ms) being monitored in real time with an optical spectrum analyser (OSA). The experimental setup used for characterization of the sensor is shown in Figure 5.5 together with the image of the described sensing device obtained by an optical microscope.

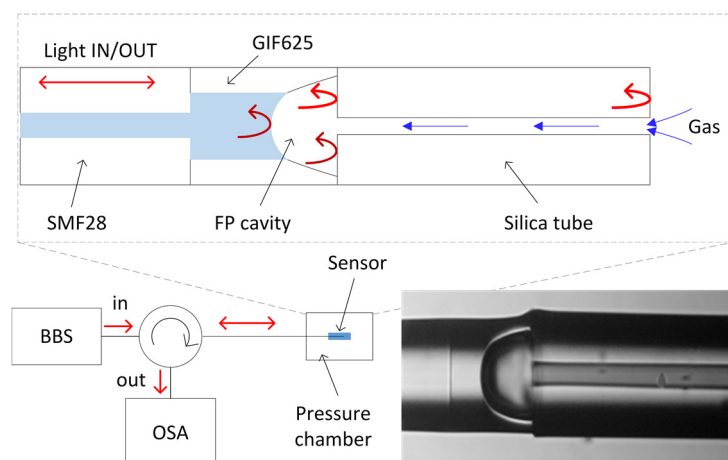


Figure 5.5 – Experimental setup used to characterize the sensor with different gaseous environment.

The experimental setup consisted of an optical broadband source (C+L bands) centred at 1550 nm wavelength with a bandwidth of 100 nm. The optical circulator was used to redirect the reflected spectrum towards the OSA (ADVANTEST Q8384) with a resolution of 10 pm to observe the spectral response of the sensing tip. The FP interference is produced with the two waves indicated by the arrows in Figure 5.5.

All the tests were performed in a stainless steel vacuum chamber where two different gases can be mixed to allow variation of the concentration by changing the partial pressures of O_2 and CO_2 (Linde Portugal, Lda) both with purity levels of 99.995 % which were monitored with a pressure gauge (model KELLY ECO 1). The chamber is connected to a primary vacuum pump to remove the air inside, clean all the pipes in the system, maintaining the purity of the atmosphere. The fibres were placed inside the chamber with a feedthrough that is used to isolate the sensing device from atmosphere medium.

– Results and Discussion

The spectrum obtained when the sensor is placed in CO_2 environment at the atmospheric pressure is depicted in Figure 5.6-(a).

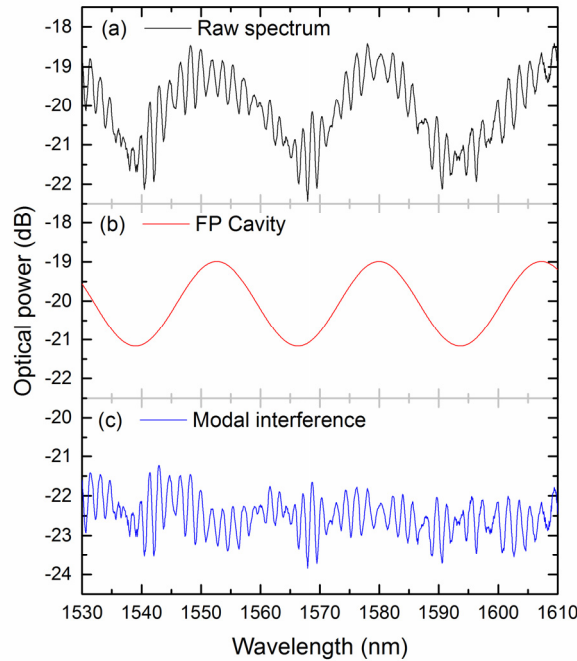


Figure 5.6 – (a) Spectrum of the light returned from the sensing device in a 100% CO_2 atmosphere at 100 kPa pressure; (b) and (c) corresponds to the Fabry-Perot and the modal interference components, respectively.

The result is a superposition of two different interferometric components, one created in the FP cavity (b) and the other in the silica tube (c). The low finesse FP cavity spectrum was obtained by adjusting the original spectrum to a sine function while the mode interference spectrum was obtained by subtracting the original curve to the sine function which appears to be very stable along time for different pressure measurements

The sensing tip was then characterized inside a pressure chamber with two different gases, O_2 and CO_2 . For each one the pressure was changed from 0 to 600 kPa with steps of 100 kPa.

The results are presented in Figure 5.7-(a) and Figure 5.7-(b) considering both gases studied and the two interference patterns generated at the sensing tip, showing that in both cases a wavelength shift arises as function of the gas pressure. Figure 5.7-(a) shows the results obtained with O_2 , while Figure 5.7-(b) shows the results obtained with CO_2 . The wavelength shift observed when the gas pressure increases is due to the change of the refractive index, which depends on the gas density and the compressibility factor of each gas considering the same wavelength. The error bars corresponds to the same size of the symbols and are not shown. From the literature, the refractive index value at atmospheric pressures for O_2 is 1.000274 (at 502 nm) while for CO_2 is 1.000452 (at 509 nm) [174]. The wavelength shift $\Delta\lambda$ was obtained by measuring the centre of the FWHM of the same fringe at 1550 nm for each induced pressure.

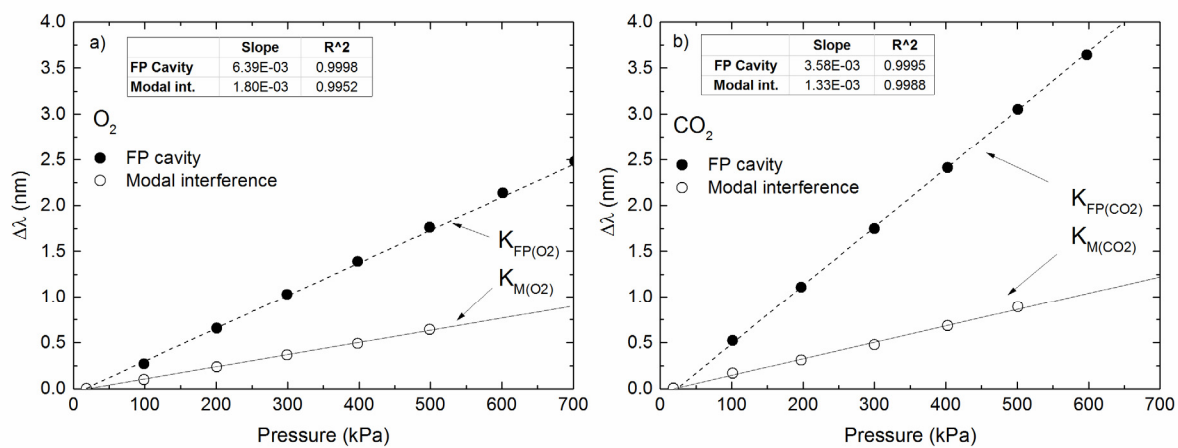


Figure 5.7 – Wavelength shift obtained with pressure variation for both interferometers using: (a) pure O_2 and (b) pure CO_2 .

Since the sensing tip was characterized for each gas independently, and due to the distinct linear behaviour of the spectral shifts observed for the different pressures applied, it is possible to use this

sensing device for simultaneous measurements of the two gases. Therefore, the matrix method can be applied regarding the discrimination of the two parameters [175, 176].

In the specific case of the gas sensor with two different partial pressures of O_2 and CO_2 the associated wavelength variations can be written as

$$\Delta\lambda_i = K_{O_2}^i \Delta O_2 + K_{CO_2}^i \Delta CO_2; i = FP, M \quad (5.5)$$

where $K_{O_2}^i$ and $K_{CO_2}^i$ are the sensitivity coefficients to O_2 and CO_2 for the i interferometer, respectively. The ideal situation occurs when each wavelength depends only of one parameter, O_2 or CO_2 . Since this is not the case, the non-ideal situation takes form through the equation (5.6) where both wavelengths depend on the two measurands.

$$\begin{bmatrix} \Delta P_{CO_2} \\ \Delta P_{O_2} \end{bmatrix} = \frac{1}{D} \begin{bmatrix} K_{O_2}^{FP} & -K_{O_2}^M \\ -K_{CO_2}^{FP} & K_{CO_2}^M \end{bmatrix} \begin{bmatrix} \Delta\lambda_M \\ \Delta\lambda_{FP} \end{bmatrix} \quad (5.6)$$

The K_j^i are the sensitivities achieved for both interferometers, considering $i = FP, M$ and $j = O_2, CO_2$, and $D = (K_{O_2}^{FP} K_{CO_2}^M) - (K_{CO_2}^{FP} K_{O_2}^M)$ is the matrix determinant. Introducing the above parameters the equation (5.7) is obtained.

$$\begin{bmatrix} \Delta P_{CO_2} \\ \Delta P_{O_2} \end{bmatrix} = \frac{1}{2.05} \begin{bmatrix} 6.39 & -1.80 \\ -3.58 & 1.33 \end{bmatrix} \begin{bmatrix} \Delta\lambda_M \\ \Delta\lambda_{FP} \end{bmatrix} \quad (5.7)$$

The concept was applied with the sensor inserted in an environment of O_2 and CO_2 mixture and the concentration, ΔC_j , of each gas in the mixture was changed from 0 to 100 % v/v with a constant pressure of 480 kPa. The concentration of O_2 and CO_2 in the mixture is given by equations (5.8).

$$\Delta C_{CO_2} = \frac{\Delta P_{CO_2}}{\Delta P_T} \times 100 \quad \Delta C_{O_2} = \frac{\Delta P_{O_2}}{\Delta P_T} \times 100 \quad (5.8)$$

The results corresponding to the wavelength shift observed for the different concentrations are represented in Figure 5.8-(a) in function of time. The concentration of O_2 was changed and monitored in the first period of 50 minutes, while the concentration of CO_2 was changed and monitored in the second period of 50 minutes.

The matrix method was applied to monitor the concentration in the mixture with equation (5.9) by using the K values of the pure gases (Figure 5.7).

$$\begin{bmatrix} \Delta C_{CO_2} \\ \Delta C_{O_2} \end{bmatrix} = \frac{1}{2.05} \begin{bmatrix} 6.39 & -1.80 \\ -3.58 & 1.33 \end{bmatrix} \begin{bmatrix} \Delta \lambda_{M/C} \\ \Delta \lambda_{FP/C} \end{bmatrix} \quad (5.9)$$

The wavelength variations observed with both interferometers for the mixture is presented in Figure 5.8-(a).

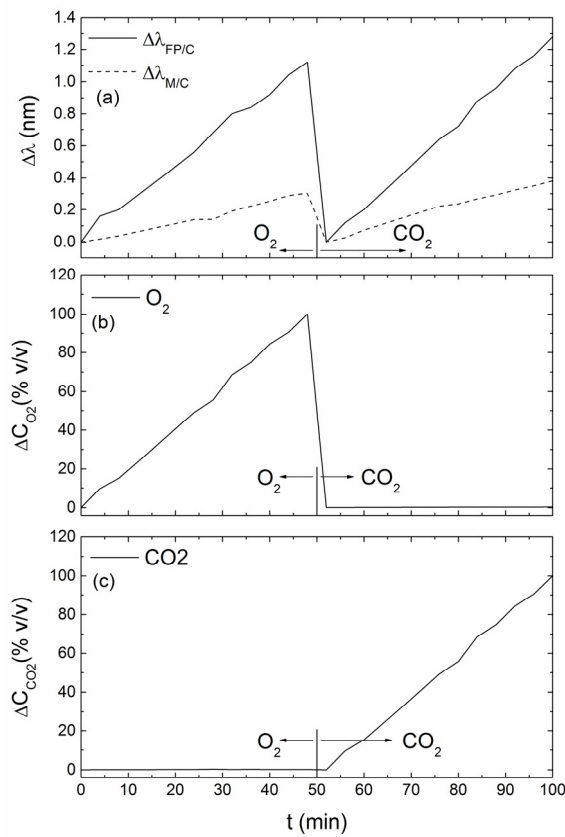


Figure 5.8 – Time response of the sensor obtained with a mixture of O_2 and CO_2 : (a) wavelength shift of both cavities spectra for the gases; (b) result for O_2 detection; (c) result for CO_2 detection.

Each gas can be monitored independently in the same mixture with the same sensing device, as demonstrated with the results given in Figure 5.8-(b) and Figure 5.8-(c), obtained from equation (5.9). In Figure 5.8-(b), the presence of O_2 is monitored in the first period where the signal grows with the concentration of O_2 , while in the second period, the signal is close to zero. Figure 5.8-(c) shows the opposite behaviour, in the first period the signal is close to zero, while in the second period the signal grows with the concentration of CO_2 . The performance of this simultaneous measurement

configuration was experimentally determined by undertaking O_2 (or CO_2) partial pressure variations in a range from 0 to 600 kPa at a fixed CO_2 (or O_2) partial pressure (300 kPa). The partial pressure measurement deviation achieved with O_2 and CO_2 were found to be 20.1 Pa and 48.7 Pa, respectively.

5.3 Fibre Optic Hydrogen Sensor based on an Etched FBG Coated with Palladium

One of the most wanted energy sources is based on pure hydrogen (H_2) because when it burns in air reacts with oxygen releasing only energy and water making it green fuel, unlike the fossil fuels giving off mostly hydrocarbons and carbon dioxide, thus contributing to the global warming.

Besides the well-known fuel cells, H_2 has been used in many chemical processes in a wide range of fields such as aerospace, aircraft and automotive industries. It can be produced from water by splitting the molecule into hydrogen and oxygen mostly by electrolytic or thermochemical processes. Other methods include biomass gasification or photo biological using microorganisms such as green microalgae.

5.3.1 Hydrogen Properties

Hydrogen in the liquid state is extremely volatile and flammable and can be explosive in a wide range of gaseous concentrations at room temperature and pressure [97] from 4 % v/v (lower explosive limit) to 75 % v/v (higher explosive limit).

Therefore, H_2 detection is extremely important and hard to implement in hazard environments where the usual electrical sensing devices are impossible to be used due to the risk of explosion.

Hydrogen fibre sensors can overcome this drawback allowing remote sensing in locations where the risk of a leak is an issue, e.g. the containers and pipelines. Several distinct working principles have been developed, such as interferometric [177], intensity [178] and grating-based systems [179], which became a growing researching area [180].

One of the best ways to detect H_2 with high selectivity is by using palladium (Pd) as an active medium. It is capable to absorb H_2 up to 900 times its own volume due to the high and selective

affinity [181]. When Pd is exposed to H_2 , its molecules are dissociated into two hydrogen atoms in the Pd surface with a high efficiency rate. The hydrogen atoms are rapidly diffused into the Pd thin film, converting it into palladium hydride (Pd_xH_{1-x}). The hydration of Pd leads to crystallographic modifications giving rise to an increment of the lattice parameters, changing the mechanical, electrical and optical properties [182].

The Pd metal becomes saturated with H_2 when the H/Pd atomic ratio is about 0.6 commonly represented by $PdH_{0.6}$ depending on the temperature and the gas pressure. In this range the face-centred cubic (fcc) lattice changes between two distinct phases α and β of the phase diagram or assuming both phases $\alpha + \beta$ [183]. The $\alpha - \beta$ transition on pure Pd in the presence of H_2 leads to fatal fractures on the thin film coating. The number of fractures increase with high levels of humidity at the surface due to the higher hydrogen concentration at the Pd surface.

Up to now, some attempts to avoid this issue have been studied mostly by alloying Pd with other metals as Ni [180] which affects the sensitivity. Recent advances have been developed using the highly sensitive plasmonic effect [184], in particular using nanowire waveguides [185], with Mach-Zehnder interferometers [186] or using microfibre knots [187].

The H_2 sensor in this work has interesting properties and characteristics thought is fabricated in theoretical and experimentally well known material and techniques. It is based on a robust and reliable strain sensor coated with pure Pd, and is protected against moisture by a cheap, robust and chemical inert Teflon over coat.

Recent works have been reported using Pd and Pd alloys. Microfibre Bragg gratings with diameter of 3.3 μm coated with Pd layers [188] could reach sensitivities of 216 pm/%v/v, approximately 10 times higher than the obtained in the present work due to the difference in the fibre diameter. However, the fragility of such structure would make it difficult to handle. Several configurations of fibre optic based H_2 sensors using either Pd-alloys have been reported recently showing a reduction in the sensitivity compared to the Pd [189]. The works proposed by Lee [190] or by Dai [191] have shown that the Pd-Ni alloys can improve the sensitivity to H_2 for very low concentrations around 0.01% but for higher concentrations pure Pd coatings still present better performance even when using an FBG with 17 μm diameter. Nanocomposites of Pd/SiO₂ and AuPd/SiO₂ have been reported as a solution for H_2 sensing using the well-known interaction with the fibre evanescent field where the H_2 adsorption leads to spectral modifications of the silica matrix [192].

The sensing concept here studied is based on monitoring the optical response of FBGs due to the mechanical forces applied in the fibre during the physical expansion. FBGs are very sensitive to strain variations which changes the grating period and the peak position, consequently is sensitive to temperature variations due to the thermal expansion of the silica. When the FBG is coated with a Pd layer a red shift is observed when the hydrogen adsorption process occurs.

The sensing scheme consists of two inline FBGs separated by 1 cm, working in reflection. The cladding around the two FBGs was reduced by chemical etching being one coated with a palladium layer using an electron beam evaporator in order to sense hydrogen below the lower explosive limit. This configuration was explored with the objective to eliminate temperature cross-sensitivity. Furthermore, specific design on the sensing device has been developed in order to reduce the level of degradation of the Pd film. A thorough analysis is performed regarding the changes in specific parameters in order to optimize the sensitivity to H_2 . Studies concerning the humidity effect on the palladium hydride structure are presented as a cheap solution to minimize this drawback.

5.3.2 Experimental Procedures

The sensing device is based on two in-line FBGs with 60% reflectivity centred at the standard C-band telecom window (1530nm-1565nm) inscribed in a hydrogenated standard communication single mode fibre (SMF28e, Corning), following the procedure described in section 3.1.1 with a UV laser and a phase mask both with the same length and separation of 10 mm. Since the gratings have a well-known sensitivity to thermal variations of $\sim 11 \text{ pm}/^\circ\text{C}$, the two in line FBGs were placed in a system, one for sensing and the other for calibration. In two different systems the fibre cladding was reduced down to $80 \mu\text{m}$ and $50 \mu\text{m}$, at 55 % humidity and 22°C during 24 and 34 minutes respectively, following the etching process described in section 3.1.2. The FBG used for temperature compensation was kept uncoated, using a single mask, while the other was coated with 5 nm of titanium (Ti), to improve the adhesion, and with a thick layer of a palladium, both performed with the electron beam evaporator described in section 3.1.3. The sensing structure and the configuration setup are depicted in Figure 5.9 (the inset is a SEM of the etched FBG showing the reduced diameter transition).

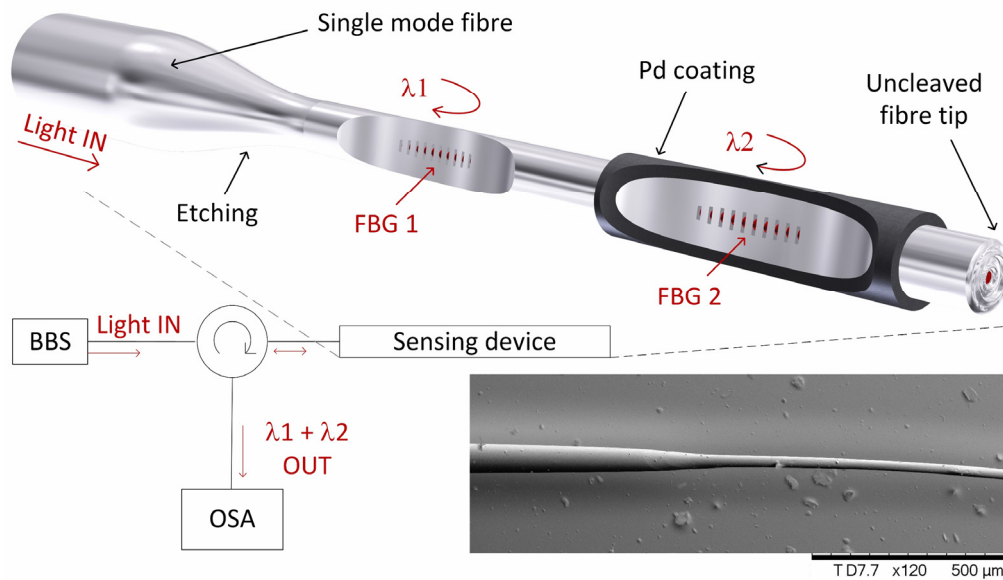


Figure 5.9 – Scheme of the setup used including a broad band optical source, an optical spectrum analyser and an optical fibre sensing device. Inset is a SEM picture of the etched FBG.

The sensing device operates in a reflection configuration and only the bands corresponding to λ_1 and λ_2 , due to the Bragg interferometry at FBG 1 and FBG 2 respectively, should be reflected so the fibre tip is damaged to avoid the Fresnel reflection.

The sensors were interrogated in a reflection using a very stable broadband light source (BBS) to illuminate the sensing device in the telecommunication C-band, an optical circulator and an optical spectrum analyser - OSA (Model ANDO AQ6315A) to measure the reflected signal. For long time stability tests a Braggmeter FS2200 SA (HBM FiberSensing S.A., Portugal) was used providing fast acquisition and processing the FBGs signals in real time.

The reflected signal containing λ_1 and λ_2 , was collected by the OSA and the wavelength shift of FBG 1 was utilized to monitor temperature variations so the wavelength shift of FBG 2 corresponding to the Pd expansion can be compensated to the effects of this parameter.

5.3.3 Results and Discussion

– Effect of the Cladding Diameter on the Sensor Sensitivity

A study of the effect of the cladding thickness on the sensitivity of the sensor was performed. Figure 5.10 shows the results for FBGs with different cladding diameter coated with a 350 nm thick Pd film for a H_2 concentration up to 4% in N_2 . For the thickness of the Pd film the value of 350 nm was chosen because it is known to provide improved sensitivity [193].

It is visible that the small cladding diameter presents the highest shift in the presence of H_2 . However, above 2% of H_2 the thin film coating becomes damaged and the fibre loses some strain. This behaviour was observed for the fibre diameters considered. High concentrations of H_2 lead to the $\alpha-\beta$ transition with high expansion of the film in the cylindrical geometry which will lead to the formation of cracks in the thin film. Up to 2% of H_2 the sensor sensitivity for the FBG with cladding diameter of 50 μm is much higher than the sensitivity for thicker claddings.

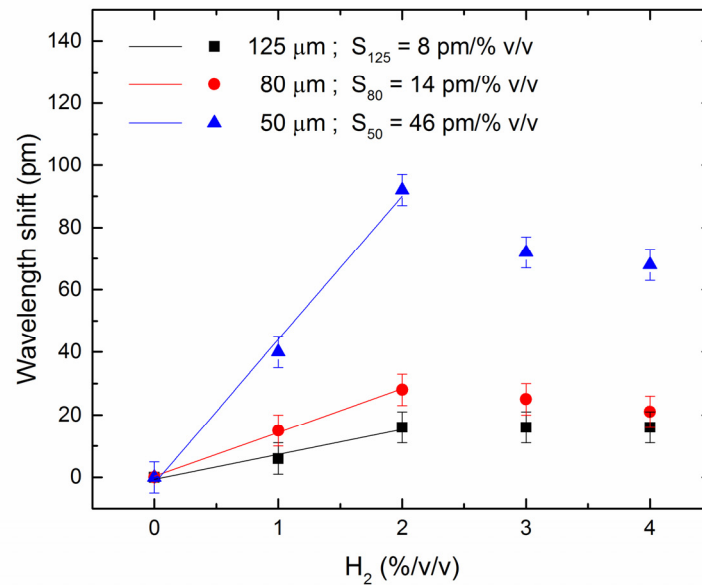


Figure 5.10 – Wavelength shift of the Bragg peak when the H_2 concentration is increased from 0 to 4% considering different fibre diameters.

The cladding reduction improves the sensitivity to H_2 by allowing the silica fibre to expand with less constraints. The 50 μm diameter keeps the shape of the FBG and provides a robust physical structure. Thinner fibre diameters would give better sensitivity results, although a trade must be set

because thinner cladding may lead to the destruction of the coupling conditions affecting the FBG resonance shape.

Figure 5.11 shows the wavelength shift of a FBG sensing device with 50 μm diameter and coated with 10 nm of Ti and 100 nm of Pd at 300 kPa of pressure in contact with different H_2 concentrations using two different sets of gas mixtures (1% H_2 while the other with 4% of H_2 in N_2). The pressure was raised to reduce the concentration deviation. The sensing device presents the same linear behaviour up to 1% H_2 using the two distinct H_2 mixtures while above this value it became saturated for a constant thickness of Pd, meaning that the working point is at the higher limit of the linear $\alpha - \beta$ phase from the phase diagram [183]. When both quantity of Pd and the gas pressure are maintained the transition between the phases is dependent of the H_2 concentration. The same behaviour can be observed in Figure 5.10 for different conditions.

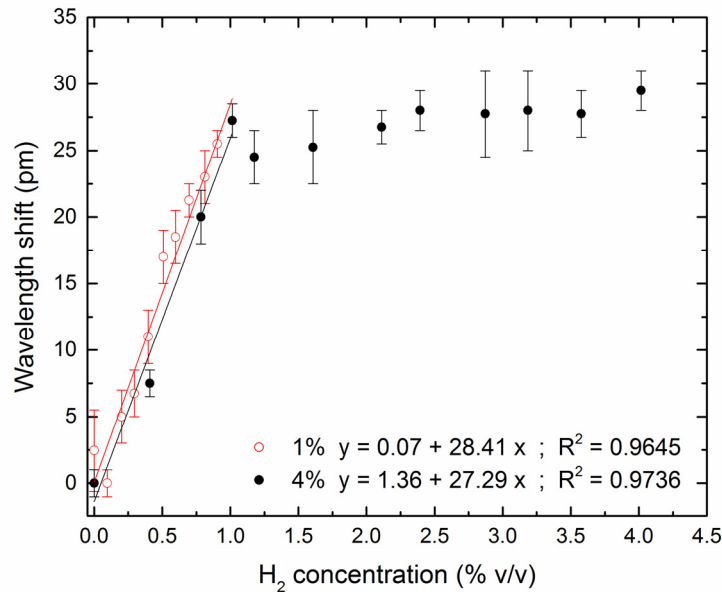


Figure 5.11 – Sensitivity to H_2 using two different gas concentrations: 1% and 4% H_2 (v/v).

– Stability Tests

Several stability tests were performed with cycles between pure N_2 and 1% of H_2 in N_2 with a pressure of 100 kPa to avoid variations along time by changes with the external medium. Two FBGs were inscribed in the same optical fibre as close as possible to allow a better temperature compensation, both etched until 50 μm cladding diameter, one without any coating for temperature measurements and another with 100 nm of Pd. The optical spectrum of both the FBGs are represented

in Figure 5.12 and is visible the wavelength shift on the FBG 2 due to the H_2 atmosphere while the FBG 1 kept the same position. The inset is the temperature calibration of each FBG with and without Pd coating. In spite of the linear thermal expansion coefficient α be $11.6 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ for Pd and $0.55 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ for fused silica [194], the small thickness of the Pd layer on the FBG is not high enough to overlap the silica expansion.

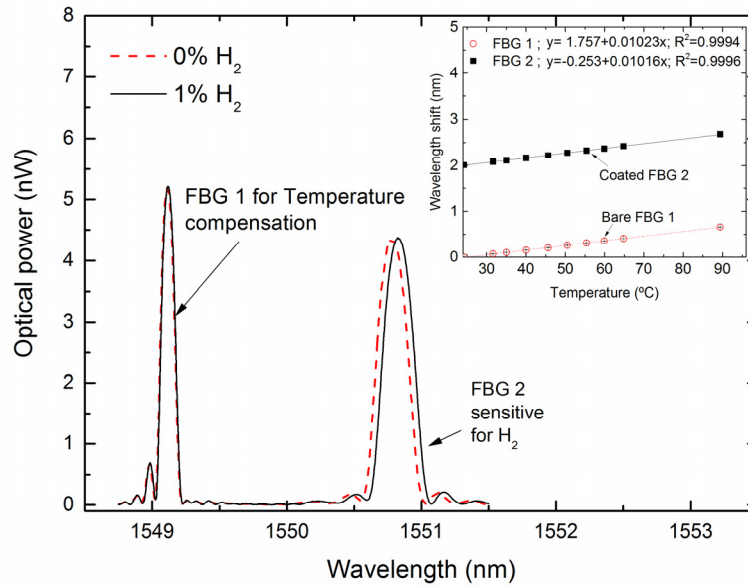


Figure 5.12 – Optical spectrum of both FBGs with 50 μm diameter, uncoated for temperature compensation and coated with 100 nm of Pd for H_2 sensing, for pure N_2 and for 1 % of H_2 ; Inset: temperature calibration of both gratings.

Figure 5.13-(a) presents absorption/desorption cycles. During the first two hours the FBG peak shifts $\sim 8 \text{ pm}$ with a relatively fast response.

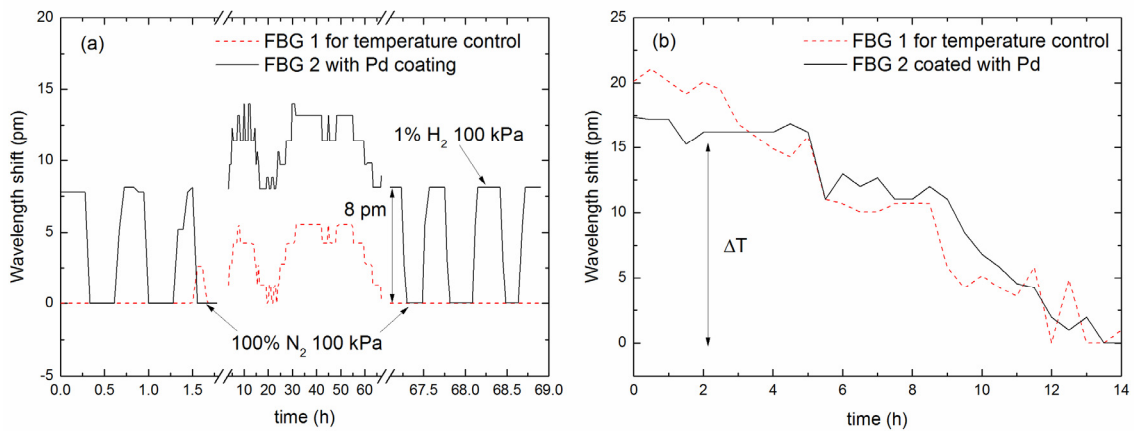


Figure 5.13 – a) Stability results in time with a 50 μm cladding FBG coated with 100 nm of Pd with absorption / desorption cycles of 1% of H_2 in N_2 , up to 70 hours in the H_2 environment; b) thermal variation along time.

The sensor was then kept in hydrogen atmosphere during 60 hours. After this time it was subjected to new absorption / desorption cycles and the same shift of 8 pm is observed which is a sign of a good integrity of the film. The FBGs wavelength variation along 14 hours is shown in Figure 5.13-(b) while the external temperature drops. As expected the temperature variation affects both FBGs in the same way.

According to the study provided by Johansson [183] the partial pressure adsorption of H₂ by the Pd layer depends exponentially on the temperature. At 200 °C the influence of the temperature variation is visibly high while at low temperatures it is much smaller. In addition, temperature variations up to 2°C around 22°C have low influence on the phase transition.

– *Simulation of Hydrogen Sensing with Palladium Coating*

Theoretical simulations of the wavelength shift of the FBG by increasing the H₂ pressure and for several values of the Pd thickness were performed in order to be compared with the experimental results. The model was proposed by Butler et al. in 1988 [181], and define the Bragg wavelength shift as a function of the H₂ partial pressure for specific fibre characteristics:

$$\Delta\lambda_B = 0,026 \times \frac{\sqrt{p}}{K} \times \left[\frac{E_{Pd} \cdot (b^2 - a^2)}{E_{Pd} \cdot (b^2 - a^2) + E_F \cdot a^2} \right] 0,78 \lambda_B \quad (5.10)$$

where a is the fibre diameter ($\sim 50 \mu\text{m}$), $b - a$ is the coating thickness (from 50 to 200 nm), $E_F = 72\text{GPa}$ [195] and $E_{Pd} = 121\text{GPa}$ [196] are the Young modulus of the silica fibre and the palladium, respectively.

The theoretical and experimental results are plotted in Figure 5.14, considering the same parameters. Four sensors are compared with 50 μm cladding diameter FBGs and Pd coating thicknesses from 50 to 200 nm, for pressures from 0 to 700 kPa of 1 % H₂ in N₂.

As expected, high dependence on the fibre diameter and the Pd thickness was found. The experimental results follow the theoretical data with good agreement. Small differences in the chemical etching rate and in the metal coating thickness could originate different sensitivities.

The sensitivity to H₂ increases with the Pd thickness until reaches a breaking point. It is possible to observe that the FBG with 200 nm presents a blue shift after 400 kPa indicating a destruction of the fibre coating. From the experimental results the FBG with 150 nm of Pd presents the highest

sensitivity without coating degradation. For this structure the experimental results indicate that the maximum sensitivity is reached with 150 nm of Pd without the coating degradation.

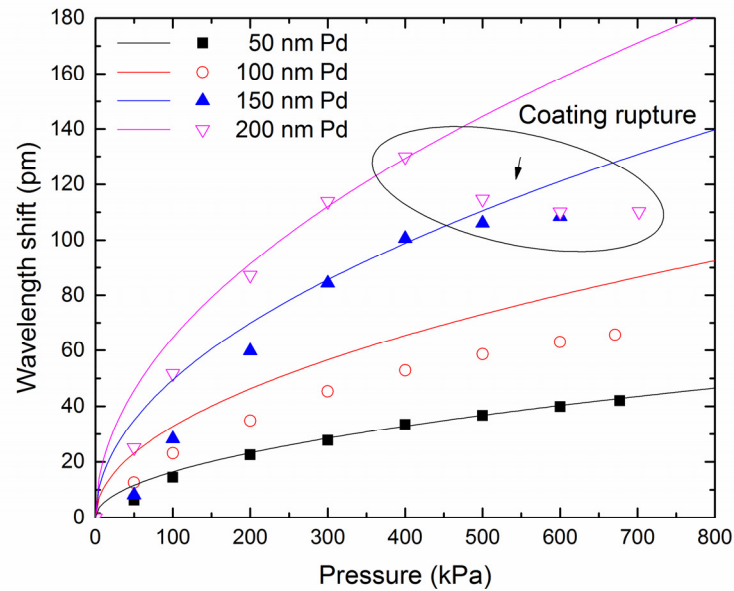


Figure 5.14 – Theoretical (continuous line) and experimental dependence of Bragg wavelength shift with the pressure variation for FBGs with 50 μm cladding diameter and different Pd coating thicknesses.

– Effect of Humidity in the Hydride Component

The humidity issue is one of the most challenging topics addressed in Pd based H_2 sensors. The effect of moisture on the Pd thin film was studied by placing the sensing device coated with 100 nm of Pd inside the vacuum chamber on top of a glass petri-dish full of water 1 mm above the surface in the presence of hydrogen with concentration of 1% in N_2 at atmospheric pressure. This way a high humidity level was created inside the chamber and surrounding the palladium hydride film.

Figure 5.15 shows the results of the tests along time for air and H_2 environment steps. During the first two hours the sensor responds to the H_2 with an environmental low humidity level. The inset in the left side is a picture of the sensor taken after these first cycles showing a pristine coated surface. Afterwards, moisture level was increased due to the presence of water inside the chamber. The coated FBGs were maintained in the same conditions with humidity and 1% of H_2 for the next 70 hours. After that time the atmosphere in the chamber was again subjected to cycles of H_2 , air and vacuum and the sensitivity to H_2 was measured. During this last period the water was removed and after the environment was totally dried the same cycles were performed and the results were the same. The

growing insensitivity of the sensor to H_2 was due to the degradation of the Pd film occurred after the hydride formation in high humidity level environment. The inset on the right side is a picture of the surface after being subjected to high level of moisture. At this point the thin film of Pd became fractured and detached from the silica substrate.

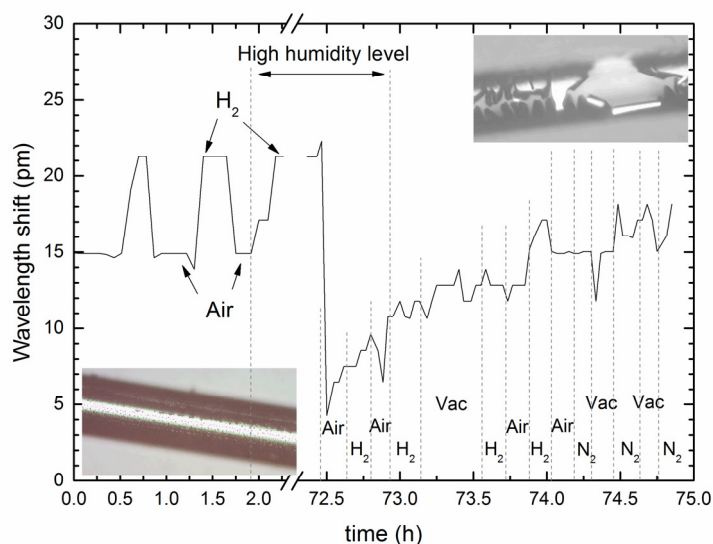


Figure 5.15 – The effect of humidity in the palladium hydride component: time response before and after contact with high humidity level for several cycles of 1% H_2 absorption/desorption. Inset pictures of the fibre before (left-bottom) and after (right-top) the hydrogen exposition in the humidity environment.

To verify the quality of the thin film, the surface of a similar sensing device was analysed by Energy-dispersive X-ray spectroscopy (EDS) technique after the degradation has started. Figure 5.16 presents the energy spectra considering two different regions of the fibre, while the inset is a SEM image of the surface containing those two regions (A and B). Region A is an undamaged coating section (red curve) while region B is a damaged coating section (black curve). From the spectra it can be conclude that region B is totally uncoated, with the lines corresponding to ^{14}Si and 8O well defined. The spectra of region A possesses four lines indicating the presence of ^{46}Pd along with the ^{14}Si and 8O lines.

In order to address the moisture constrain the coated sensing device was protected between two thin polytetrafluoroethylene (PTFE, known as Teflon) membranes with 20 μm thickness fixed by two metal plates to avoid leaks (Figure 5.17). The Teflon layer was used to decrease the effect of H_2O on the Pd coating layer allowing the diffusion of H_2 to the Pd surface. It was choose from a set of other materials as polydimethylsiloxane (PDMS) and Low Density Polyethylene (LDPE) due to its permeability coefficient P, which is low for water vapor (33.3 Barrer) while is maintained reasonable

5.3 - Fibre Optic Hydrogen Sensor based on an Etched FBG Coated with Palladium

high for H_2 (9.3 Barrer) (Goodfellow, Inc), as well as due to its mechanical strength, chemical properties and easiness to manipulate ($1 \text{ Barrer} = 10^{-10} (\text{cm}^3 (\text{STP}) \text{ cm}) / (\text{cm}^2 \text{ s cmHg})$).

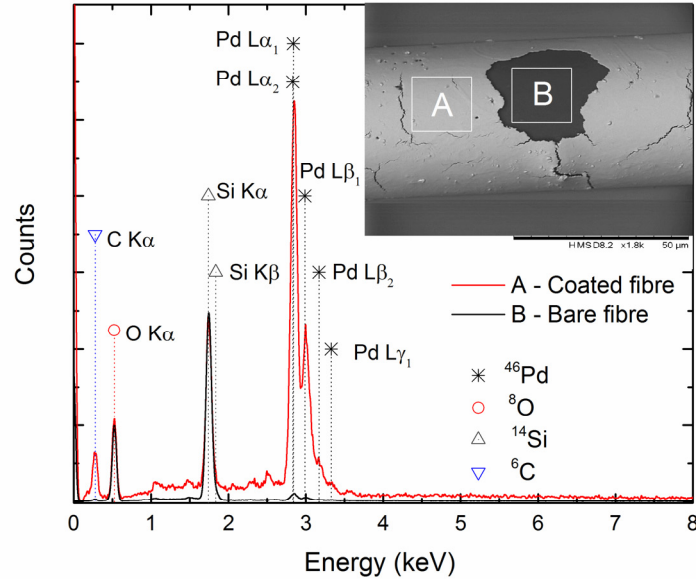


Figure 5.16 – EDS spectra of two different surfaces: silica uncoated fibre and the Pd coating. Inset is the SEM image of the fibre regions considered in the chemical analysis.

The sensor to be tested was coated with 150 nm of Pd and designed with an overall cladding diameter of 50 μm . The H_2 sensitivity of $\sim 20 \text{ pm}/\%v/v$ achieved with this sensing device at 100 kPa of pressure is in agreement with the prediction from simulations and previous measurements (Figure 5.14).

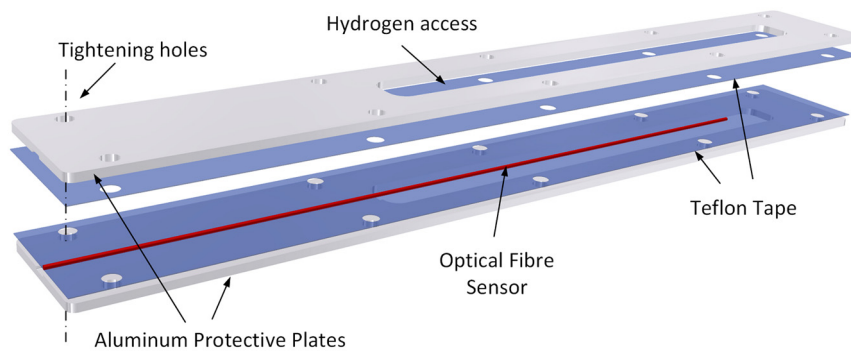


Figure 5.17 – Scheme of the protective structure of the sensing device to prevent the humidity damaging.

Figure 5.18-(a) shows several cycles between pure N_2 and 1% H_2 before the high humidity level exposition. The sensing device was then protected with the Teflon layers and placed in the same high

humidity level as before during 70 hours. The results after this process are presented in Figure 5.18-(b). Initially, the chamber was filled with air and after 10 minutes it was flushed with pure N_2 which has slightly lowered the temperature and it was observed until 20 minutes. After this the atmosphere was changed between pure N_2 and 1% H_2 at an atmospheric pressure. The temperature was reduced when the N_2 expanded which cool down the whole chamber but after this point expected variations are observed and match the temperature of the entrance of the gases.

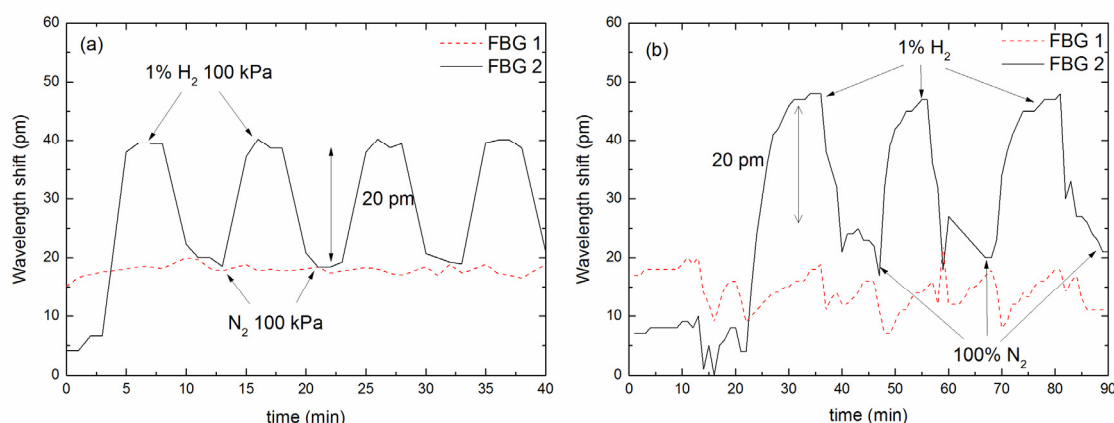


Figure 5.18 – Sensitivity results of the sensing head to H_2 a) before the high humidity level exposition and b) after 72 hours in a high humidity environment with the sensor protected with Teflon tape.

The time response of the sensing device related to the H_2 absorption process by the Pd coating is around 2 minutes from Figure 5.18-(a). When using Teflon it is observed in Fig. 10-b) that the time response rises up to 10 minutes which can be justified by the low diffusion coefficient of the hydrogen molecules through Teflon. Although this drawback, the sensitivity to 1% of H_2 did not change, Teflon only introduces a delay in the time response.

5.4 Vapour Sensing of Ethanol and Hexane

The fabrication of sensors for the detection of volatile organic compounds is of significant interest in monitoring industrial, environmental and physiological processes, like detection of explosive or pollution gases, and medical breath analysis. An ethanol vapor detection probe [96], a gas sensor of amine [197] toluene and benzene odors [198] and a toluene sensor for use with water contamination [199] were demonstrated using LPFGs functionalized with a polyelectrolyte multilayer, calixarenes thin films and metal oxide nanoparticles. Zinc oxide (ZnO) is an interesting material for the

implementation of chemical sensors [200]. Conductivity changes induced on ZnO surface due to adsorption of organic vapours or active gases, such as ozone, gasoline, toluene and ethanol, has led to electrically interrogated sensors [157]. Optical interrogation based on ZnO thin films, nanoparticles and nanorods were demonstrated for ethanol, methanol and isopropanol vapour sensing using surface plasmon resonance, micro-ring resonators and LPFGs schemes [96, 158, 201].

In this work an LPFG sensor coated with 290 nm thick ZnO layer was fabricated and optically interrogated at the C-band for the detection of volatile organic compounds, ethanol and hexane.

5.4.1 Materials and Methods

The measurement of the vapour sensitivity of the LPFGs sensors was accomplished using the arrangement illustrated in Figure 5.19. The set, comprising a glass bottle, valves and a gas cell, was placed inside an oven, whose temperature was controlled within ± 0.1 °C, and has an opening for the fibres and the vacuum tube. Before being positioned inside the chamber, the sensors were held under tension by clamping both ends to a 10 cm long glass slide with epoxy.

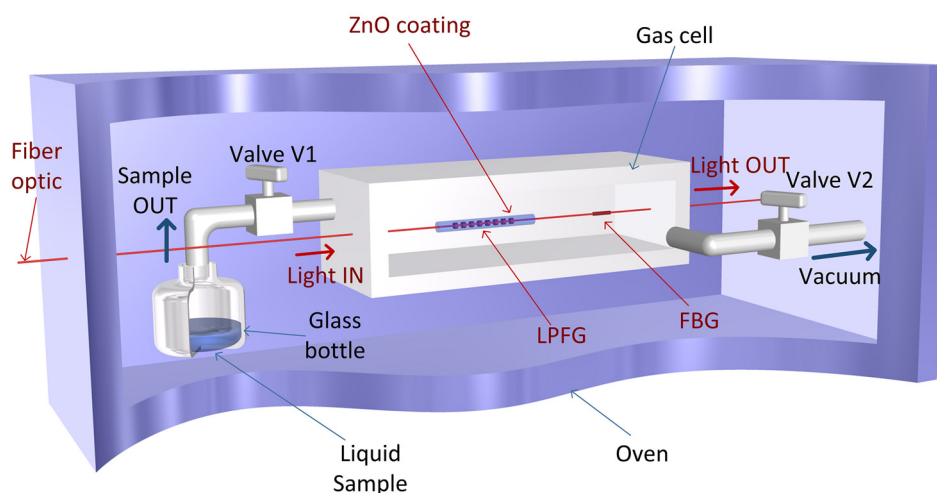


Figure 5.19 – Setup for the characterization of the sensor constituted by a glass bottle, valves and a gas cell placed inside an oven. A broadband source and an optical spectrum analyser are not shown.

Initially, the temperate of the oven was set to 25 °C and left to stabilize while, with valves V1 and V2 open, both the glass bottle and the gas cell were pumped down to 10^{-1} mbar and at that time both valves were closed. Then a volume of 100 mL of liquid of one of the volatile organic compounds was injected into the glass bottle and temperature was left to stabilize again. When the valve V1 is

open the ethanol vapour moves into gas cell and, simultaneously, the liquid ethanol evaporates until vapour pressure, given by Antoine equation (5.11) [202], is reached:

$$\log_{10} p = A - \frac{B}{C + T} \quad (5.11)$$

where p is the vapour pressure, T is the temperature and A , B and C are constants obtained from the *Dortmund Data Bank* [203]. From the values of the vapour pressure and the volume, the calculation of the vapour concentration in the gas cell is straight forward. An increase in the temperature of the oven led to an increase in the vapour pressure, and therefore a wide range of vapour concentration may be attained.

The LPFGs along with the FBGs were characterized in transmission mode with the OSA (ANDO, model AQ 6315B) by coupling light from a super luminescent diode source (SLD) model S5FC1550S-A2 (Benchtop SLD – Thorlabs, Inc., Germany).

5.4.2 Experimental Results and Discussion

– *Sensitivity of the Sensors to Ethanol*

The ZnO overlaid LPFGs sensors were first tested for their ethanol sensitivity. After a sensor has been placed inside the gas cell, the set glass bottle/gas cell was pumped down and the oven was set to 25 °C and left to stabilize for 20 minutes. Afterwards several reference transmission spectra were recorded at constant time intervals.

After the liquid ethanol is in thermal equilibrium with the set glass bottle/gas cell the temperature of the oven was risen in 0.5 °C steps and for each vapour pressure value (or concentration) the LPFG spectrum was again recorded at constant time intervals. The increase in ethanol concentration in the gas cell gives rise to wavelength shift and attenuation variation of the resonant bands of the LPFG, as is illustrated in Figure 5.20 for the LP₁₆ mode of a 290 nm thick ZnO coated LPFG for ethanol vapour concentration from 0 to 174 g.m⁻³.

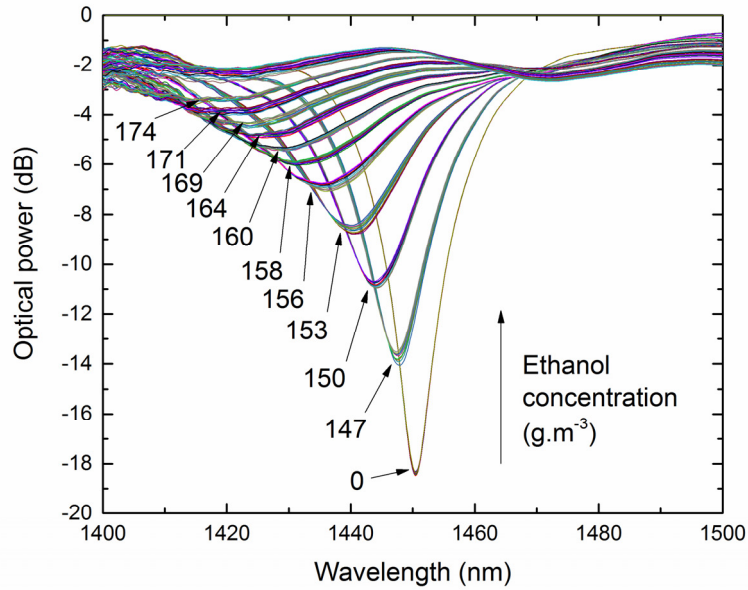


Figure 5.20 – Spectra of the LP_{16} mode of a 290 nm thick ZnO coated LPFG from 1400 to 1500 nm as a function of the ethanol concentration.

The correspondent wavelength shift and the optical power shift of the attenuation band as a function of the ethanol concentration are presented in Figure 5.21. From Figure 5.21-(a) an average sensitivity of 0.99 nm/g.m^{-3} for the wavelength shift was calculated from the linear fit ($R^2 = 0.95$) and a nonlinear trend was found for the variation of the optical power with the concentration. The combination of the optical power and wavelength shifts of the attenuation band for a given ethanol concentration have returned the nonlinear trend shown in Figure 5.21-(b), characteristic of the ethanol.

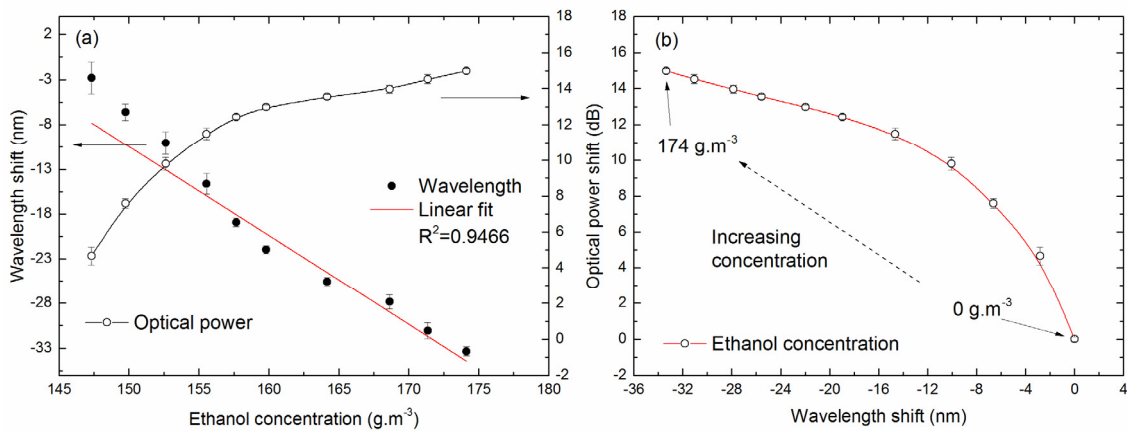


Figure 5.21 – Normalized curves of the LPFG coated with 290 nm of ZnO, considering the LP_{16} mode, in function of the ethanol concentration a) wavelength shift and b) optical power shift.

When a metal oxide such as ZnO is left unprotected, oxygen from air is absorbed on the surface transferring negative charge to the oxygen and leaving a positively charge surface barrier to electron flow at each grain boundary in the metal oxide [204]. When the ZnO thin film are exposed to reducing gases such as ethanol, they will react with the adsorbed oxygen ions, leading to the release of the trapped electrons to the conduction band and an increase of the carrier concentration [205]. The ethanol induced electronic mobility in the ZnO thin film results in conductivity change, related to the concentration and chemical composition of the reducing gas, which in sequence is directly associated with optical absorption and refractive index changes [96].

Additionally, it was found that ethanol adsorption on ZnO results in shorter Zn-O bounds, which can be correlated with strain induced refractive index changes [206]. Consequently, the adsorption of ethanol onto ZnO thin film structures induces both electronic and structural modifications which leads to refractive index and optical absorption variations. While the ZnO refractive index is modified, affecting both visibility and spectral position of the LPFG attenuation band, optical absorption will mainly induce variation on the attenuation visibility. This may be a reasonable explanation for the change of the LPFG band intensity and wavelength shift presented in Figure 5.20.

Commercial available optical spectrum analyser with 2 pm resolution would make feasible the detection of an ethanol concentration of $\sim 0.002 \text{ g.m}^{-3}$. However, the spectral resolution has to be taken into account. From the data shown in Figure 5.22-(a) spectral resolution better than 3.2 g.m^{-3} was calculated [161].

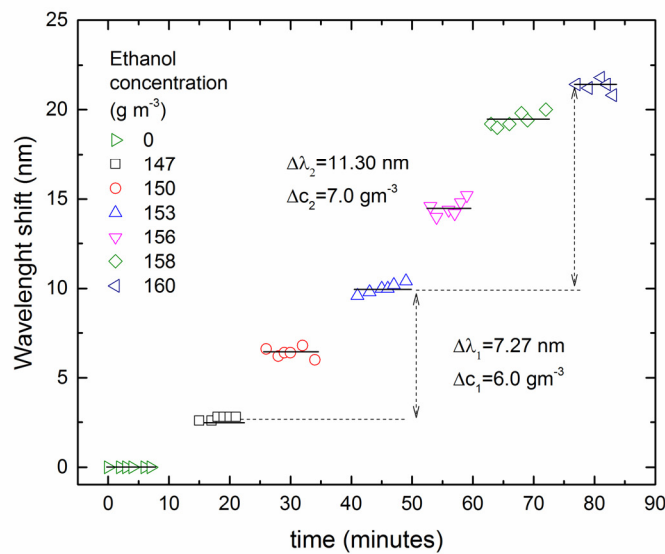


Figure 5.22 –Wavelength shift of the dip of a 290 nm thick ZnO coated LPFG when the ethanol concentration undertakes step variations.

– *Sensitivity of the Sensors to Hexane*

A preliminary investigation of the selectivity of the sensor was carried out using hexane following the same procedure as detailed above. The saturated vapour pressure of hexane curve for Figure 5.23 illustrates the wavelength shift and optical power variation of the attenuation band minimum of the LPFG for increasing hexane concentration up to 1989 g.m^{-3} .

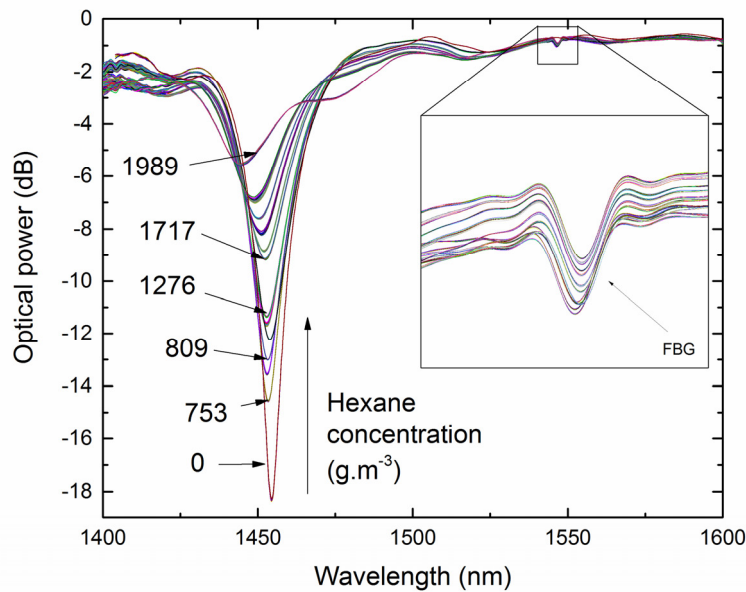


Figure 5.23 – Optical Spectra of the LP₁₆ mode with 290 nm thick ZnO coated LPFG from 1400 to 1600 nm as a function of the hexane concentration. Inset is the FBG in transmission for temperature compensation.

The inset of Figure 5.23 shows the transmission spectrum of the FBG in series with the LPFG used to calibrate the system to the temperature.

The analysis of the attenuation band according to the wavelength and optical power shifts for hexane concentrations from 0 to 1989 g.m^{-3} is presented in Figure 5.24. From Figure 5.24-(a) while there is a noticeable decrease of the dip of the resonance band with increasing hexane concentration the corresponding wavelength only shifts slightly for low hexane concentration. The wavelength sensitivity for hexane considering concentrations up to 1780 g.m^{-3} is $0.003 \text{ nm / g.m}^{-3}$, a value much smaller than the corresponding for ethanol ($0.99 \text{ nm / g.m}^{-3}$). Although, the optical power shift shows a good linearity up to the same concentration. The optical power of the attenuation minimum as a function of the wavelength shift for the range of hexane concentration follow a similar curve shape, although non-overlapping, comparing to the ethanol as shown in Figure 5.24-(b).

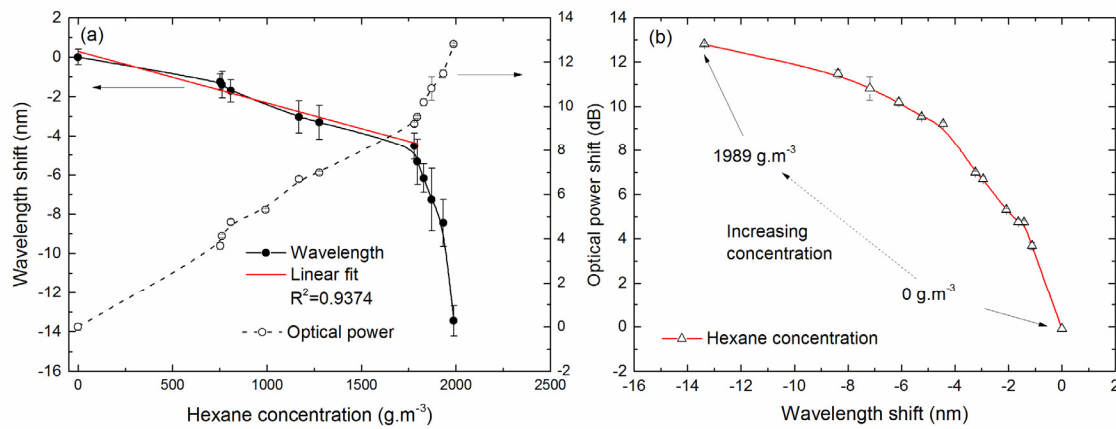


Figure 5.24 –Normalized wavelength shift and attenuation of the coated LPFG LP₁₆ mode.

Although the increasing in the temperature was very slow and monitored with the FBG there are always fluctuations from the different thermal conductivities in the system, which introduce deviations in the concentration calculation. This is reflected in the spectral resolution calculated around 220 g.m⁻³.

5.5 Conclusions

Studies using three different configurations as hybrid FP/modal interferometers, FBGs, and LPFGs to the detection of gases and volatile compounds were presented and discussed.

The hybrid interferometer was used for simultaneous measurement of the partial pressures of O₂ and CO₂ which consists on the combination of an FP cavity and a modal configuration. The intrinsic FP structure was created by splicing an SMF to a GIF section that was later subjected to chemical etching, creating an air FP cavity. The modal interferometer is based on a splice of silica tube in series with the FP. Due to the design and distinct gas compressibility factors, different sensitivities were achieved, enabling the discrimination of the partial pressures of the gases. The resolutions were found to be 48.7 and 20.1 Pa for P CO₂ and P O₂ measurements, respectively.

A thorough study using FBG coated with palladium for hydrogen detection for concentrations below lower explosion limit was presented. A sensitivity of ~20 pm/%(v/v) was attained due to an optimized design associated with a reduction of the fibre cladding from 125 μm to 50 μm by chemical etching process and Pd coating with 150 nm thin film. The study of high level humidity in the palladium hydride transition for long time operations had shown irreversible damage in the

coating causing a decrease of the sensor performance. It was demonstrated that the approach of using protective Teflon layers is a good solution to prevent the coating damaging.

A room temperature vapour sensing probe for ethanol and hexane was presented employing a ZnO thin film as a chemosorptive material overlaid onto LPFGs. When working in the wavelength shift mode of operation the sensitivity of 0.99 nm/g.m^{-3} and a spectral resolution better than 3.2 g.m^{-3} was measured. From the highest visibility of the attenuation band to its extinguish the response for both gases allow to cover different concentrations showing a superior wavelength sensitivity toward ethanol when compared to hexane.

Chapter 6

Fabrication and Characterization of Metal Oxide Coated Long Period Fibre Gratings

Real time monitoring of metals oxidation is performed for a set of metals deposited over long period fibre gratings and annealed up to 600 °C in air with a small furnace. The new sensing structures have improved sensitivity to the external refractive index which depends on the thickness and the morphology of the coating material.

6.1 Introduction

Transition metal oxides are widely used in laser optics as micro mirrors, anti-reflection coatings, band pass filters, etc. The most commonly used materials are silicon dioxide (SiO_2) and titanium dioxide (TiO_2), which are both electrically insulators that in some applications might be a drawback. Some other materials as zinc oxide (ZnO) or copper oxide (CuO / Cu_2O), both semiconductors, are attracting attentions due to their intrinsic properties. Furthermore, metal oxides in general are interesting high RI coating materials due the available range of RI values, the robustness in the thin film geometry and the variety of growth techniques. In addition, a few metal oxides undertake

variations of their physical properties upon chemical adsorption, thus making themselves interesting solutions for chemical and biochemical sensing applications [96, 207].

Zinc oxide (ZnO - zincite) is a transparent, wide-bandgap semiconductor oxide. It has several promising properties depending on its dimension, morphology and crystallinity, including good transparency, high electron mobility, and strong room-temperature luminescence [208, 209]. Copper oxides can be classified into two well-known structures, tenorite (CuO) and cuprite (Cu₂O) [210]. At 200 °C the formation of Cu₂O occurs while at 350 °C in air may exist a total conversion of Cu₂O to CuO [211]. Nickel (Ni) is a ferromagnetic transition metal and it is known that it oxides to the chemically stable nickel oxide (NiO - bunsenite) [212]. Titanium dioxide (TiO₂ - rutile/anatase) have been used in several types of fibre sensors as in surface plasmon resonance devices to allow the working spectrum position to higher wavelengths (Chapter 8) or to enhance the sensitivity of LPFGs (Section 4.3.1) which happens when the refractive index of the coating layer is higher than that of the cladding. Aluminium oxide (Al₂O₃ - corundum) is the most well-known oxide ceramic material with a set of particular properties as very efficient electrical insulation, bio-inert, food compatible and low density. A very thin alumina layer is always formed on the top of an aluminium metal surface acting as a protecting layer against corrosion. Moreover, the low refractive index couple with high optical transparency (>80%) in a wide range of wavelengths, therefore it is often used to improve the efficiency in solar cells [213]. Other oxides have great importance due to its features as, for example, chromium oxide (Cr₂O₃ - eskolaite).

The real time monitoring of the oxidation process of a set of metals is presented using coated long period fibre gratings (LPFGs) placed in an furnace with controlled temperatures up to 600 °C, below the melting point of pure silica. LPFGs coated with thin films of Cu, Zn, Ni, Ti, Al and Cr were annealed together with planar silicon (Si) samples coated with the same metals for further analysis using Scanning Electron Microscope (SEM), Energy Dispersive X-ray Spectroscopy (EDS), X-ray Photoelectron Spectroscopy (XPS) and X-ray diffraction (XRD) techniques. After the oxidation process the attenuation band of the coated LPFG was monitored in terms of their optical properties (wavelength position and optical power) by varying the surround refractive index (SRI) from 1.300 to 1.640.

6.2 Materials and Methods

The sensing devices were produced in single mode fibre for optical communications (SMF28e, Corning, Inc.) where LPFGs were inscribed and coated with a set of metals following the procedures described in sections 3.1.1 and 3.1.3 respectively. Simultaneously, the same metals were deposited on Si substrates for further morphological, chemical state and optical properties analysis. Each LPFG was produced with a period of $387\text{ }\mu\text{m}$ and a length of $45\pm 5\text{ mm}$, to provide an attenuation band with peak attenuation above -20 dB , corresponding to the antisymmetric 6th order cladding mode around 1480 nm [153].

The coated fibres with a 30 nm thick metal film were then positioned in the central section of a 20 cm long, 520 W furnace (Termolab, Portugal), being clamped in one end while at the other end the fibre was kept stretched at a constant tension with a 5 g weight, therefore avoiding bending effects. Figure 6.1 shows the scheme of the oxidation process.

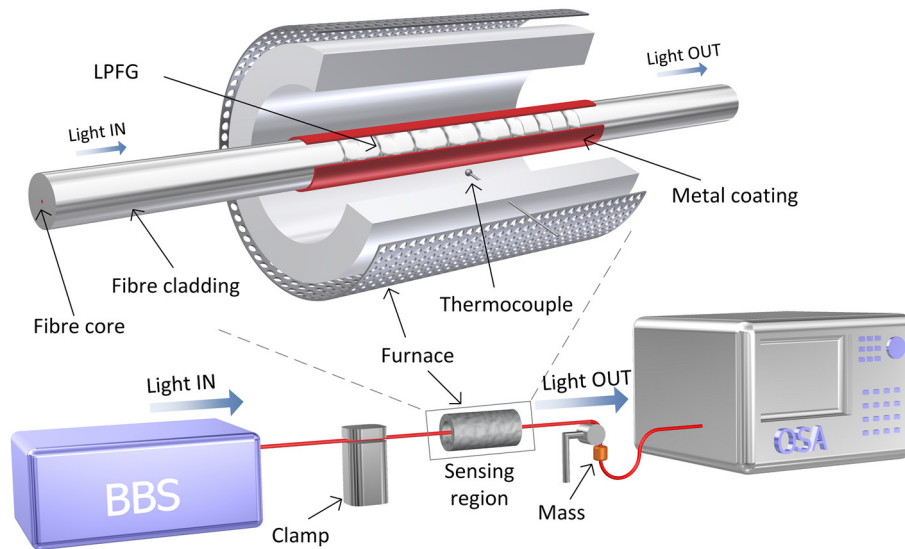


Figure 6.1 – Scheme of the oxidation setup using a furnace and a LPFG working in transmission comprising a broadband source (BBS), an optical spectrum analyser (OSA) and the grating sensor.

To monitor the oxidation process each fibre was illuminated with a super luminescent diode source (Benchtop SLD model S5FC1550S-A2 – Thorlabs, Inc., Germany) and the LPFG attenuation band was record in transmission mode with an optical spectrum analyser (OSA) model Yokogawa AQ 6370D. The temperature was controlled with a thermocouple located in the middle of the heating section close to the thin film coating. The oxidation takes place by thermal annealing process in air up to $600\text{ }^{\circ}\text{C}$ for 1 h , following the procedure described in [214]. Heating and cooling were

maintained at an approximate rate of about ~ 4 °C per minute. As the furnace had both ends open, the metal oxidation took place in an air atmosphere. The Si substrates coated with the same metals and thickness were placed simultaneously in the furnace, which were then measured with the surface profiler model DektakXT (Bruker Co., U.S.A.) in order to determine the final oxide thickness. The step profile of thin films on Si substrates was measured with the surface profiler model DektakXT (Bruker Co., U.S.A.).

The methods already described in section 3.2 were used, namely: SEM/EDS (model models QUANTA 400 FEG, FEI, U.S.A./ Pegasus X4M, EDAX, U.S.A.); XPS (model AXIS Ultra HAS, KRATOS, U.K) using the Al $\text{K}\alpha_1$ transition at 1.486 keV; and XRD (model X'Pert Pro, PANalytical, Netherlands) equipped with Cu $\text{K}\alpha$ radiation. In addition, each LPFG coated with oxide metal was placed in the setup presented in section 4.3 (Figure 4.7) for optical characterization with a set of refractive index calibrated oils (Cargille-Sacher Laboratories Inc., NJ. U.S.A.) and a V groove as described in section 4.3.

The oxidation process can be monitored by following the attenuation band of the LPFG while the temperature rises. There are structural modifications on the coatings which lead to variations in the optical response.

The surface analysis returns a significant amount of data which needs to be presented for its importance to the final conclusions. The results for each method of analysis are presented for all the metal samples of Cu, Zn, Ni, Ti, Al and Cr as deposited and after thermal annealing.

The optical response of all the LPFGs coated with the final oxides to the external refractive index are also presented and compared.

6.2.1 Real Time Monitoring Oxidation of Metals with Long Period Fibre Gratings

The thermal process leading to oxidation of the metal thin films gives rise to wavelength shift and intensity variation of the attenuation bands of the LPFG as illustrated in Figure 6.2 for the LP₁₆ cladding mode where, for example, two LPFGs were coated with 30 nm of Zn (a) and Ni (b) respectively. The red dashed curves are related to the bare LPFGs while the red solid curve shows the same after the metal coating indicating a considerably reduction in the intensity of the attenuation band of the LPFG.

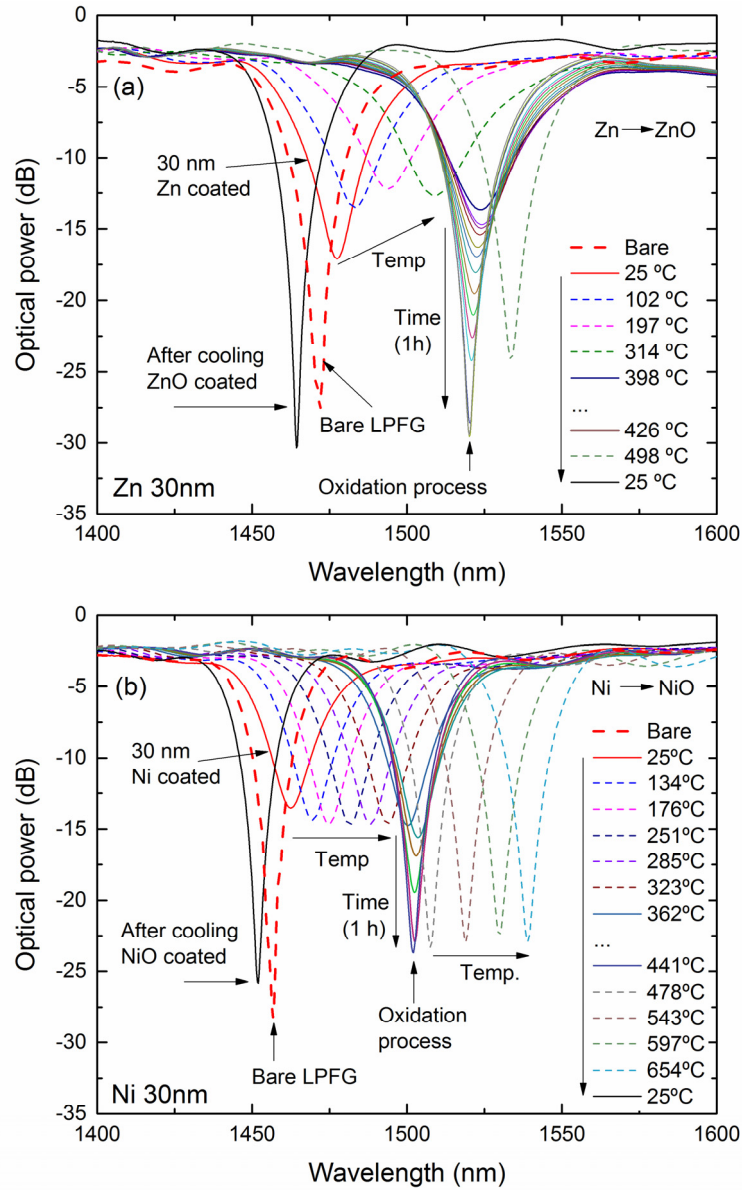


Figure 6.2 – Real time oxidation spectra of the LP₁₆ mode from 1400 to 1600 nm of LPFGs coated with 30 nm of metals annealed with a range of temperatures: (a) Zn from 25 to 498 °C and (b) Ni from 25 to 654 °C. Also shown, for comparison, the spectrum of the LP₁₆ mode of a bare LPFG (uncoated) at 25°C.

The metal coating becomes a mirror to the evanescent field causing light to be coupled back to the fibre core mode. With heating, the band shifts to higher wavelengths, as expected due to the intrinsic thermal sensitivity of LPFGs, but the attenuation maintains approximately the same optical power level. For temperatures above 350 °C the intensity of the attenuation band starts to increase, an indicator of the oxidation process, with a decrease in the coating reflectivity, until reaches the level of the starting point at room temperature. Increasing even more the temperature a red shift is observed

while the minimum of the attenuation band maintains the same optical power level. This level of attenuation is maintained when the room temperature is reached, after the cooling process, with a slight shift in wavelength which was expected due to the change of the effective refractive index in the fibre boundary.

In order to illustrate how the coated LPFG spectral features changes when the temperature rises and oxidation takes place the minimum of the attenuation band was monitored and is presented in Figure 6.3 for the Zn in terms of optical power (a) and wavelength position (b). The red round symbols are related to the bare LPFG and compared to the metal coated LPFG with the blue squared symbols.

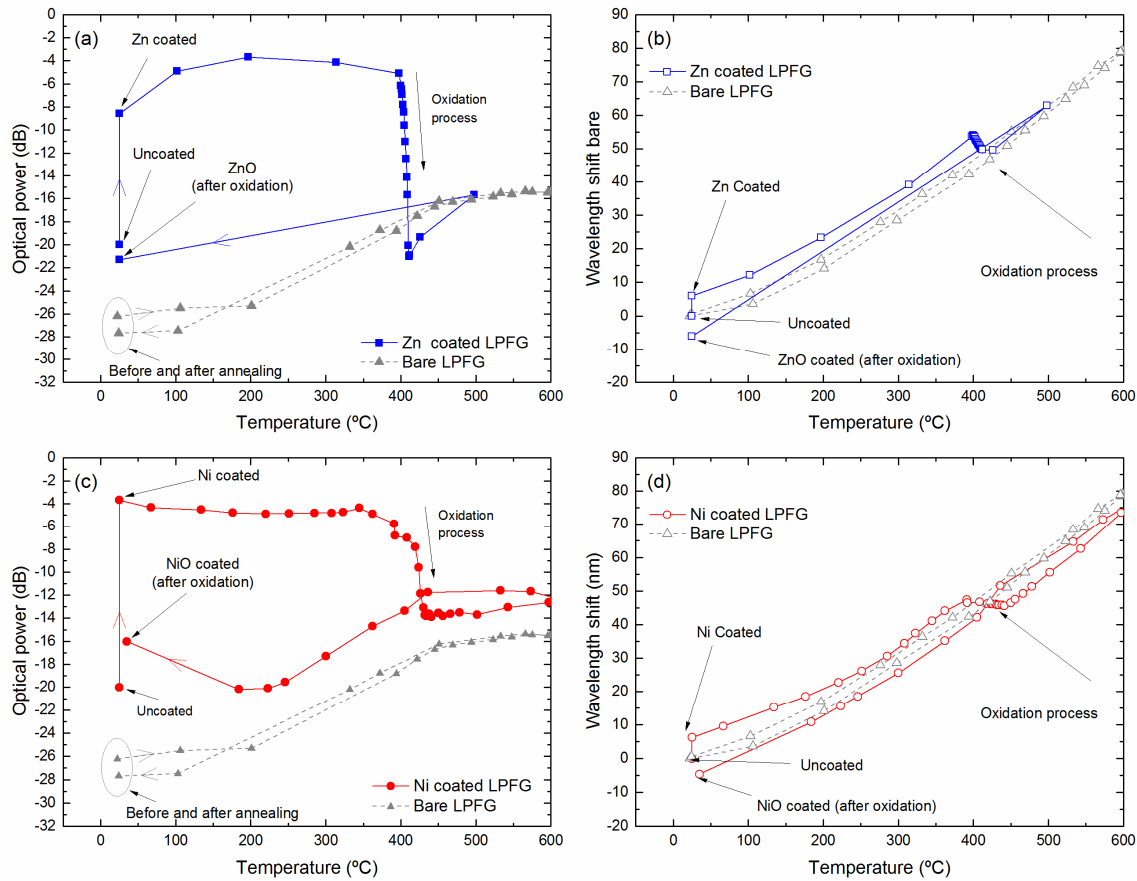


Figure 6.3 – The LP₁₆ mode spectral features of a bare and of a 30 nm thick Zn and Ni coated LPFG as function of temperature up to 600 °C: (a) and (c) optical power; (b) and (d) normalized wavelength shift.

After the metal coating there is a small shift in wavelength position but a huge reduction in the optical power of the band is observed due to less light being coupled to the high order cladding modes. The oxidation process is evident around 400 °C where the attenuation band visibility increased more than 18 dB. In addition, the wavelength shift behaviour is maintained with the same slope as with the bare

LPFG for the same temperature range up to 500 °C. The oxidation process causes a translation effect in the wavelength shift curve around 400 °C due to the refractive index changes but the thin coating is unable to change substantially the thermal sensitivity of the LPFG. At ~498 °C a red-shift of resonance band is established again at a rate similar to the bare LPFG. It is reasonable to assume that this final red-shift is only temperature driven and the Zn thin film is completely oxidized.

During cooling the LPFG coated with Ni oxide moves to shorter wavelengths showing ~4 dB reduction in intensity and ~5 nm blue-shift relatively to the initial position of the bare LPFG at the same conditions. A blue-shift and a decrease of the attenuation were predictable [148]. The resonance wavelength depends on the effective RI of the cladding modes which, in turn, depends on the SRI, being higher sensitive as the SRI approaches the cladding refractive index (CRI). The formation of a metal oxide thin film on the LPFG induces a re-distribution of the cladding modes that leads to wavelength and amplitude shifts of the attenuation bands.

The same methodology was applied to the oxidation of the other metal coatings as Cu, Ti, Al, and Cr and presented in Figure 6.4.

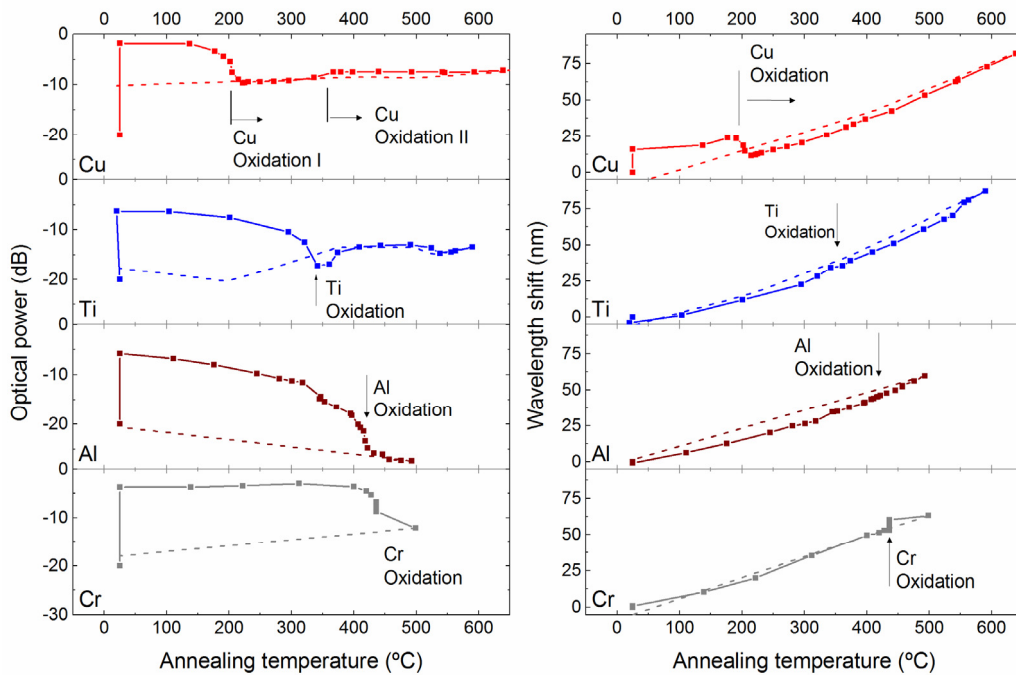


Figure 6.4 – Transmission response with temperature variations for LPFGs coated with Cu, Ti, Al and Cr metal thin films respectively: (a) Optical power shift, (b) Wavelength shift.

The intensity variations of the attenuation band for each metal coating is depicted in Figure 6.4-(a) where at a certain temperature level the attenuation increases suggesting oxidation reaction. It can be

observed that the different metals show oxidation at distinct temperatures. The sensitivity to temperature is shown in Figure 6.4-(b), in average have the same nonlinear behaviour of the bare LPFG. Nevertheless, is possible to identify a small negative shift when the oxidation occurs. The optical power shift curve of Cu shows two steps I and II at 200 and 350 °C, characteristic temperatures of the Cu oxidation states CuO and Cu₂O as discussed above.

6.2.2 Chemical and Morphological Characterization of Metals and Oxide Samples

– Scanning electron microscopy coupled with energy dispersive X-ray spectroscopy

SEM photographs with magnification of 200 000 of 67.5 nm thick metal samples before and after annealing are presented in Figure 6.5 and Figure 6.6, respectively.

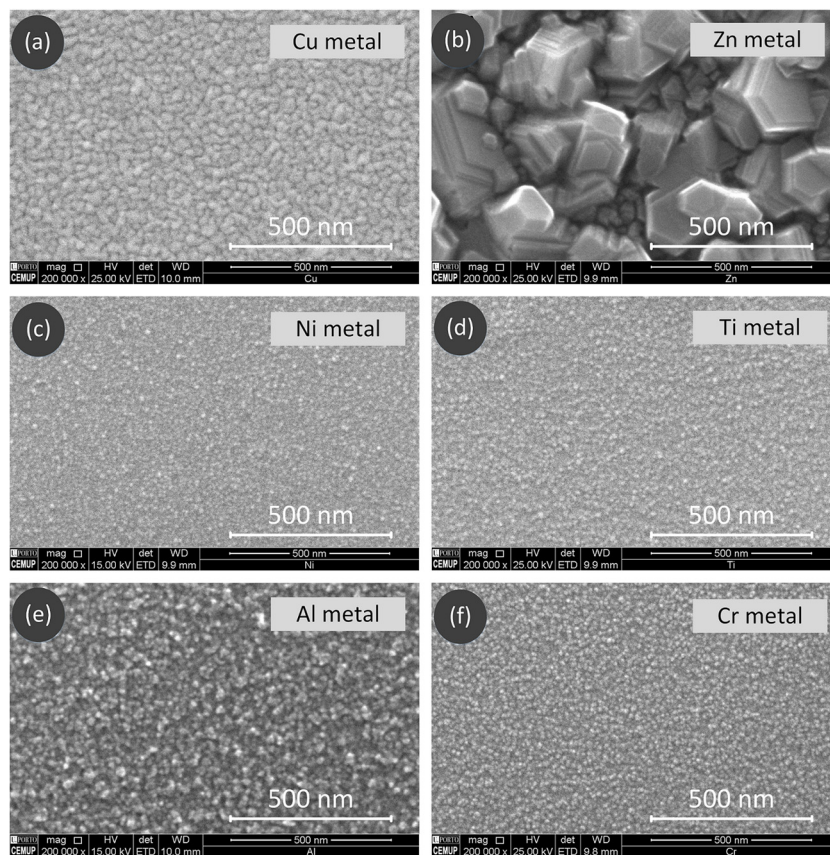


Figure 6.5 – SEM photographs with 200 000 X of magnification of a 67.5 nm thick metal film as deposited: (a) Cu, (b) Zn, (c) Ni, (d) Ti, (e) Al and (f) Cr.

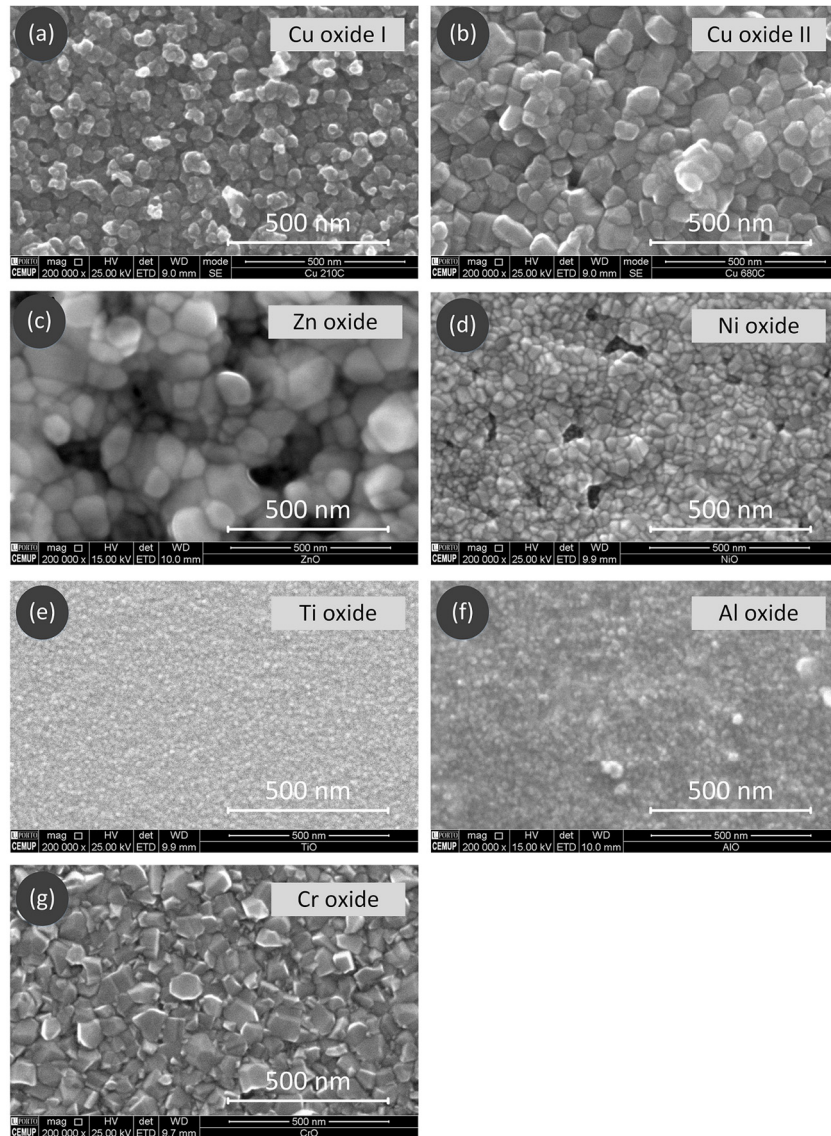


Figure 6.6 –SEM photographs with 200 000 X of magnification of 67.5 nm thick metal film samples after annealing: (a) Cu at 225 °C for 1 hour; and after annealing at 600 °C: (b) Cu, (c) Zn, (d) Ni, (e) Ti, (f) Al and (g) Cr.

Figure 6.5-(a) to -(f) presents images of the metal thin film samples of Cu, Zn, Ni, Ti, Al and Cr, respectively, as deposited.

Although the procedure to evaporate Zn metal is the same, with a rate ~ 0.02 nm/s, a high surface inhomogeneity is visually evident for the Zn metal coating when compared to the others. It occurs at a lower temperature range (Table 3.1), where the electron beam energy is more unstable, and more chunks of material could leave the crucible instead of single atoms. These could be one of the reasons to the inhomogeneity observed in the Zn metal coating. All the other metal samples present a relatively smooth surface with low grain size.

In the oxide phase of Figure 6.6 the roughness is different from sample to sample. It increases for the Cu, Cr and Ni samples, decreases for the Zn sample while the Ti and Al samples maintains the same surface profile. The Cu samples Figure 6.5-(a) and -(b) corresponds to annealing temperatures of 225 °C (I) and 600 °C (II), respectively, showing considerable differences in the morphology and suggesting two different oxidation states.

The grain size of all the samples was calculated using the image software analysis ImageJ (National Institutes of Health, U.S.A.). For the Zn sample before annealing, an average particle diameter of 157.9 ± 62.2 nm was measured, which diminishes to 106.6 ± 38.7 nm after the annealing process. This behaviour is opposite to the other samples where the annealing leads to an increase on the grain size diameter. The average particle diameter calculated for all the metals before and after annealing are presented in Table 1. In general, a tendency to increase the surface inhomogeneity with the oxidation process is observed. The Zn sample is an exception where the average particle diameter decreases after the annealing process maintaining a wide range of values.

Table 6.1 – Average particle diameter observed in the metal samples and the associated oxides by analysing the SEM images.

Sample	As deposited		After annealing	
	Average diameter particle (nm)	Standard deviation (nm)	Average diameter particle (nm)	Standard deviation (nm)
Cu	33.4	5.9	(at 225 °C) 41.7	5.9
			(at 600 °C) 67.9	14.0
Zn	157.9	62.2	106.6	38.7
Ni	<12	--	46.6	11.4
Ti	<12	--	11.5	2.3
Al	18.2	2.4	21.3	3.5
Cr	17.3	2.6	80.6	9.3

In order to estimate the thickness of the oxide layer on the LPFGs after oxidation the thickness of the metal coated Si samples was measured before and after oxidation using the surface profiler leading to ratios of 1.98 ± 0.1 for Cu at 225 °C, 2.38 ± 0.2 for Cu at 600 °C 2.9 ± 0.1 for Zn, 2.1 ± 0.2 for Ni, Ti and Cr and 1.1 ± 0.1 for the Al sample.

The EDS analysis of Cu, Zn, Ni, Ti, Al and Cr as deposited on Si substrate and compared with the same samples after annealing are shown in Figure 6.7. The thin metal films do not possess a significant number of impurities. Besides the bands related to the metal under concern - the substrate (band Si K), the adhesion layer (bands Cr K and Cr L) and oxygen (line O K α) - only a band related to carbon contamination (band C K) is present. The well-defined band around 1739.98 eV corresponds to the K α_1 , K α_2 and K β_1 lines of the Si K band and the low intense peaks above 5 KeV are the Cr K lines from the adhesion layer [124].

In the Cu sample (a), after the annealing process, three bands are shown with energies of 514.48, 524.9, 949.8 and 1739.98 eV corresponding to O K, Cu L and Si K lines respectively. Is important to observe that increasing the annealing temperature more oxygen is transferred to the matrix leading to changes in the Cu/O ratio, which is in agreement with the oxidation phase transitions between Cu₂O and CuO.

The Zn sample (b) shows the same kind of behaviour with three bands at 514.48, 1014.45 and 1739.31 eV corresponding to O_K, Zn L and Si K lines, respectively. The spectral position of all the lines and bands referred were compared with published values and found to be in good agreement [215] [124].

Figure 6.7-(c) and -(e) display the spectra of Ni and Al before oxidation with intense bands (neglecting the Si K band) at 850.14 and 1486.64 eV corresponding to the Ni L and Al K bands, respectively. The band at 524.90 eV in Figure 6.7-(e) can be allocated to the O_{K α} line, indicating the presence of oxygen in the Al film before the oxidation process, probably due to the time delay between deposition of the Al film and the EDS measurement associated with the well-known formation of a stable layer of Al₂O₃ at room temperature [216]. The same but less intense O K α line may be observed in the Ni spectrum [Figure 6.7-(c)]. After oxidation the intensity of the O K α line increases in both metal films, confirming the presence of high quantities of oxygen.

Concerning Ti and Cr, Figure 6.7-(d) and -(f) show bands with peaks at ~517 and ~519 eV corresponding to the overlap of Ti L and Cr K bands with O K α line [124]. This overlapping doesn't allow the semi-quantitative analysis of the elements, however, the existence of Ti and Cr can be established by the presence of the Ti K α and Cr K α lines at 4510.16 and 5415.52 eV, respectively. After oxidation the intensity of Ti L and Cr K bands increased due to oxygen incorporation in the matrix.

The EDS analysis is able to confirm the presence of high quantities of oxygen after the thermal annealing. It is not a quantitative analysis technique but once those peaks are well defined without overlapping it is possible to give semi-quantitative analysis of the elements showing, for example, for Zn oxide atomic percentage of Zn and O around 41.45 and 58.55 %, respectively, while the atomic percentage of Cu oxide at 225 °C were calculated as ~ 32.20 % and ~ 67.80 % for Cu and O respectively, while at 600 °C these values changed to ~ 49.19 % and ~ 50.81 %.

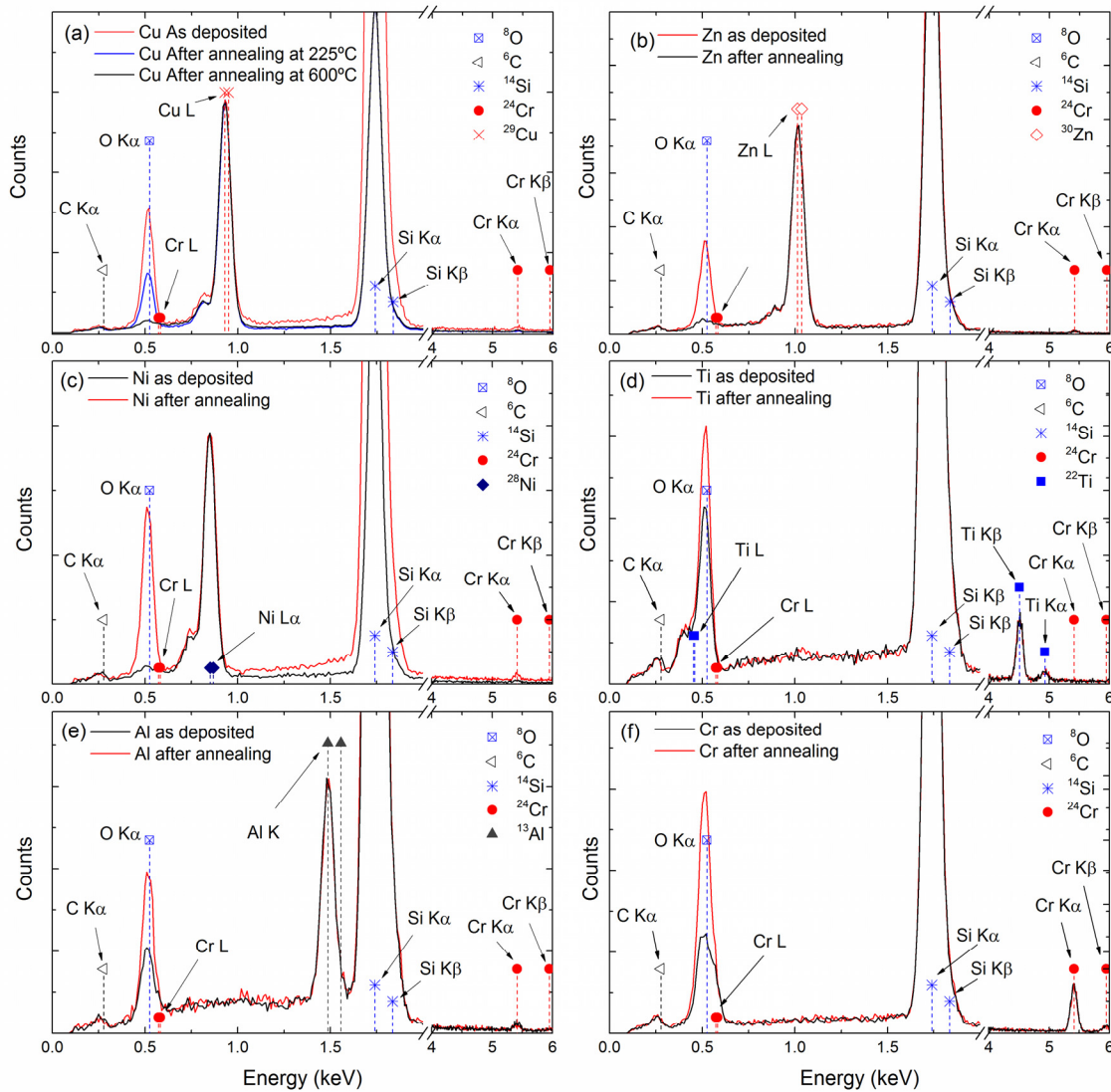


Figure 6.7 –EDS spectrum of thin film samples as deposited and after annealing in air for 1 h: (a) Cu at 225 °C and 600 °C, and (b) Zn (c) Ni, (b) Ti, (c) Al and (d) Cr at 600 °C.

In both samples the estimated ratio metal/oxygen is lower than 1, exhibiting an excess of oxygen in the sample which may be found on the top of the Si substrate, in the C=O bonds and at the adhesion layer.

– *Characterization by X-ray photoelectron spectroscopy*

The survey spectrum of a sample shows all the elements present on the surface and allows setting up subsequent high-resolution XPS spectra acquisition. In order to illustrate the quality of the samples the survey spectrum of the Zn sample after annealing is shown in Figure 6.8.

The more relevant peaks are the Zn 2p and O 1s corresponding to the grey boxes. Besides the presence of carbon (C) this survey shows a very clean sample surface.

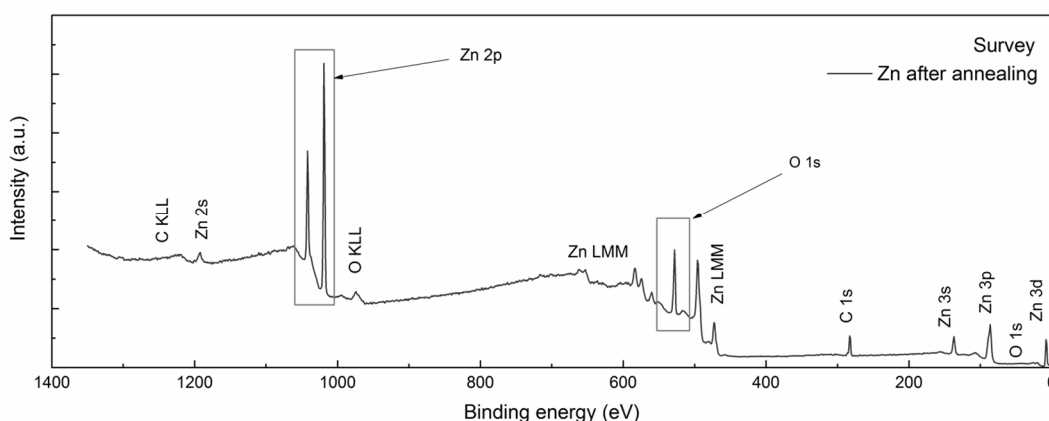


Figure 6.8 –XPS spectrum survey of an Zn thin film sample on silicon wafer after annealing at 600 °C for 1 h..

The high-resolution XPS spectra acquisitions corresponding to the orbitals 2p and O 1s from all samples after annealing are shown in Figure 6.9 and Figure 6.10, respectively.

Figure 6.9-(a) shows the binding energy spectrum, from 1010 to 1060 eV, with two peaks that can be identified as Zn 2p_{1/2} and Zn 2p_{3/2} electrons with energies of 1044.36 and 1021.31 eV, respectively [131, 133]. The measured difference between the two lines is ~23 eV which is in agreement with the standard reference value of ZnO oxidation state [217].

Figure 6.9-(b) exhibits a binding energy spectra of the Cu samples after annealing at 225 and 600 °C, respectively. The last one (solid black line) with two main peaks (1,4) and satellites (5, 6) corresponding to the Cu 2p_{3/2} at 933.87 eV and Cu 2p_{1/2} at 953.78 eV, respectively, which is a characteristic of the CuO oxidation state [218]. The spin-orbit splitting separation between Cu 2p_{3/2} and Cu2p_{1/2} is 19.91 eV, which is a common value between the metallic Cu and the oxidation states

CuO and Cu₂O [219]. Nevertheless, the presence of satellites on the high binding energies at ~9 eV of the Cu 2p_{1/2} peak confirms the presence of CuO [218]. However, the sample with annealing temperature limited to 225 °C (dash blue line) shows a similar Cu 2p spectrum with two main peaks and satellites which is not characteristic of the Cu₂O.

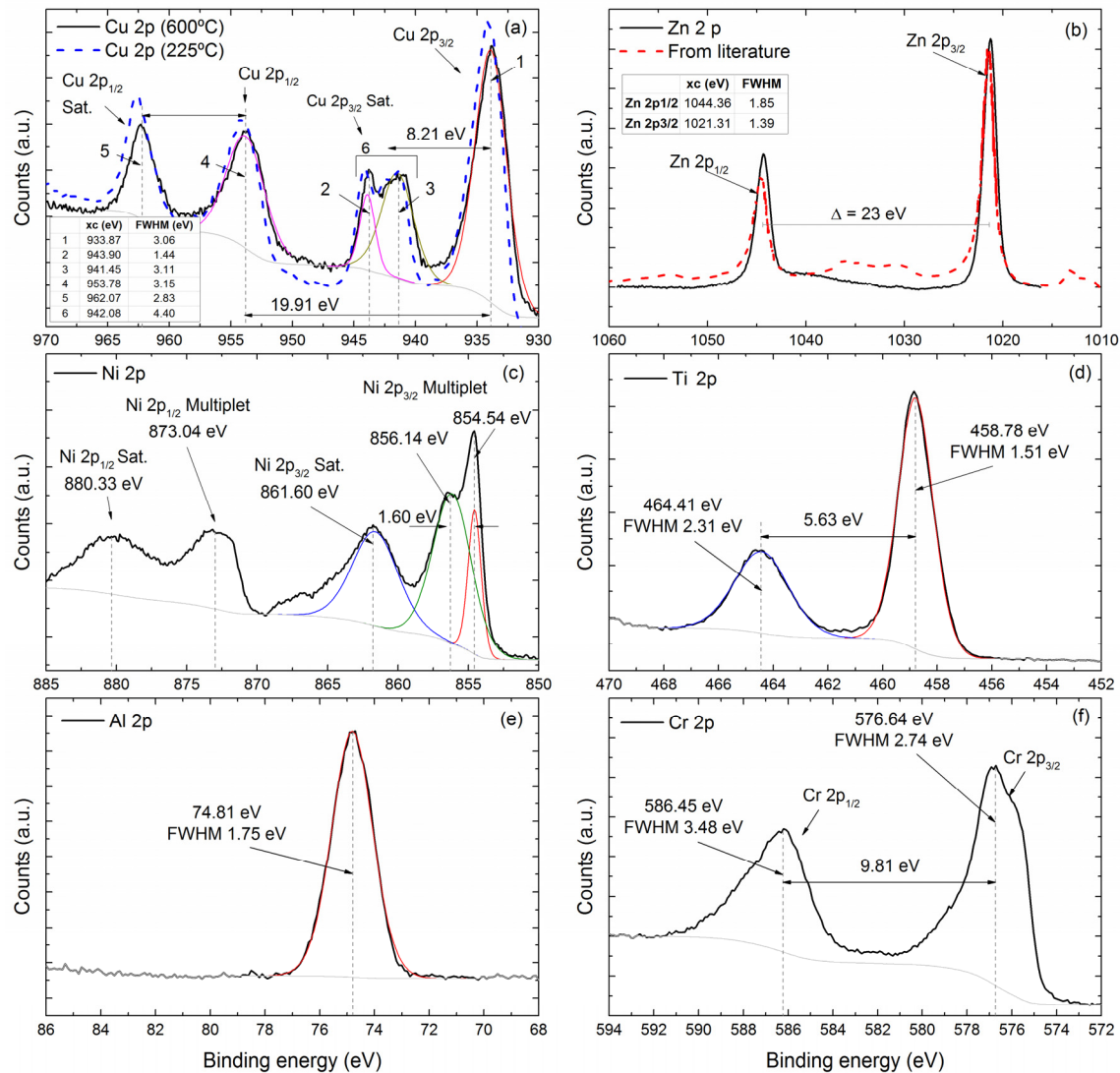


Figure 6.9 – Binding energy spectrum of 2p electrons obtained by XPS of thin film samples after annealing in air at 600 °C for 1 hour acquiring specific oxide phases: (a) CuO and Cu₂O, (b) ZnO, (c) NiO, (d) TiO₂, (e) Al₂O₃ and (f) Cr₂O₃. The grey curves correspond to the baseline.

Figure 6.9-(c) represents the binding energy spectrum of the Ni 2p electrons exhibiting the typical features of Ni²⁺ ions [220]. The spectrum is composed by multiplet splitting and satellite structures. The main contributions of the complex structure are at 854.54, 856.14 and 861.60 eV associated with 2p_{3/2} multiplet-split. The splitting of the 2p_{3/2} photoemission of ~1.6 eV is a common feature for NiO

oxidation state [221]. The band at 873.04 eV corresponds to the $2p_{1/2}$ multiplet-split [222] and the two bands at 880.33 and 861.60 eV are due to charge-transfer multielectron excitation.

The photoelectron spectrum displayed in Figure 6.9-(d) contains the bands of the Ti 2p electrons characteristic of TiO_2 . The $2p_{3/2}$ and $2p_{1/2}$ spectral bands are composed of a single peak at a binding energy of 458.78 and 464.41 eV, with a FWHM of 1.51 and 2.31 eV, respectively, meaning the Ti element in the oxide mainly exist as Ti^{4+} . Moreover, the separation between the $2p_{3/2}$ and the $2p_{1/2}$ lines is 5.63 eV, characteristic of the TiO_2 phase, as reported in [223].

The spectra illustrated in Figure 6.9-(e) containing a single line with peak at 74.81 eV and FWHM of 1.75 eV can be assigned to the Al 2p electrons and is characteristic of aluminium (III) oxide (Al_2O_3) [131].

The pattern of Figure 6.9-(f) is formed by two main bands associated to the Cr $2p_{3/2}$ and the $2p_{1/2}$ electrons with peaks at 576.64 and 586.45 eV and FWHM of 2.74 and 3.48 eV, respectively, which can be assigned to the Cr_2O_3 chemical state [224]. The band shift of these two peaks is 9.81 eV, which is in good agreement with previously reported data and confirms the existence of Cr_2O_3 chemical state [225]. A detailed analysis of these bands need to consider the multiplet splitting as well as satellite structures [226].

The spectrum of O 1s of the Zn sample after annealing was deconvoluted into three peaks, as shown in Figure 6.10-(b). The component peak corresponding to 530.20 eV is related to the *wurtzite* structure of the O^{2-} ion in the Zn-O bounding in the lattice and to the typical ZnO structure [227] while the components at 531.63 eV and 532.69 eV are associated to the existence of OH^- groups at the ZnO surface, respectively, and to the presence of C=O bonding originated by molecules adsorbed on the surface [228, 229]. Figure 6.10-(b) shows the O 1s signals of the annealed copper samples at 225 ° and 600° C. The two curves show an energy shift of 0.69 eV. The lower binding energy peak at 529.76 eV corresponds to the Cu_2O phase, while the major peak of red curve at 530.15 eV could be assigned to the CuO phase which is in agreement with the literature [230, 231]. The low intensity peaks in both curves corresponding to higher binding energies are associated to undecomposed copper acetate and water containing species as hydroxyl groups and oxygen atoms in the carboxyl groups [232].

An overview of the four remaining spectra reveals that all lines may be deconvoluted into two gaussian curves. From the calculation was found that for the metals, Ni (c), Ti (d), Al (e) and Cr (f), the value of the binding energy of the O 1s electrons, associated with metal-oxygen bond is (value

of the FWHM in parenthesis) 530.23 eV (0.98 eV), 530.10 eV (1.69 eV), 532.63 eV (2.04 eV) and 530.13 eV (1.04 eV), respectively, in close agreement with [131, 220, 223, 224]. The value of the remaining curve that resulted from each deconvolution is 531.12 eV (2.36 eV), 531.47 eV (0.99 eV), 531.63 eV (1.55 eV) and 531.25 eV (2.51 eV) for Ni, Ti, Al and Cr, respectively, as reported in [131, 220], and can be attributed to emission from oxygen-containing species adsorbed at defects, such as OH⁻ [217, 223].

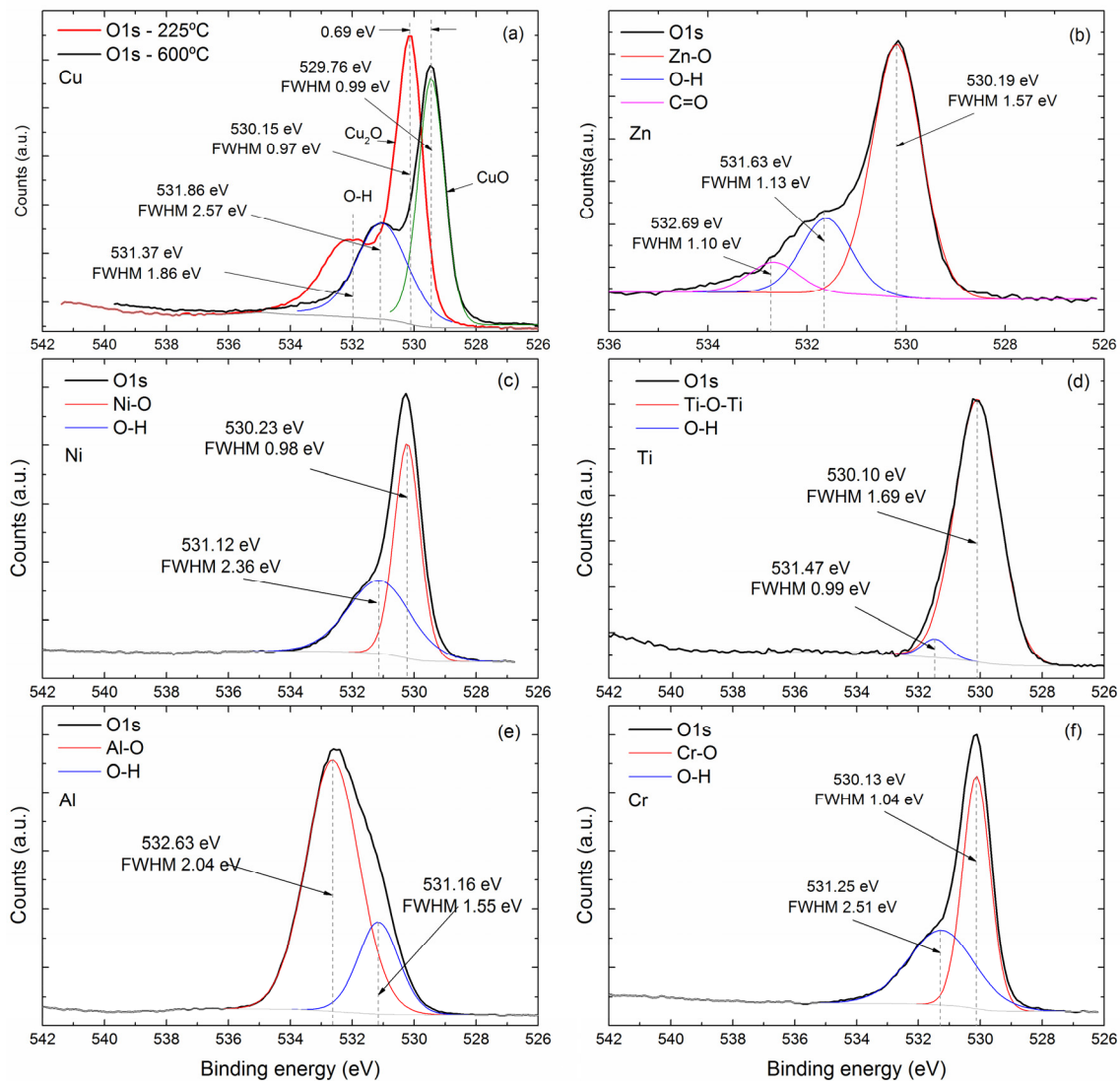


Figure 6.10 – Binding energy spectrum of O 1s electrons obtained by XPS of thin film samples as deposited and after annealing in air at 600 °C for 1 hour: (a) CuO and Cu₂O (at 225 °C), (b) ZnO (c) NiO, (d) TiO₂, (e) Al₂O₃ and (f) Cr₂O₃.

– *Characterization by X-ray diffraction*

The X-ray diffraction patterns of the oxide thin films on Si substrate after annealing are shown in Figure 6.11 and Figure 6.12 together with the identification of the peaks consistent with the corresponding metal oxides using data presented in the RRUFF database [233].

Figure 6.11 shows the two Cu samples with different annealing temperatures, at 225 °C (a) and 500 °C (b) for 1 h. The diffraction patterns of both samples are in perfect agreement with the RRUFF database given by the triangle shape symbols. At 225 °C a strong peak at 36.5 ° corresponds to the (111) direction which is characteristic of Cu₂O (cuprite). At 500 °C the structure changes completely showing two strong peaks at 35.7 ° (111) and 38.8 ° (-111) plus one at 49.0 ° (-202). The cross symbols (-×-) shows the peak positions of the plane directions corresponding to the metal phase which is not detected in the spectrum.

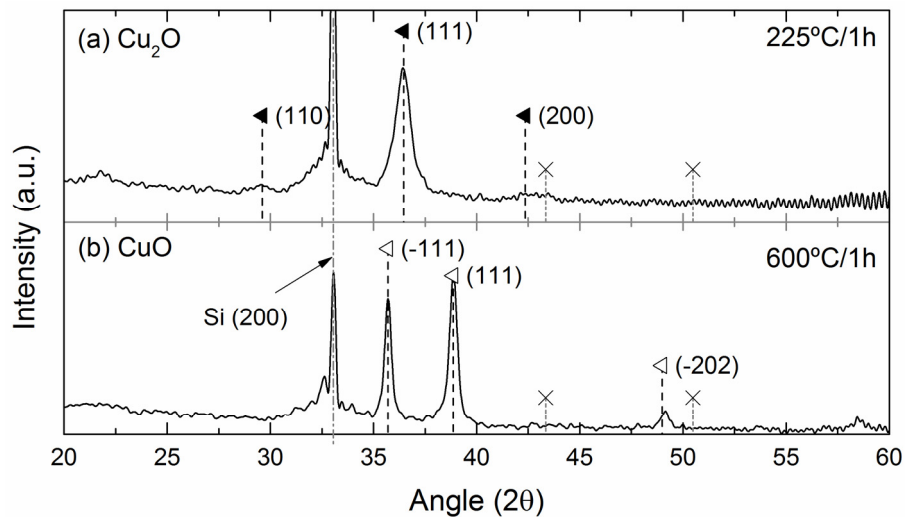


Figure 6.11 – XRD of thin film samples after annealing in air for 1 hour together with database values (RRUFF database): (a) Cu₂O at 225 °C, (b) CuO at 600 °C. The symbol (×) corresponds to the planes of the Cu metal.

The noticeable peak of the Si 200 reflection at about $2\theta \approx 33.1^\circ$ for Si (100) substrates can be observed in all X-ray patterns. It is known that this reflection and the Si (222) reflection at $2\theta \approx 58.9^\circ$ for Si (111) substrates are basis-forbidden reflections. Even though the reason for the occurrence of both reflections has been known for many decades, especially concerning the Si 200 reflection daring explanations can still be found in recent publications: for example, that it occurs only when the Si lattice is distorted (or that it stems from the Si 400 Bragg reflection of half the wavelength of the Cu K α radiation [234].

The diffraction patterns of the Zn, Ni, Ti, Al and Cr thin films deposited on Si substrates after annealing are shown in Figure 6.12. The absence of metallic phase in the samples can be established from a preliminary survey of the four figures. In addition, the low annealing temperature lead to the formation of partially amorphous thin films.

After annealing at 400 °C in air for 1 h, the diffraction patterns of Zn disappear, as shown in -(a), and the metallic zinc is completely transformed into ZnO (zincite). Six peaks appear at 2θ from 20° to 65° and they correspond to the (100), (002), (101), (102), (110) and (103) directions of the hexagonal ZnO crystal structure [214]. The XRD analysis of a ZnO thin film indicated that oxidizing a Zn thin film at 400 °C in air for 1 h the metallic zinc is completely transformed into ZnO (zincite).

The spectrum of the Ni annealed sample [Figure 6.12-(b)] shows clearly visible NiO (111) and NiO (200). Although very small, both peaks are narrow pointing to a reasonable crystallite size.

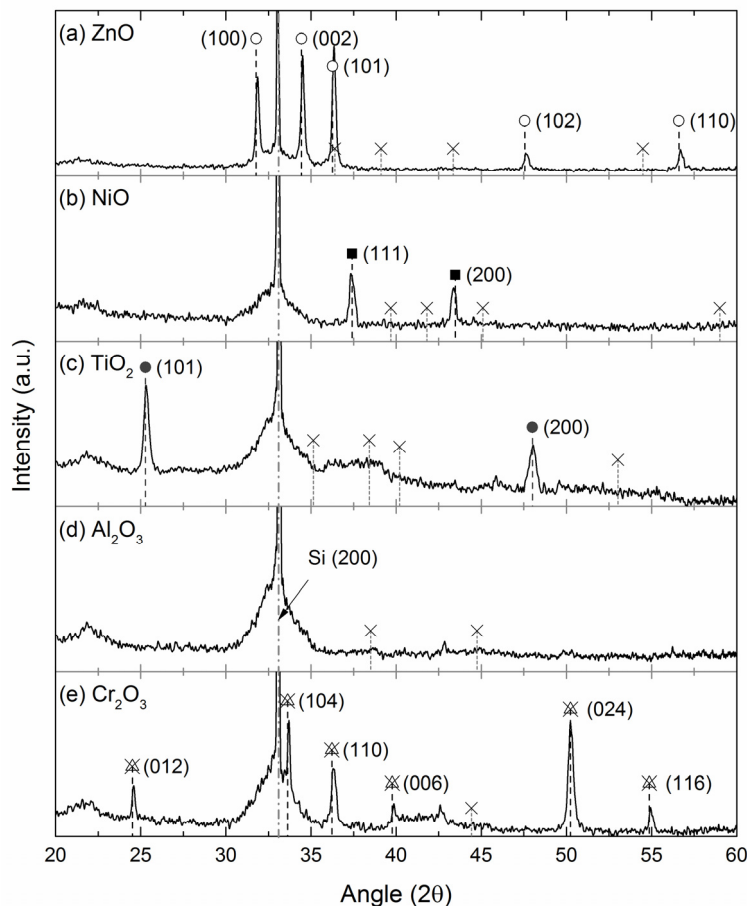


Figure 6.12 –XRD pattern of thin film samples after annealing in air at 600 °C for 1 h together with the RRUFF database values: (a) ZnO, (b) NiO, (c) TiO₂, (d) Al₂O₃ and (e) Cr₂O₃. The symbol (×) corresponds to the planes of the metal.

The starting of the formation of the anatase phase is evident from the presence of the TiO_2 (101) and TiO_2 (200) peaks in Figure 6.12-(c) compatible with reported data for TiO_2 films annealed at different temperatures [235]. The pattern displayed in Figure 6.12-(d) point to the formation of a fully amorphous Al_2O_3 thin film, which was expected because it is known that transformation to γ -, θ - and α -alumina phases requires a temperature higher than 600 °C [236]. The annealing of the Cr film produced a partially amorphous oxide layer whose X-ray pattern, shown in Figure 6.12-(e) has a few peaks matching the chromium (III) oxide (eskolaite) [233, 237].

6.2.3 Optical Characterization with LPFGs

The optical characterization of the LPFG coated with the oxides produced by the thermal annealing from metal thin films is based on the optical features of the attenuation band. It has been already presented in section 4.3 systematic studies using LPFGs coated with the oxides TiO_2 and ZnO for a set of coating thicknesses. While the ZnO thin film was produced by the procedure here described, the previous TiO_2 thin films were produced inside the vacuum chamber with an oxygen atmosphere. Nevertheless, the ZnO results should be highlighted considering approximately the same thickness to allow the comparison with the other metals.

From the chemical and morphological analysis presented above the new coating structures can be assumed to be in the form of Cu_2O , CuO , ZnO , NiO , TiO_2 , Al_2O_3 and Cr_2O_3 , with refractive indices at 589.3 nm found in the literature of 2.670, 2.630, 2.006, 2.020, 2.620, 1.769, and 2.551, respectively [159, 238-241]. The wavelength shifts and intensity variations of the attenuation band before and after the oxide coating process are combined in Figure 6.13-(a) for all the coatings studied in this work depending on the refractive index of the structure of each oxide layer.

A negative wavelength shift higher than 8 nm is observed for all the coating oxides with the exception of Al_2O_3 which presents a positive shift. In average, is observed an attenuation reduction while for ZnO and Al_2O_3 an increase up to ~2 dB occurred. The changes in the characteristics of the optical spectrum of the coated LPFG leads to improvements of the sensitivity to higher SRI in the liquids range.

The optical power shift due to the formation of the oxide phase is shown in Figure 6.13-(b). With the exception of the Cr_2O_3 , the optical power shifts increases with the increase of the RI of the oxides. For the particular case of Cu annealing it is well visible the difference in optical power of 2.5 dB

between the two phases Cu_2O and CuO although the similar RI value according to the literature [238, 240] .

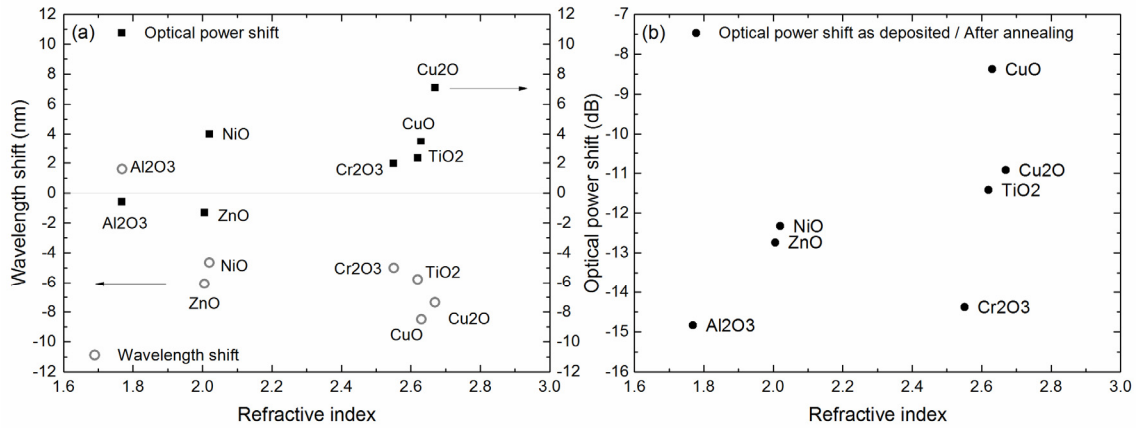


Figure 6.13 – Variation of as a function of the oxides RI: (a) wavelength and optical power shifts before and after the oxide coating and (b) optical power shift before and after the metal oxidation.

Figure 6.14 and Figure 6.15 presents the measured transmission spectra, from 1350 to 1600 nm, corresponding to LP_{16} mode of LPFGs coated with all the metal oxides, for SRI values from 1.300 to 1.600 at 589.3 nm of wavelength. A blue-shift of the resonance band is observed until the value of the SRI is common to all samples and comparable to the CRI (1.457) of the fibre. For SRI higher than the CRI a shift for higher wavelengths is observed together with a substantial reduction in the attenuation bands. Even though for SRI higher than the CRI the attenuation band shows a relatively high intensity. This behaviour is similar for bare and coated LPFGs although the wavelength shift and the attenuation variation with the SRI are clearly more evident for the coated LPFG due to the higher effective SRI.

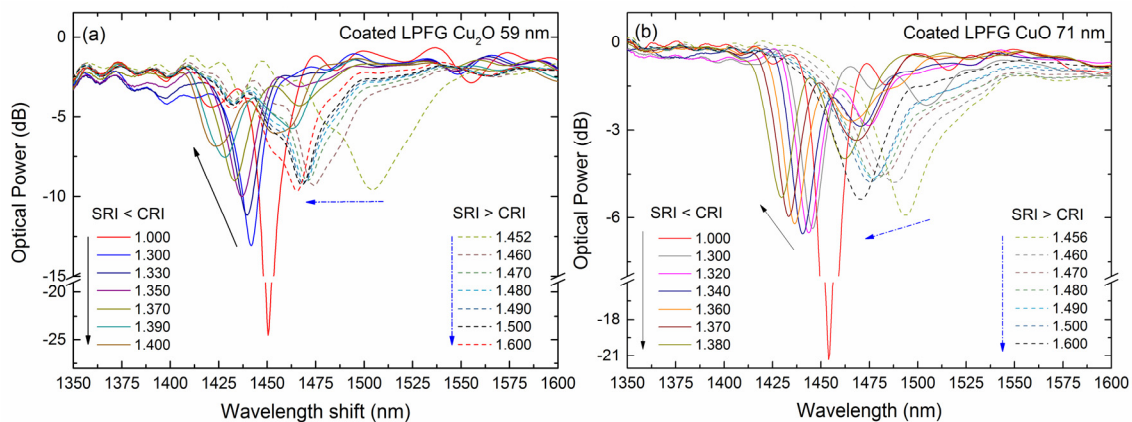


Figure 6.14 – Spectral response from 1350 to 1600 nm, corresponding to LP_{16} mode of LPFGs coated with Cu after annealing (a) at 225 °C – Cu_2O and (b) 600 °C - CuO .

The spectral characterization of the coated LPFGs with 67 nm of Cu_2O -(a) and CuO -(b) from Figure 6.14 reveals differences in the optical response. It is visible a strong reduction of the optical power of the attenuation band common to both sensors, however while the SRI increases the both bands assume slightly different behaviour. All the others LPFGs in Figure 6.15 assumes differences in the optical response.

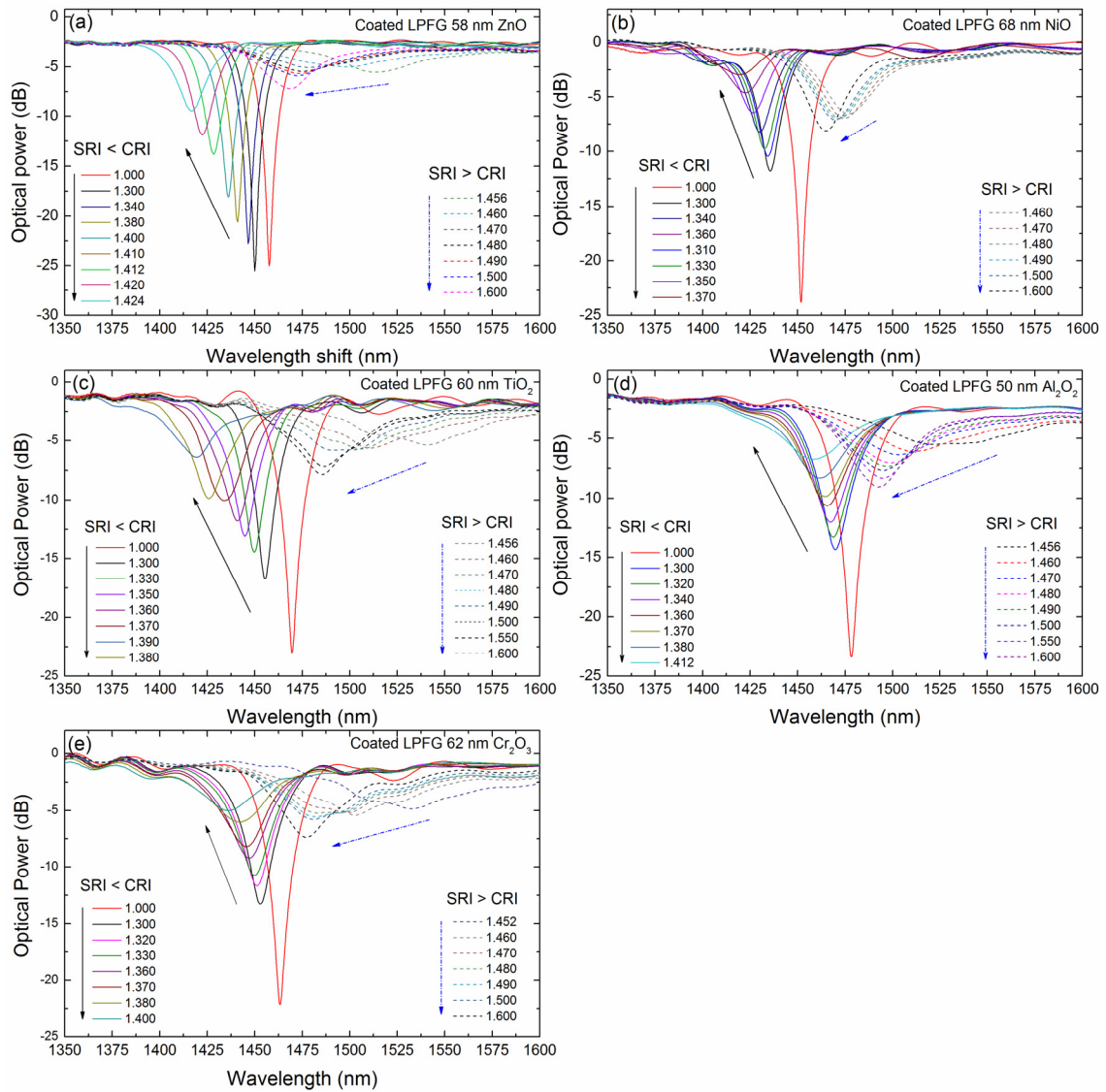


Figure 6.15 – Transmission spectra, from 1350 to 1600 nm, corresponding to LP16 mode of LPFGs coated with (a) ZnO , (b) NiO , (c) TiO_2 , (d) Al_2O_3 and (e) Cr_2O_3 for SRI values from 1.300 to 1.600.

The wavelength shift and the optical power of the attenuation band minimum normalized to the initial state ($\text{RI}=1.000$) is presented in Figure 6.16 and Figure 6.18, respectively, for all oxide samples

compared to the bare LPFG. The expected sensitivity improvement is observed in all cases. The two oxidation phases of Cu with variations in the composition leading to different optical properties which are reflected in Figure 6.16-(a). The CuO oxidation phase presents an average higher sensitivity to the SRI below the CRI but is limited to 1.360, while with the Cu₂O is possible to measure up to 1.420. In addition, for SRI higher than the CRI, CuO offers a higher wavelength shift than Cu₂O. However, the superior sensitivity exists in a narrower range.

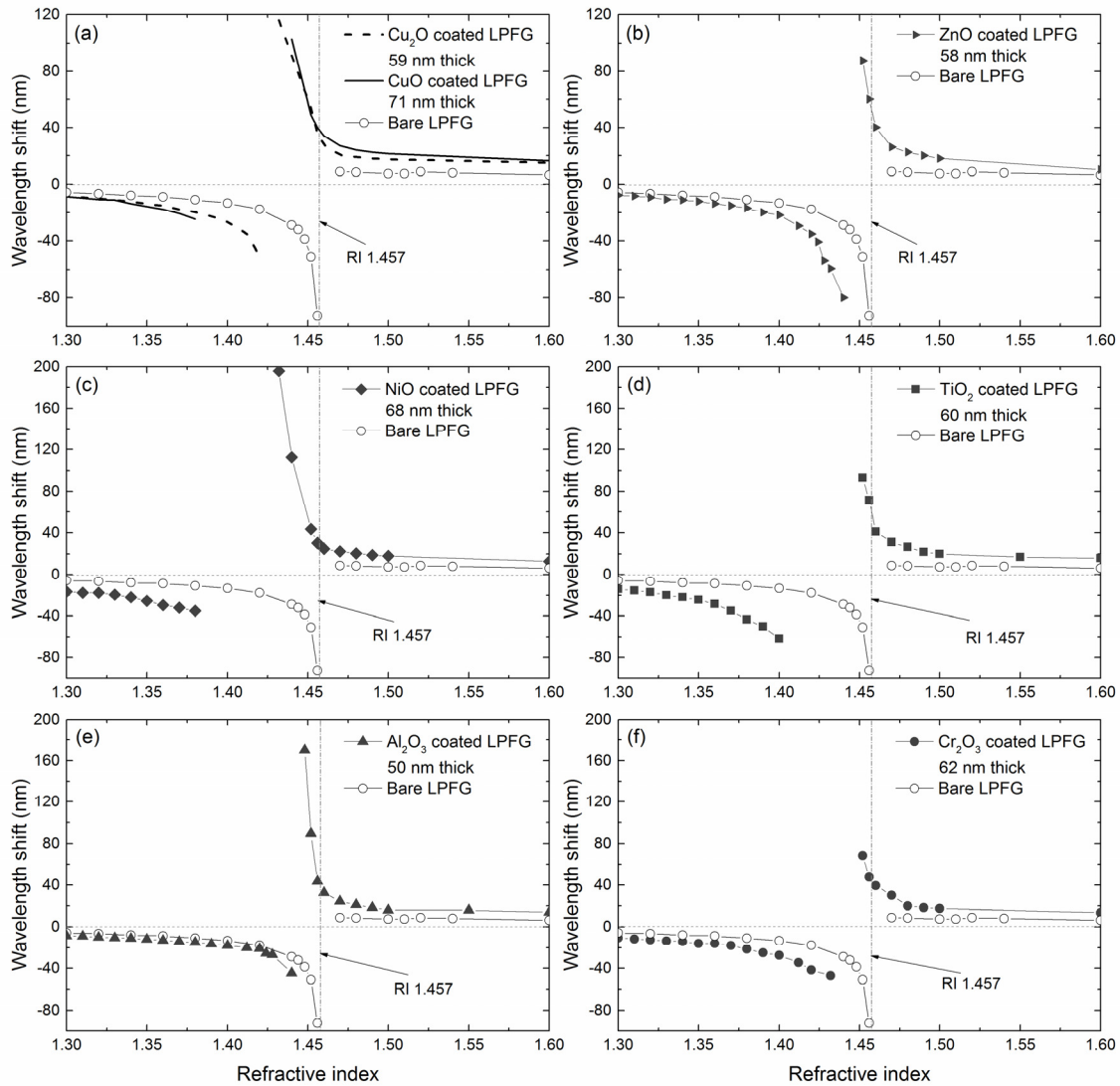


Figure 6.16 – Wavelength shift normalized to the initial state (RI=1.000) from 1350 to 1600 nm, corresponding to LP₁₆ mode of a bare LPFG and of LPFGs coated with (a) Cu₂O and CuO, (b) ZnO, (c) NiO, (d) TiO₂, (e) Al₂O₃ and (f) Cr₂O₃ for SRI values from 1.300 to 1.600.

The sensitivity to the external refractive index with an LPFG coated with 58 nm of ZnO [Figure 6.16–(b)] is increased in the entire range of RI when compared with the bare LPFG as discussed in section 4.3.2. The LPFGs show an increased wavelength shift for SRI lower than CRI, particularly for NiO (a), TiO₂ (b) and Cr₂O₃ (d) coatings. For example, in the 1.340-1.380 region, the average shift is less than 9.7 nm for a bare LPFG while for NiO, TiO₂ and Cr₂O₃ coating the average shift is in the 32-36 nm range.

Both the TiO₂ and Cr₂O₃ coatings provide the highest shift for SRI higher than the CRI, the TiO₂ coating seems to be a better solution for applications where the SRI is smaller than the CRI. For instance, for a 60 nm thick TiO₂ and 62 nm thick Cr₂O₃ coatings, the shift for a SRI of 1.470 is about 31.1 and 30.1 nm, respectively (where a bare LPFG is virtually useless). On the other hand, at RI of 1.400, the TiO₂ shifts the attenuation band 61.5 nm which is the double provided by the Cr₂O₃. The LPFG coated with 50 nm of Al₂O₃ shows, as illustrated in Figure 6.16-(c), very low improvement in the wavelength shift compared to the bare LPFG in the lower RI range. Nevertheless, for a RI of 1.448 a wavelength shift of 170 nm is attained.

The sensitivity level of the LPFGs coated with the different oxides in the SRI range from 1.300 to 1.600 is calculated with the 1st derivative of the data plotted in Figure 6.16 and shown in Figure 6.17. It can be easily observed that the behaviour of the sensitivity is different for each coating, thus being possible to choose an optimized metal oxide coating depending on the SRI to be measured. The Figure 6.17-(a) and -(b) show the results for lower SRI (left side of the 1.000) and higher SRI (right side of the 1.000), respectively.

While the CuO coated LPFGs shows sensitivities up to 500 nm/RIU for RI of 1.375, the Cu₂O reach 2000 nm/RIU around 1.420.

For SRI smaller than the CRI the sensitivity can be as high as 1050 nm/RIU at 1.420, 10437 nm/RIU at 1.432, 1150 nm/RIU at 1.400 and 875 nm/RIU at 1.420 for LPFGs coated with 58 nm of ZnO, 68 nm of NiO, 60 nm of TiO₂ and 62 nm of Cr₂O₃, respectively. Moreover, a very high sensitivity of 20125 nm/RIU at 1.448 is achievable using a 50 nm thick Al₂O₃ coating. For SRI higher than the CRI the sensitivities coated LPFG are 1937 nm/RIU, 6801 nm/RIU, 5762 nm/RIU and 3051 nm/RIU at 1.457 for the Ni, Ti, Al and Cr oxides, respectively. The sensitivity decrease as the RI increase but are far higher than the bare LPFG.

In section 3.1.3 the fabrication and characterization of TiO₂ coated LPFG was presented where the oxide layer has been grown by evaporation of pure titanium in an oxygen rich atmosphere. The

reported sensitivity is smaller for either SRI smaller or higher than the CRI. For instance at 1.360 and at 1.470 the reported sensitivities were 350 and 460 nm/RIU, respectively, while the corresponding sensitivity measured in this section are 525 and 725 nm/RIU, respectively.

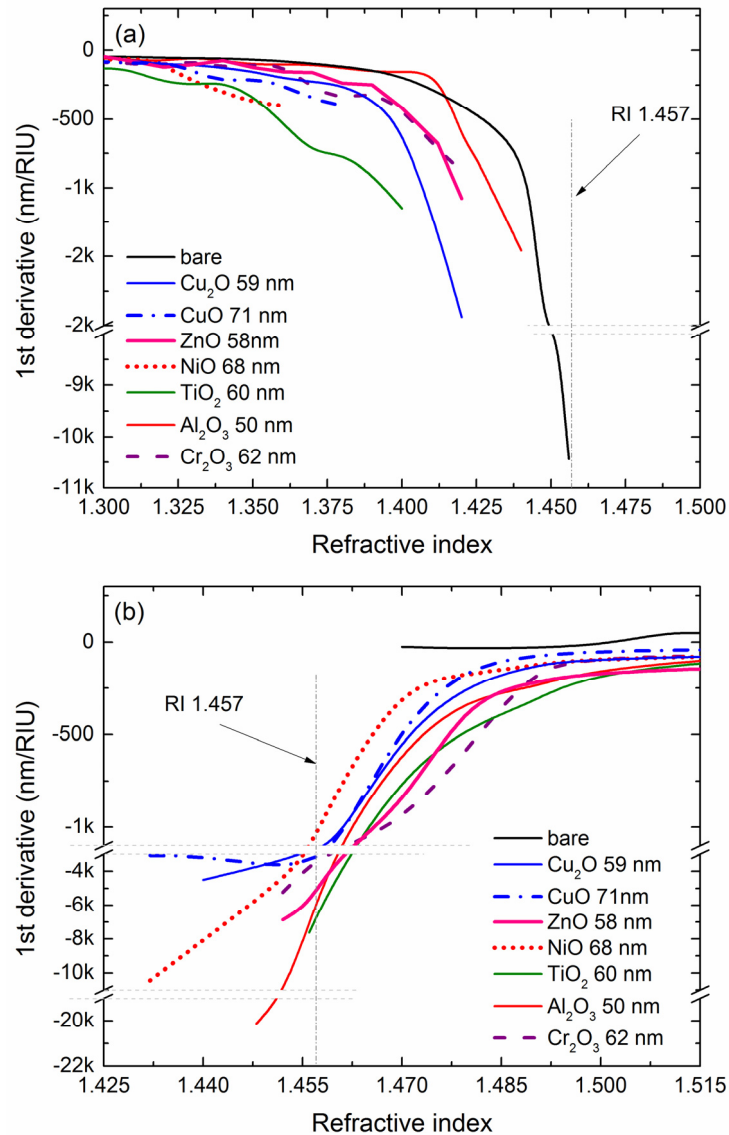


Figure 6.17 – Wavelength sensitivity as a function of the surrounding refractive index for a bare LPFG and for LPFGs coated with Cu₂O, CuO, ZnO, NiO, TiO₂, Al₂O₃ and Cr₂O₃ from (a) 1.300 to 1.500 and (b) 1.425 to 1.515.

The sensitivity to the SRI exhibits also a variation in the minimum of the attenuation band, as can be seen in Figure 6.18, meaning that the LPFG could be used as an intensity sensor in a wide range of RI values. The sensitivity is larger for higher order modes, as observed in [146]. For the LPFGs of Figure 6.18 and for SRI smaller than the CRI it can be observed a region where a reasonable linear fit

was obtained. The optical power shift of the Cu_2O and CuO depicted in -(a) is reduced down to 30 % of the value in air. Cu_2O shows a linear behaviour in the wide SRI range 1.300 to 1.420, with a sensitivity of 69.38 dB/RIU. For CuO the intensity shift of the attenuation band is not significant in the same RI range.

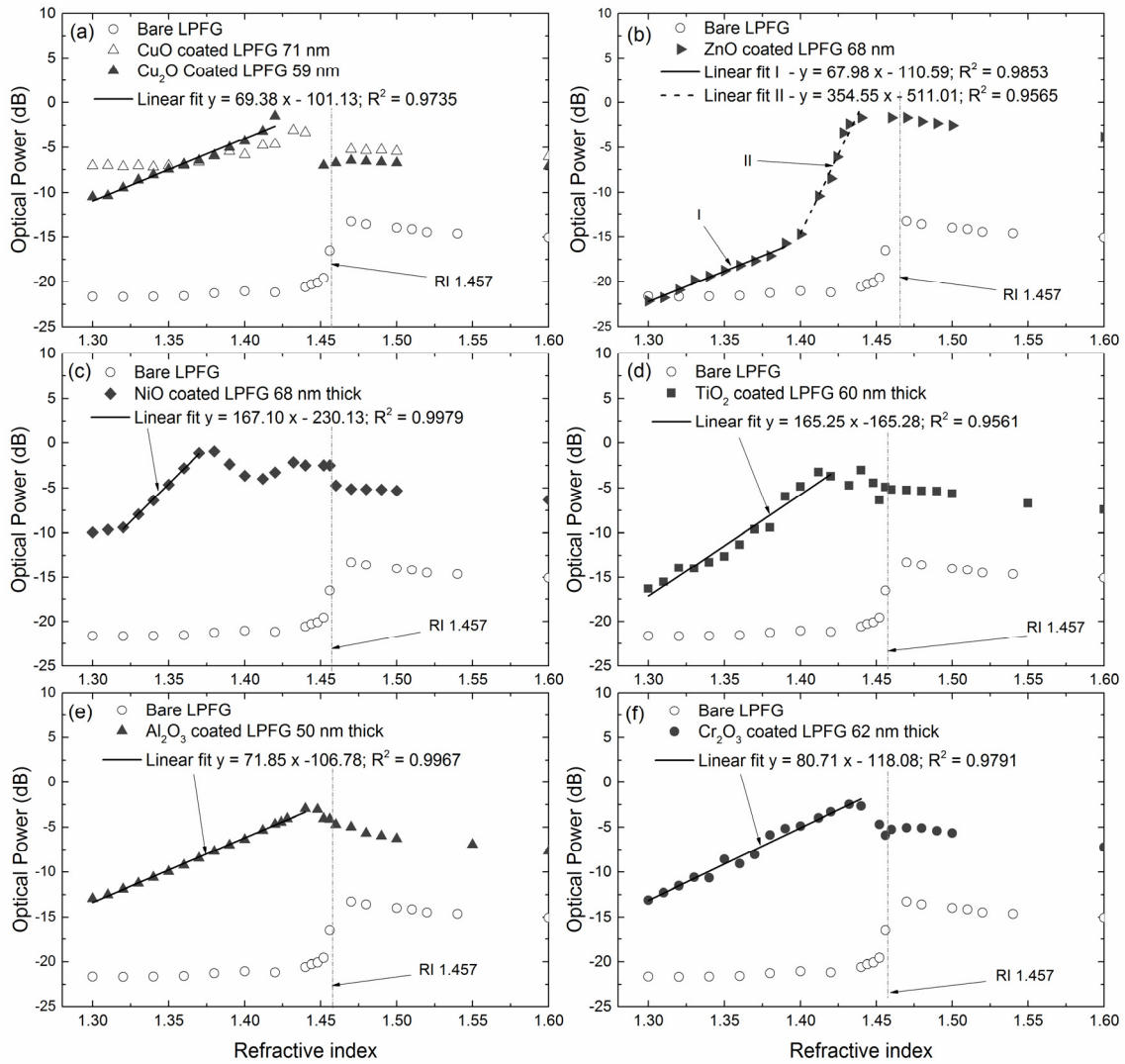


Figure 6.18 – Optical power variation of the resonance band corresponding to the LP_{16} mode of a bare LPFG and of LPFGs coated with (a) Cu_2O and CuO , (b) ZnO , (c) NiO , (d) TiO_2 , (e) Al_2O_3 and (f) Cr_2O_3 oxides for SRI values from 1.300 to 1.600.

The ZnO [Figure 6.18-(b)] shows a total optical power variation above 20 dB in the same RI range with linear behaviour in two regions I (1.300-1.400) and II (1.400-1.435) with sensitivities of 67.98 and 354.55 dB/RIU respectively. The NiO coating [Figure 6.18-(c)] shows a high sensitivity (~ 167 dB/RIU) and linearity ($R^2=0.994$) in a band from 1.320 to 1.370. The working range is limited

but in an adequate region for chemical and biosensing. Larger RI intervals are achievable using TiO_2 with 165.25 dB/RIU or with lower sensitivities of 72 and 80.7 dB/RIU using Al_2O_3 [Figure 6.18-(e)] or Cr_2O_3 [Figure 6.18-(f)] respectively, in the range from 1.330 to 1.440.

In bare LPFGs the cladding mode suffers the influence of the SRI while using a certain oxide coating there is a combination of all the RI near the cladding surface. Above a certain value of the RI coating when the effective RI is equal to that of cladding no guided modes are supported by the cladding mode and no attenuation bands are observed [147]. For higher RI coatings when placed in high SRI the attenuation bands can be explained by the existence of leaky modes due to the RI profile. Increasing the SRI the leaky mode became better confined with additional attenuation [14].

6.3 Conclusions

Real time monitoring oxidation of coatings using LPFGs was studied for a set of metal thin films as Zn, Cu, Ni, Ti, Al and Cr. The optical properties of the metal coated LPFG were analysed when subjected to a certain annealing temperature oxides into a specific structure. The transmission spectra of the LPFG allows to obtain, in real time, the oxidation phase transition of all the metals in study and the correspondent temperature level was identified. It was demonstrated that using a single LPFG coated with a thin film of metal is possible to estimate the oxidation state by measuring the intensity of the attenuation band during the process. The metal samples before and after annealing at specific temperatures were analysed by its morphology and chemical state showing good indicators of full oxidation into ZnO , CuO , Cu_2O , NiO , TiO_2 , Al_2O_3 and Cr_2O_3 .

The LPFGs coated with the different oxides were able to enhance the intrinsic sensitivity to external refractive indices which depends on their morphology and chemical state which induce variations on the effective refractive index, leading to the sensitivity improvement.

In particular, considering the Cu oxide into two different phases, CuO and Cu_2O at distinct annealing temperatures, 225 and 600 °C respectively, the optical characterization based on the LPFG transmission signal was able to distinguish the two phases returning slightly different optical response to the external refractive index medium.

Measurement of the transmission spectrum allowed the calculation of the wavelength and attenuation sensitivity as a function of the refractive index of the surrounding medium in the 1.300 to 1.600

range, thus adding an extra degree of freedom in the design of LPFG sensors to be used as refractometers of liquid mixtures of either water based solutions or liquid organic compounds.

Wavelength sensitivities of about 10437 nm/RIU at 1.432, 1150 nm/RIU at 1.400, 20125 nm/RIU at 1.448 and 875 nm/RIU at 1.420 were achieved for LPFGs coated, with 68 nm of Ni, 60 nm of TiO₂, 50 nm of Al₂O₃ and 62 nm of Cr₂O₃, respectively. For surrounding RI higher than the cladding RI, the wavelength sensitivities are 1937 nm/RIU, 6801 nm/RIU, 5762 nm/RIU and 3051 nm/RIU at 1.457 for the Ni, Ti, Al and Cr oxides, respectively.

Working as intensity sensing devices, sensitivities up to 167 dB/RIU with the NiO coating at ~1.350 and of 354.55 dB/RIU with ZnO at ~1.420 were found for thickness layers up to 68 nm.

The two Cu oxide phase leads to different optical responses with better performance in the Cu₂O coated LPFG for both wavelength and intensity modulation. Nevertheless, the CuO phase shows a slightly higher range for SRI higher than CRI.

It can be concluded that metal oxide coated LPFGs leads to wavelength and intensity sensitivity enhancement comparing to bare LPFGs. In addition, metal oxide coated LPFGs may be used in systems with RI higher than the fibre cladding, a region where bare LPFGs are insensitive.

Chapter 7

A Study of the Quality of Olive Oils with Coated Long Period Fibre Gratings

In this chapter a sensing device based on a TiO_2 coated LPFG is used to detect variations on liquid samples with refractive index higher than the optical fibre cladding and applied to evaluate the quality of edible oils. With this target two different experimental studies are presented, one intends to monitor the thermal deterioration of an extra virgin olive oil, while the second one addresses the study of how contaminants as hexane influence the properties of edible oils permitting to access their quality.

7.1 Introduction

One of the most controlled markets in the world is the food industry where all the processes must be efficient and reliable to preserve the quality of the final products. Edible oils (EO) are a particular category in this industry with a long list of different sources with specific functions either uncooked or to be used in the food preparation. The production of EO is increasing, as reported by the Food and Agriculture Organization (FAO) [242]. Edible oils find application in the food industry as well

as in biofuel production, which will drive the EO demand in the next years [243]. Edible oils and fats are virtually omnipresent in food processing, either naturally present in foods or added as ingredients that convey functional properties. Although ingestion levels of oils and fats must be controlled in order to avoid health problems, such as obesity, however, along with proteins and carbohydrates, are one of the three macronutrients and therefore an essential part of a healthy diet [244]. Edible oils can be characterized by the colour, taste, smell, chemical composition and refractive index (RI). The intrinsic RI of some common edible oils @ 589.3 nm is presented in Table 7.1 in the range from 1.450 to 1.4800.

Table 7.1 – Refractive index of common edible oils

Oil	RI	Ref.	Oil	RI	Ref.
Coconut Oil	1.4490-1.4510	[245]	Hemp seed oil	1.4723	[245]
Palm Oil	1.4530-1.4580	[245]	Soybean Oil	1.4729	[246]
Sesame Oil	1.4650-1.4690	[246]	Poppy seed oil	1.4730-1.4760	[245]
Olive Oil	1.4679	[246]	Corn Oil	1.4735	[246]
Sunflower oil	1.4670-1.4690	[246]	Castor oil	1.4770	[246]
Peanut Oil	1.4697-1.4719	[245]	Cod-liver oil	1.4810	[246]

Extra Virgin Olive Oil (EVOO) is a particular edible oil with a strong presence in the so called Mediteranium diet. This special oil is made from fruits of the olive tree (*Olea europaea L.*) by mechanical processes (crushing, malaxation and centrifugation) and can be consumed by humans without additional treatments [247]. EVOO is recognised as a healthy foodstuff due to its capacity to prevent pathologies, such as cancer and cardiovascular diseases [248]. EVOO is a significant source of mono- and polyunsaturated fatty acids, tocopherols and phytosterols. Even though EVOO is a very stable foodstuff, autoxidation takes place leading to hydroperoxides, usually called primary oxidation products. Later the breakdown of these compounds leads to alcohols, aldehydes (mainly responsible for flavours and odours), ketones, lactones, hydrocarbons, fatty acids (secondary and tertiary oxidation products) and, in the last stage, the polymerization products is observed [249].

The enhanced optical spectral sensitivities achieved with the titanium coated long period fibre gratings (LPFG), makes them good candidates to be used to monitor the quality of edible oils. The range of RI of the common edible oils presented in Table 7.1 fits the high sensitivity spectral region of the coated LPFG as shown in Figure 4.15 (Section 4.3.1) which displays the spectral

characteristics of the attenuation band near 1550 nm, corresponding to the LP_{16} cladding mode. The bare LPFGs are virtually insensitive to surrounding refractive indices (SRI) higher than that of the fibre cladding (CRI), however, with a thin layer of TiO_2 the sensitivity to SRI can be increased to levels where edible oils can be monitored.

The wavelength shift as a function of the SRI, from 1.250 to 1.650, for a bare LPFG and for a LPFG with 30 nm thick TiO_2 film is shown in Figure 7.1. The data corresponds to the LP_{16} cladding mode and was normalized to the initial state ($n = 1.000$). In the 1.460 to 1.480 range, which fits to the majority of edible oils, the measured average sensitivity is about 800 nm/RIU. The shift in wavelength was calculated with an error smaller than 0.1 nm.

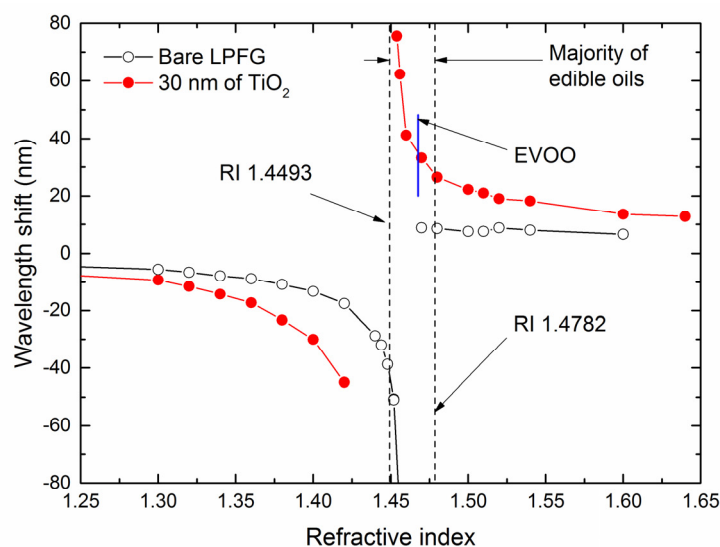


Figure 7.1 – Normalized wavelength shift as a function of the surrounding refractive index for a bare LPFG and for a LPFG with 30 nm thick TiO_2 film. Data corresponds to the LP_{16} cladding mode.

The enhanced properties of the TiO_2 coated LPFG device are used in this chapter to monitor the thermal deterioration of EVOO and its adulteration with organic solvents. Therefore, it was fabricated a LPFG with an overlay of 30 nm of TiO_2 following the procedures described in sections 3.1.1 and 3.1.3. The spectral characterization of the device was performed by an optical spectrum analyser (OSA) (ANDO, model AQ 6315B) and the RI range from 1.300 to 1.640 was considered in the studies described next sections.

7.1.1 Thermal Deterioration of Edible Oils

Uncooked EVOO keeps all its nutritional components, such as vitamins, essential fatty acids and antioxidants. However, EVOO is also frequently used for baking and cooking in Mediterranean countries where deep frying is a popular method for food preparation, either in traditional or in fast-food restaurants [250, 251]. During frying the oils change colour, thicken and acquire an unpleasant taste and odour [252].

During frying at high temperature edible oils in general and EVOO in particular, absorb oxygen and water suffering a wide range of reactions namely hydrolysis, oxidation, isomerization, and polymerization [252-256]. These reactions lead to an increase of polar substances, decomposition of essential fatty acids and in an increase in *trans* isomers [257]. The degradation substances formed during frying have nutritional and toxicological consequences in human health. Therefore, frying oils have to be substituted before substantial deterioration has taken place.

Several methods were developed to determine the deterioration threshold of frying oils, such as the measurement of free fatty acids, total polar compounds, alkaline materials, anisidine value, peroxide value, and mono- and diglycerides [252, 258]. However, most of these methods have the disadvantage of being expensive, time consuming, unsuitable for online monitoring and do not provide results in a short time interval. Therefore, accurate inexpensive and real-time methods of frying oil deterioration monitoring are required.

It has been reported by several authors an increase of the refractive index (RI) after frying EVOO along with an increase in free fatty acids and peroxide value and a decrease of natural anti-oxidants (phenols and α -Tocopherol) [259, 260]. It was also reported an increase of the RI after thermo-oxidative degradation of vegetable shortening [259], canola oil [261] and of sunflower oil [262].

Optical techniques, such as Raman, fluorescence and absorption spectroscopy are reagentless, non-destructive analytical techniques [263]. Namely, near infrared (NIR) and Fourier transform infrared (FTIR) spectroscopy found application across a wide range of fundamental [264] and applied sciences [265] and production lines in industry [266]. FTIR spectroscopy has been used to monitor the thermal stability of sunflower and canola oils [267] and to study the kinetics of EVOO deterioration [268, 269].

The detection of small levels of adulteration or accurate monitoring of thermal deterioration of edible oils could be achieved by LPFGs provided that the high wavelength sensitivity to SRI variations

could be used as sensing mechanism. However, most edible oils have RI higher than the CRI of optical fibres. Coating the bare LPFG with a thin film with RI higher than the CRI could lead to the realization of a chemical sensor for the food industry.

7.1.2 Adulteration of Edible Oils

The production of EO consists of two separate processes, extraction and refinement. During extraction, oil is removed from healthy and intact seeds, nuts or fruits and after that refinement alters its appearance, texture, taste, smell or stability to meet consumer expectations [270]. There are three main processes of EO extraction, pressing (using an expeller press), decanter centrifuge and chemical solvent extraction [244]. High quality EO extracted by cold pressing have high tocopherols, sterols, carotenoids, and phospholipids concentrations [271], and a few, such as extra virgin olive oil [272], can be directly consumed unrefined by humans. However, since the oil pomace obtained by pressing still retains 3 to 15 % of residual oil, it is desirable to carry out a more complete extraction with organic solvents.

Modern commercial methods of chemical extraction use volatile purified organic solvents, such as iso-propanol, ethanol, acetone and, especially, the various grades of petroleum benzin, commonly known as petroleum ether or commercial hexane [273]. In fact, a major part of the global EO production in commercial applications derives from chemical extraction processes which have been extensively used in the food industry [274]. These techniques are less expensive, quicker and lead to higher extraction yields [270].

After extraction the oil is separated from the solvent (which is recycled back to the extractor) and then processed using conventional refining techniques such as, degumming, neutralization, washing, drying, bleaching, filtration and deodorization. These processes are intended to remove minor components such as phospholipids, free fatty acids, colouring pigments, proteins and oxidation products [275].

Crude EO contains residual solvents, which raises safety and operational issues during storage and processing. As storage tanks are usually kept at normal pressure, without any inert gas system, the residual solvent may thus accumulate in the vapour phase. The eventual formation of flammable mixtures inside confined volumes may result in explosion in the case of accidental ignition [276]. Recently, several identified accidents involving mixtures of EO with hexane were reported, of which

more than half occurred in extraction plants during regular process stages. Two tragic accidents occurred in vegetable oil refineries in Italy in 2006 and in Spain in 2007, due to accidental ignition of flammable mixtures in EO storage tanks [276].

The introduction of optical fibre sensors in this kind of environments can avoid some of these problems. In this chapter, the wavelength response of a long period fibre optic grating coated with a layer of titanium dioxide (TiO_2) is used to screen the RI change caused by the thermal deterioration of EO and to monitor the concentration of organic solvents in these oils.

7.2 Detection of Extra Virgin Olive Oil Thermal Deterioration

7.2.1 Materials and Methods

The deteriorated samples were produced from a commercial extra virgin olive oil which was heated at 180 and 225 °C for periods of time from 1 to 57 hours. A glass beaker with 350 ml of oil was placed on a hotplate fitted with a temperature controller (± 1 °C) and continuously mixed with a magnetic stirrer. At each sampling time a 6 ml sample was collected and stored in dark glass vial at room temperature (~ 21 °C) in order to prevent modifications with the light exposition. Measurements of each sample were accomplished within 48 hours so they can provide comparable results.

The visible (VIS) and NIR absorption spectra were acquired from 345 to 1700 nm with a resolution of 3 nm. A tungsten halogen light source equipped with a cuvette holder and a connector for a patch cord was used (Avantes, AvaLight-Hal, Netherlands). Spectra were collected using two diode-array fibre optic spectrometers (USB4000 and NIRQ5120 from Ocean Optics, USA, respectively) and a bifurcated cable (SPLIT400-VIS-NIR, Ocean Optics, USA). The spectra acquisition was performed by pipetting ~ 3 ml of oil into a plastic cuvette. Each measurement was repeated twenty times and averaged using the software that controls the equipment. The white light spectrum was recorded and the raw spectra normalized accordingly and the absorbance expressed in dB/cm.

7.2.2 Sensing Device and Experimental Setup

The EVOO samples were characterized with the TiO_2 coated LPFG with a similar setup to the one described in section 4.3 and presented in Figure 7.2.

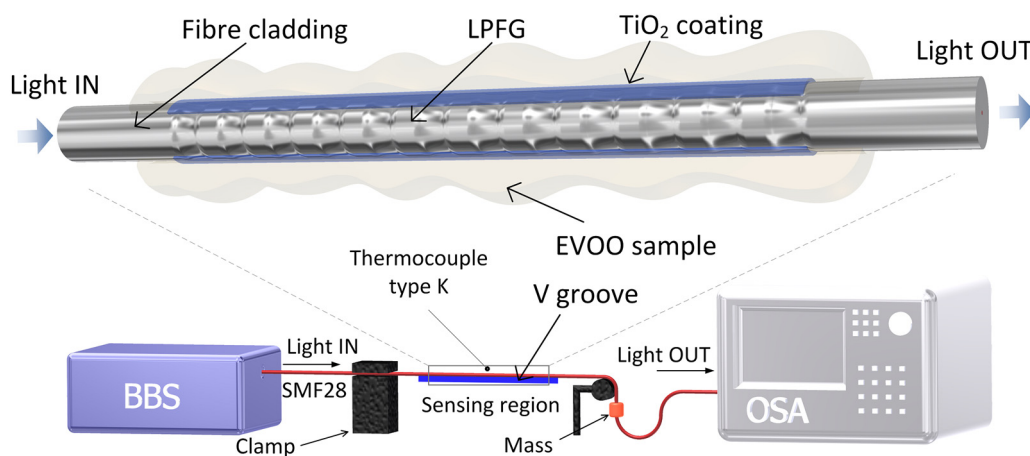


Figure 7.2 – Scheme of the sensing device and of the measuring set-up. (BBS-broadband source, OSA-optical spectrum analyser, SMF – single mode fibre.)

Each oil sample to be tested was placed in a glass V groove aligned with the sensing region in the fibre covering the entire LPFG length. After each measurement both fibre and the V groove were flushed with acetone to avoid contamination to the next oil sample. The temperature of the setup was monitored with a thermocouple type K and kept constant within ± 1 °C.

7.2.3 Results and Discussion

– Spectroscopic characterization

The VIS and NIR absorption spectra can be considered a fingerprint of the olive oil [277]. The spectroscopic data can be processed for obtaining a correlation with quality indicators, origin of production, as well as to oxidation or thermal deterioration [278].

Figure 7.3 represents the VIS absorption spectra of samples before heating and after heating at 180 °C. The inset presents the corresponding NIR spectra. For the sake of clarity not all the heating times are presented. The curve labelled “Pure” was taken from an unheated sample while curve labelled “0 h” corresponds to a sample taken after the oil reached the pre-stablished temperature (30 and 45 minutes for 180 and 225 °C, respectively).

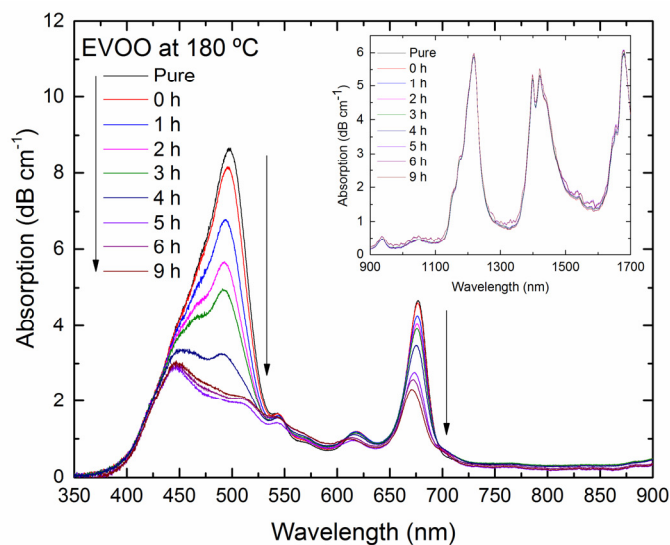


Figure 7.3 – Visible absorption spectra of olive oil samples before heating and after heating at 180 °C. The inset presents the corresponding near infrared absorption spectra.

The effect of thermal deterioration is clearly seen in the decreasing of the absorption band centred at ~677 nm, attributed to chlorophyll A [279]. Figure 7.4 shows the decrease of the integral of the band calculated between 640 and 740 nm as a function of the heating time for both temperatures.

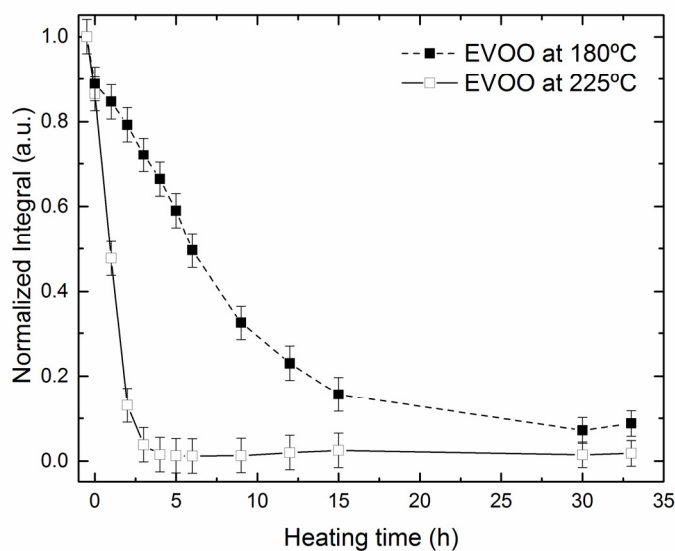


Figure 7.4 – Integral of the absorption band between 640 and 740 nm as a function of the heating time for 180 and 225 °C.

The integral decreases at a rate greater for a higher heating temperature. Also, absorption bands, between 400 and 550 nm, attributed to chlorophyll B and their derivatives (pheophytins), carotenoids

and flavonoids, such as anthocyanins, present a clear decrease with increasing heating time and temperature.

The NIR spectrum presents a band near 1218 nm, characteristic of the 2nd overtone of C-H stretching vibration of various chemical group (-CH₂, -CH₃, -CH=CH-) [280]. The bands near 1177 nm were assigned as the 2nd overtone of the C-H absorption of pure fatty acids containing *cis* double bonds (e.g., oleic acid). The region from 1300 to 1600 nm shows two weak bands centered near 1399 and 1421 nm. These absorption bands correspond to the combination of the C-H stretching vibration with other vibration modes. The absorption band of the 1st overtone of water highly perturbs the absorption at these wavelengths. As it can be seen, the NIR spectral data does not show clear information on thermal deterioration.

– Evolution of the refractive index

Many alterations of EVOO occurring during heating may lead to RI variations. Fatty acid composition measured by gas chromatography at the beginning and the end of frying was reported [255, 269]. The phenolic composition during heating was measured [281], the authors reported that hydroxytyrosol, elenolic acid, decarboxymethyl, oleuropein aglycon, and oleuropein aglycon presented reduced concentration after thermal treatment.

The RI of the samples was measured using an Abbe refractometer. Figure 7.5 presents the measured RI variation as a function of heating time for both temperatures.

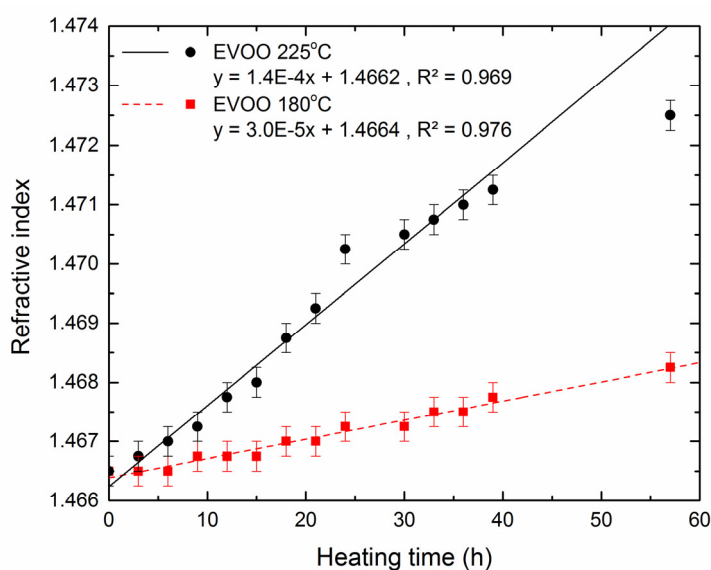


Figure 7.5 – Measured refractive index of olive oil as a function of heating time for 180 and 225 °C.

At room temperature (26 ± 1 °C) the RI was 1.46650 ± 0.00025 . However, as illustrated in Figure 7.5, the evolution of the RI with the heating time strongly depends on temperature. It increased until 1.47250 after 57 hours at 225 °C. It follows that thermal deterioration of olive oil can be monitored by measuring RI variations, which in turn can be scrutinized by measuring the wavelength shift of the LPFG based sensor described above.

– LPFG detection of thermal deterioration

Transmission spectra of the LP_{16} cladding mode of the 30 nm TiO_2 coated LPFG is illustrated in Figure 7.6-(a) from 1500 to 1620 nm with air and with EVOO as external medium, before heating and after heating for 6, 12, 30, 39 and 57 hours at 225 °C. In spite of the great increase in the transmission of the attenuation band when the surrounding medium goes from air to oil, no appreciable change could be measured for different oil samples. Nevertheless, pronounced wavelength shifts were observed for the same oil samples.

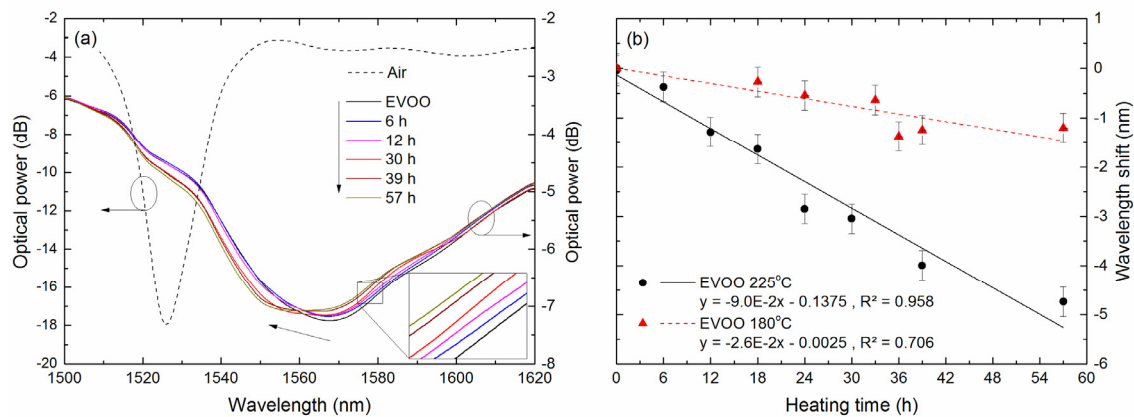


Figure 7.6 – (a) Transmission spectra of the LP_{16} cladding mode for air and EVOO as external medium (before heating and after heating for 6, 12, 30, 39 and 57 hours at 225 °C); (b) Wavelength shift of the long period fibre grating sensor for heating times from 1 to 57 hours at 180 and 225 °C.

Figure 7.6-(b) illustrates the behaviour of the sensor for heating times from 1 to 57 hours. A good linear sensitivity was observed in the first 24 hours of heating. A wavelength shift of ~ 5 nm was obtained in the refractive index range from 1.4665 to 1.4725.

The sensitivity is about 811.3 nm/RIU at 180 °C and 785.7 nm/RIU at 225 °C. These values correspond to 26 and 90 pm per hour of heating at 180 and 225 °C, respectively. Using a commercial available optical spectrum analyser with 2 pm resolution, thermal deterioration periods down to ~ 5 minutes at 180 °C and ~ 2 minutes at 225 °C could be, in principle, detected.

There is a large variety of edible oils with very distinct biochemical constitution. Likewise, extra virgin olive oils originating from different sources, made from olives in different ripening stages or kept in different conditions, possess diverse constitution and are easily distinguishable. Therefore, its refractive index and absorption spectrum, and its corresponding temperature variations, are different. Nevertheless, it was demonstrated that given a pure EVOO brand, its deterioration dynamics can be followed using a TiO₂ coated LPFG. Moreover, the time interval that the oil stayed at a certain temperature can be determined by acquisition of an initial measurement.

Given the linear shape of the sensor and its small dimensions it would be ease to fit it in an industrial frying pan. EVOO was the edible oil selected to demonstrate the feasibility, precision and efficacy of a TiO₂ coated LPFG optical sensor. Further research is needed to investigate the possibility of applying the sensor to other edible oils and to measure its properties.

7.3 Detection of Hexane in Extra Virgin Olive Oil

Typically, hybrid FBG/LPFG structures contains two fibre Bragg gratings (FBG) with wavelengths at both sides of attenuation band of the LPFG [246], but operation with a single FBG in one side of the attenuation band is also feasible under certain conditions. Recently, it was reported RI measurements using a LPFG in line with a FBG for temperature compensation [282]. The present work follows a similar configuration, focusing on the development of a hybrid optical sensing structure based on a FBG and a TiO₂ coated LPFG, combination aiming the measurement of concentration of organic solvents in EO. The introduction of the FBG coupled to the LPG generates essentially two major advantages. First, it makes the sensing device interrogation easier by measuring the optical power at the FBG wavelength. The second, is the possibility of controlling the thermal stability by tracking the wavelength position of the FBG since it is insensitive to the external RI.

The sensing device and its corresponding sensitivity and resolution performance is presented following two different interrogation modes, when operating in reflection and in transmission.

7.3.1 Sample Preparation

High quality extra virgin olive oil was acquired in the local market and mixed with *n*-hexane (CH₃(CH₂)₄CH₃) (Sigma-Aldrich, Germany), in different proportions, from 1 to 6 % V/V in 1 % V/V steps and from 6 to 20 % V/V in 2 % V/V steps. Afterwards, all samples (each one had a total volume

of 25 ml) were mixed, using a vortex mixer (model ZX3, Neu-TEC Group Inc, USA) to ensure total homogenization and were stored in dark glass vials at room temperature ($\sim 21^\circ\text{C}$). Measurements were accomplished within ~ 48 hours.

7.3.2 Experimental Setup

Prior to the oil characterization using the FBG/LPFG sensors, the RI of the samples was measured at room temperature ($26 \pm 1^\circ\text{C}$) using the Abbe refractometer with a RI resolution of 2.5×10^{-4} .

Two similar FBG/LPFG sensors (labelled SMF 1 and SMF 2) were used simultaneously to characterize the refractive index variation of the oil samples, as illustrated in the setup of Figure 7.7.

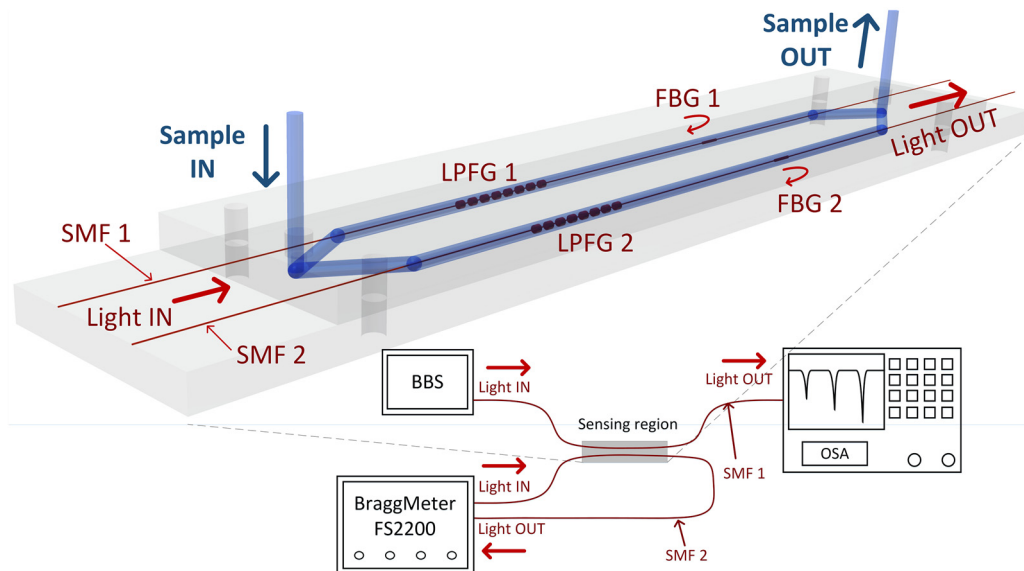


Figure 7.7 – Scheme of the measurement setup including: broadband source - BBS, optical spectrum analyser - OSA, sensors - SMF1/SMF2, FBGs interrogation unit/OSA – Model FS2200 (bottom), PMMA flow cell with two channels and six openings, four to pass the fibres and two to fill and drain liquid samples (top).

Sensor SMF 1 was intended for interrogation in transmission mode only. For that purpose it was used a homemade broadband source (BBS) and the OSA, with a resolution of 0.2 nm and a sampling rate of 1 spectrum per minute, from 1500 to 1630 nm.

Sensor SMF 2 was planned to be used as a sensing tip interrogated in reflection mode, however it was also characterized in transmission mode, as shown in Figure 7.7-(a). The spectra were measured using a computer controlled unit specifically designed to interrogate FBGs but also capable to be

used as OSA (BraggMETER FS2200 SA, FiberSensing, Porto, Portugal), with a resolution of 1 pm at a sampling rate of 1 spectrum per second, from 1500 to 1600 nm.

The setup shown in Figure 7.7-(b) is constituted by a homemade flow cell made of poly (methyl methacrylate) (PMMA) with two identical channels and six openings, four of them used to pass the fibres containing sensors and the other two to fill and to drain liquid samples. Both sensors were inserted in the cell and the FBG/LPFG structures were aligned with the centre of the channels. To avoid fibre-bending interference on the sensing response the ends of the fibres were clamped by pressing and holding the base of the flow cell against its upper half.

After each measurement the flow cell was flushed with 20 ml of ethanol and dried with filtered air to avoid contamination to the next oil sample. Then the spectrum of each sensor was monitored to ensure that the resonance dip has returned to its original spectral position.

7.3.3 Results and Discussion

The RI of the pure olive oil was 1.46650 ± 0.00025 and as the hexane concentration increases (whose RI is 1.3735), the RI of the mixture diminishes, as illustrated in Figure 7.8. From a linear fit to the data with a correlation coefficient (R^2) of 0.998, a rate of 0.076 RIU / %V/V was calculated.

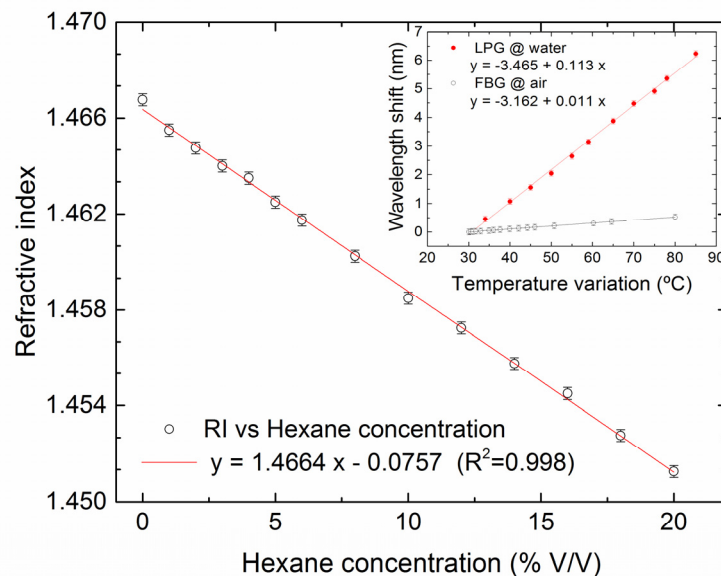


Figure 7.8 – Refractive index of the samples for hexane concentration from 0 to 20 % V/V. Inset: temperature sensitivities of both LPFG and FBG from 30 to 80 °C.

It follows that the concentration of hexane in olive oil can be monitored by measuring the RI of the mixture, which in turn can be evaluated by measuring the specific spectral characteristics of the LPFG resonance band.

– Analysis of the LPFG 1 wavelength shift with OSA

For the SMF 1 sensor, Figure 7.9 shows the spectral behaviour of the LP₁₆ band characteristic of the LPFG 1, together with the FBG 1 dip at 1539.91 nm, for increasing hexane concentration. It is also shown the LPFG spectra taken with air and with hexane as external medium. The spectral data was subjected to a fast Fourier transform (FFT) smoothing filter to reduce the noise due to the low power level of the light that reaches the OSA. As the corresponding RI decreases, the LP₁₆ band exhibits a notorious redshift.

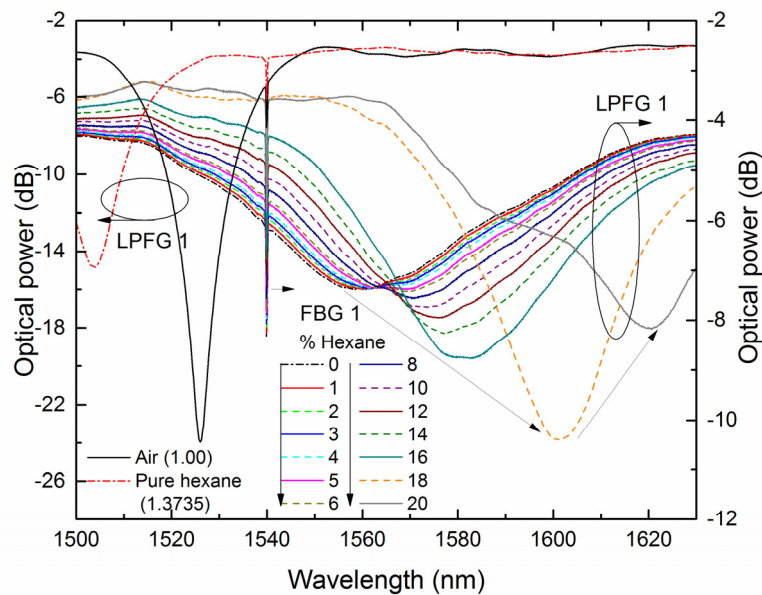


Figure 7.9 – Spectral features of the LP₁₆ band characteristic of the LPFG 1 (SMF 1 sensor), for air as external medium, pure hexane, olive oil and for mixtures with olive oil and various hexane concentrations.

For achieving the minimum of the LPFG dip in terms of wavelength and optical power care must be taken because the attenuation bands are in most cases asymmetric. However, the lower part of the bands is with reasonable accuracy a symmetric curve which can be fitted by a symmetric function. To perform this analysis the minimum optical power of the band was evaluated and then considering only the points 15% above this minimum, a Gaussian function was fitted and all the parameters were extracted, such as the wavelength position and the minimum optical power.

The experimental wavelength shift of the resonance dip is shown in Figure 7.10-(a) as a function of either the hexane concentration or the resulting RI of the mixture. In Figure 7.10-(b) the same results are presented as a function of time. For hexane concentration up to 16 % V/V the average sensitivity of 1.41 nm / % V/V (or 1881.2 nm/RIU) was calculated.

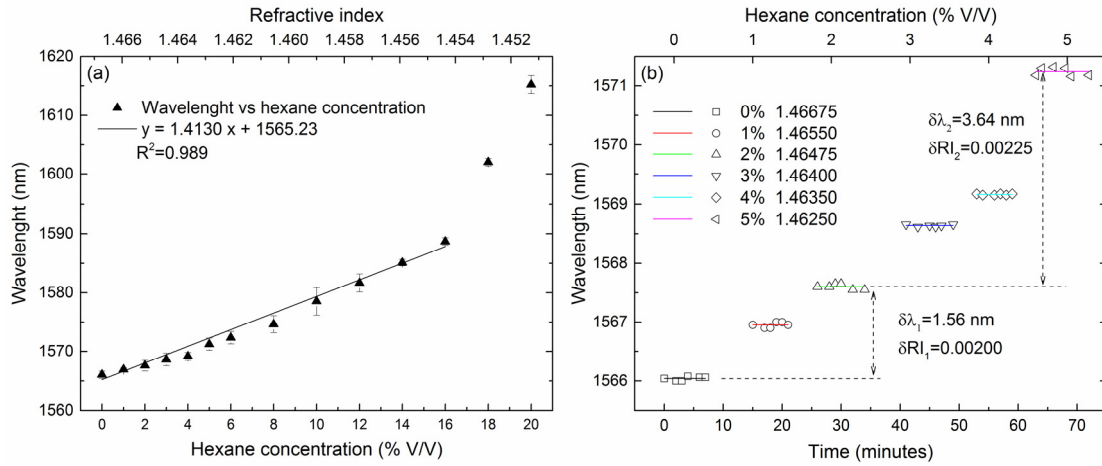


Figure 7.10 – (a) Wavelength position of the LP₁₆ band dip of the LPFG 1 (SMF 1 sensor) as a function of the hexane concentration (and of the RI). The continuous line is a linear fitting up to 16 % V/V; (b) Wavelength variation of the dip from LPFG 1 (SMF 1 sensor) when the surrounding medium undertakes step variations of hexane concentration (or RI).

The temperature around the flow cell was measured by a digital thermocouple (Model DVM1322, Velleman, Belgium) and found to increase ~ 1.5 °C during the measurements. It is well known that optical fibre gratings are sensitive to temperature variations [283]. The temperature sensitivity of the LP₁₆ band of coated TiO₂ LPFG sensor was measured from 30 to 85 °C. As shown in the inset of Figure 7.8, a linear fit was established, from which a sensitivity of 113pm / °C was measured for this specific mode. Therefore, for a temperature increase of 1.5 °C, the highest expected error in the determination of the wavelength of the LP₁₆ dip is lower than 0.2 nm.

As discussed in section 4.3.2 the resolution, R , can be calculated considering the values obtained from two measurement linked with two different values of the external RI [161] through equation (4.11).

From the two steps, shown in Figure 7.10-(b), a spectral resolution better than 0.58 %V/V (or 5.8×10^{-4} RI) was calculated. To check the stability/repeatability of the process, the same samples solutions were used to obtain several acquisitions, confirming the effectiveness of this sensing structure.

– Analysis of the FBG 1 transmission with OSA

Increasing the hexane concentration leads to a RI reduction and to a redshift of the LP₁₆ mode, which in turn conducts to an increment of the transmitted optical power in the left wing of the LPFG 1 resonance band. Also, it leads to an almost symmetrical transmission reduction on the right wing of the resonance band (see Figure 7.9). Therefore, the spectral signature at 1539.91 nm of the FBG 1 (located on the left side of the band dip) associated with the SMF1 sensor can be used to monitor the transmitted optical power through the sensor. Figure 7.11-(a) displays the variation of the optical power transmitted through the FBG 1 due to the continuous fading of the low wavelength region of the resonance band when the hexane concentration increases. The stability in time of the measurement system using the same transmitted optical power of FBG 1 is closely analysed in Figure 7.11-(b).

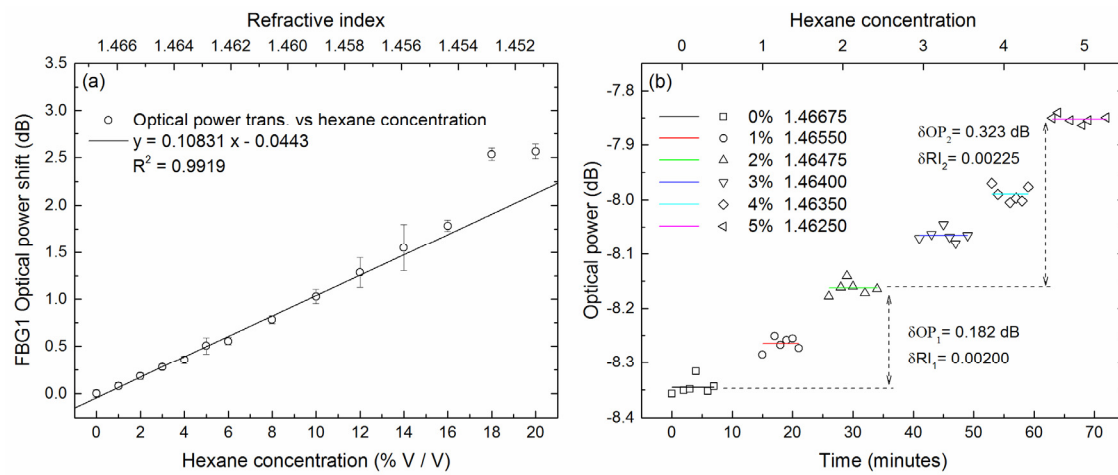


Figure 7.11 – (a) Dependence of the transmitted optical power shift of the FBG 1 (SMF 1 sensor) on the hexane concentration (and on the RI). The continuous line is a linear fitting up to 16 % V/V; (b) Variation of the optical power transmitted by FBG 1 (SMF 1 sensor) when the surrounding medium undertakes step variations of hexane concentration (or RI).

The continuous line in the graph is a linear fit to the experimental points (excluding two outlier samples corresponding to 18 and 20 %V/V), characterized by a R^2 value of 0.9919. For hexane concentrations up to 16 %V/V the sensitivity is 0.11 dB / %V/V (or 170.8 dB/RIU).

Following the procedure outlined above, the resolution of this measurement methodology can be calculated applying equation 7.1 and considering the values obtained from two measurements linked with two different values of the external RI, where δP is the difference in the output power of the FBG 1 under the RI variation (Section 4.3.2).

$$R = \frac{\sigma}{S_{RI}} = \frac{\delta RI}{\delta P} \sigma \quad (7.1)$$

From the two steps, shown in Figure 7.11-(b), a resolution of 0.29 %V/V (or 2.1×10^{-4} RI) was calculated.

– *Analysis of the data from the BraggMeter*

For the SMF 2 sensor, Figure 7.12 shows the spectral behaviour of the LP₁₆ band of the LPFG 2 after signal-to-noise improvement using the same FFT smoothing filter. Similar comments can be applied to this grating, namely, the wavelength sensitivity and spectral resolution which are of the same order of magnitude as stated above for the LPFG 1 analysed in transmission mode.

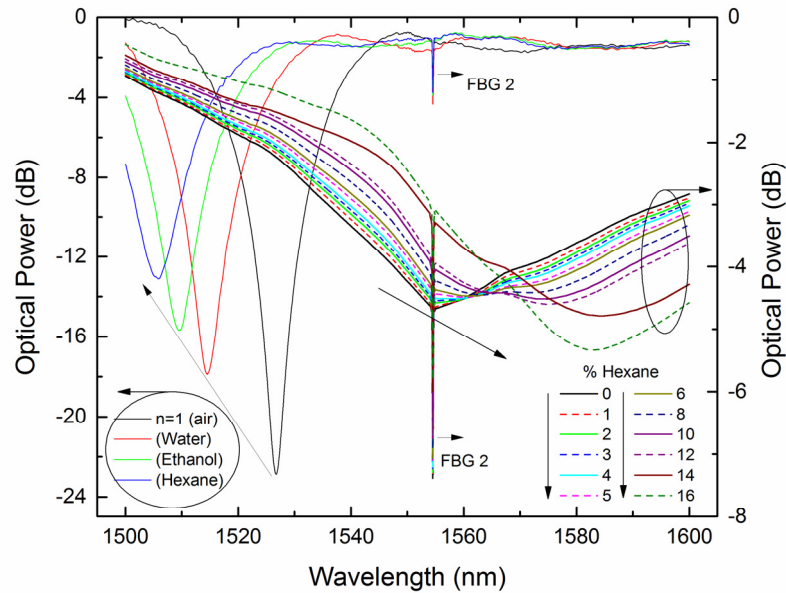


Figure 7.12 – Spectral features of the LP₁₆ band characteristic of the LPFG 2 (SMF 2 sensor), for air as external medium, pure water, ethanol, hexane, olive oil and for mixtures with olive oil and various hexane concentrations.

Sensor SMF 2 was planned to be a sensing tip. Using the concept applied to SMF 1 sensor, the continuous vanishing of the LP₁₆ band with increasing hexane concentration leads to an increase of the optical power reaching the FBG 2. The spectral feature at 1554.54 nm, characteristic of the FBG 2, is shown in Figure 7.12. Part of the radiation transmitted double crosses the LPFG 2 upon reflection in the FGB 2, being then detected by the interrogation unit (BraggMeter, FS2200 SA, HBM Fibersensing). In addition, as described above, FBG 2 can be used to monitor the transmitted optical power through the LPFG 2.

Figure 7.13 displays the magnitude of the measured optical power shift due to signal reflection on FBG 2 and due to the signal transmitted through it.

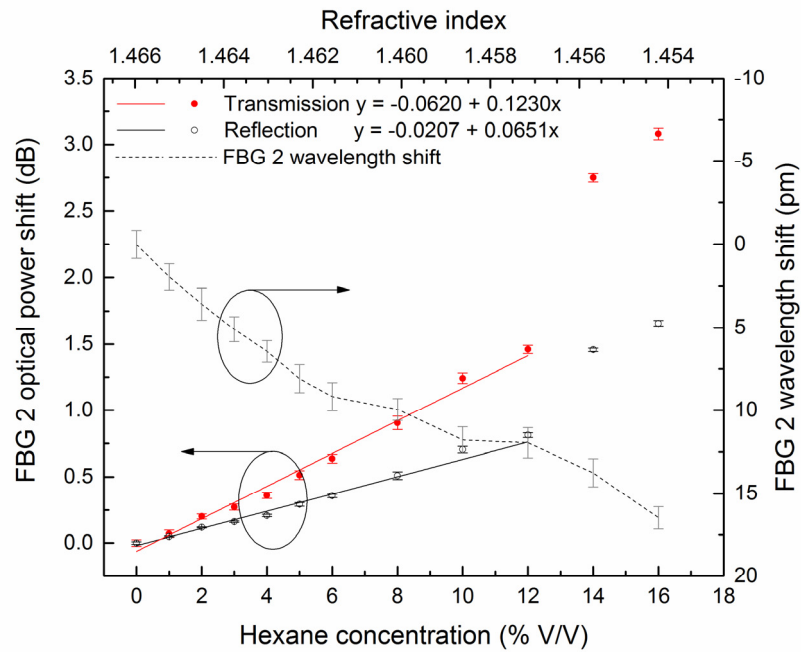


Figure 7.13 – Left axis: dependence of the transmitted and of the reflected optical power shift of the FBG 2 (SMF 2 sensor) on the hexane concentration (and on the refractive index). Right axis: FBG 2 wavelength shift during the measurements.

The continuous lines are linear fits to the experimental points (excluding two samples at 14 and 16 % V/V). For hexane concentrations up to 12 % V/V, the sensitivity in reflection is 0.07 dB / % V/V and in transmission is higher, 0.12 dB / % V/V. Both fits are characterized by R^2 higher than 0.98.

Figure 7.14 illustrates the time evolution of the sensor readout, both in reflection and in transmission, from which the calculated resolution was higher for reflection, 0.16 %V/V (or 1.4×10^{-4} RI) than for transmission, 0.31 %V/V (or 2.3×10^{-4} RI).

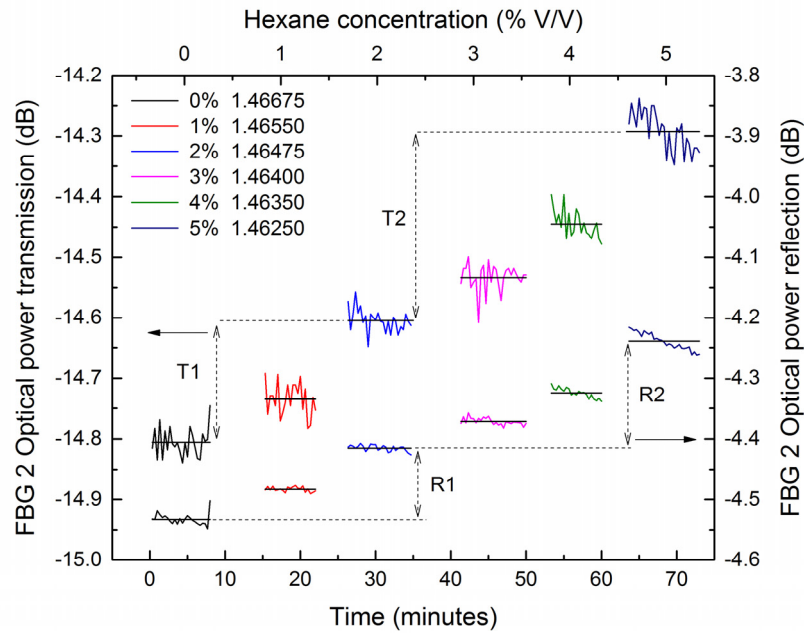


Figure 7.14 –Variation of the optical power transmitted and reflected by FBG 2 (SMF 2 sensor) when the surrounding medium undertakes step variations of hexane concentration (or refractive index).

Table 7.2 resumes the sensitivities and resolution for both sensors and measurement techniques.

Table 7.2 – Summary of the sensitivity and resolution of SMF 1 and SMF 2 sensors interrogated in both modes, transmission and reflection.

	SMF1			SMF2		
	Wavelength shift		Optical power	Optical power		Units
Sensitivity	1.41	nm / %V/V	0.11	0.12	0.07	dB / %V/V
	1881.2	nm / RIU	170.8	160.5	89.7	dB / RIU
Resolution	0.58		0.29	0.31	0.16	%V/V
	5.8×10^{-4}		2.1×10^{-4}	2.3×10^{-4}	1.4×10^{-4}	RI
Transmitted				Transmitted	Reflected	

According to the inset of Figure 7.8, the FBGs used in the present work have a temperature sensitivity of ~ 11 pm/ $^{\circ}$ C which is in agreement with the literature for the standard optical fibre (~ 10 pm/ $^{\circ}$ C) [284]. As can be observed in the right axis of Figure 7.14, a wavelength shift of 16.5 pm of the FBG 2 occurred during the experiment, from which a temperature variation of 1.5 $^{\circ}$ C within the flow cell was calculated, a value compatible with the temperature variation just outside the cell.

While the LPFG sensors are sensitive to both SRI and temperature variation, FBGs are SRI insensitive. The proposed hybrid configuration allows correction of the LPFG wavelength shift due to random temperature drifts, which may occur in crude EO storage. Moreover, in temperature dependent laboratorial or industrial processes, such as in EO chemical extraction, accurate monitoring of hexane concentration would require wavelength shift correction.

7.4 Conclusions

New sensing technologies well adapted to process control in agri-food industry was presented in this chapter using fibre optic sensors which are easy to use, robust, reusable and do not involve the use of hazardous chemicals. The studies reported in previous chapters allow the possibility of applying long period fibre gratings to monitor the quality of high refractive index edible oils when coated with TiO_2 through the changes in refractive index. The high sensitivity of the TiO_2 coated LPFG sensor to the surrounding refractive index has been used to demonstrate the feasibility of a measurement sensor of thermal deterioration and for contamination of high refractive index edible oils.

The thermal deterioration sensing system is based on the refractive index change of the EVOO induced by heating at high temperature. Visible and near infrared spectroscopy has allowed the effects of thermal deterioration to be detected, clearly seen, for example, in the decreasing of the visible absorption band centred at ~ 677 nm, attributed to chlorophyll A.

The detection of organic solvents in edible oils as EVOO was performed with an optical sensing scheme based on hybrid FBG/coated LPFG. Despite the advantages of a probe tip geometry and of the easiest of the sensor interrogation in reflection mode, the study showed that the highest sensitivity was obtained in transmission mode. The resolution, however, is lower in transmission mode as compared with reflection mode. SMF 1 and SMF 2 sensors present sensitivities between 0.11 and 0.12 dB / %V/V when interrogated in transmission mode, a value higher than the value of 0.07 dB / %V/V, achieved for the FBG readout in reflection mode. However, the lowest resolution is attained in reflection mode (0.16 %V/V).

In conclusion, the LPFG sensor coated with TiO_2 thin film is simple to fabricate, easy to implement and to interrogate and allows real time characterization of deterioration of high refractive index edible oils, such as EVOO, without chemical analysis.

Chapter 8

Surface Plasmon Resonance: Studies with Single Mode Optical Fibres

Multimode fibres provide easier and faster way to expose the evanescent wave of the group of modes that propagates in their large core, therefore has been the preferred platform to support fibre optic based surface plasmon resonance sensing devices. However, their performance may be enhanced when singlemode fibres are addressed, so in this chapter, such approach is studied considering single mode optical fibres with a reduced cladding by chemical etching.

8.1 Surface Plasmon Resonance

The general principle behind the operation of optical sensors is the modification induced by the measurand of light properties, namely intensity, phase, polarization, frequency and wavelength (these two are related but gave raise to rather different classes of sensing layouts). Additionally, there are situations where the coupling of light to other elements originate new phenomena that may be the source of new sensing approaches, most often opening paths to have access to extremely high

sensitivities derived from the fact, in such cases, the measurand acts on the coupling conditions of light to those elements, which usually shows rather sensitive dependence. The most well-known of these phenomena is the coupling of light with free electrons at a metal surface, originating a hybrid photon-electron entity, known as plasmon. It turns out this resonance interaction (*surface plasmon resonance* – SPR) is highly sensitive to the refractive index (RI) of the surrounding medium, therefore enabling the design of high performance sensing devices. By proper functionalization, many measurands, mostly related to the chemical and biological domains, can be scrutinized [285].

Plasmonics based optical sensors have been mostly supported by bulk optical elements (prisms) in a coupling layout known as Kretschmann's configuration [32, 286, 287]. However, soon has been recognized the obvious advantages of using the optical fibre as the SPR sensing platform, starting by the fact propagation in these waveguides in most of the cases is supported by total internal reflection, an effect central in plasmonic phenomena. Therefore, it has been observed a tendency to establish the optical fibres the preferred platform for the SPR detection [33]. This tendency naturally led to the idea of developing fibre based SPR sensing systems and related subjects, such as their multiplexing to achieve a spatially distributed sensing network.

8.1.1 Brief Definition

Plasmons are oscillations of free electrons in a plasma defined by traveling waves with specific wave vector and frequency. They exist under certain resonant conditions, usually called surface plasmon resonance (SPR), a phenomenon that had been systematically investigated [32, 288] and mostly used for chemical and biosensing in bulk planar waveguides through commercial products such as Biacore (GE Healthcare group, EUA) or Navi models (Bionavis, Finland).

Surface plasmon resonance is a phenomenon that gives rise to a transverse electron-density oscillation, at a given eigenfrequency, that in certain conditions exist at the interface of two media with dielectric constants of opposite signs, for example a metal and a dielectric. The electron-density oscillation and associated electromagnetic field are called surface plasmon polariton (SPP), a coupled state between a plasmon and a photon. The metals have in general a large number of free electrons which allows plasma excitation. The oscillation is associated with an electromagnetic wave, and the evanescent field at the interface decay exponentially into both metal and dielectric media. This situation is illustrated in Figure 8.1 for a planar waveguide where the perpendicular field E_z decays

exponentially. The plasmon excitation is strongly dependent on the effective RI of the combination dielectric/external medium, thus making a surface plasmon based device suitable for sensing.

Only TM-polarized incident light will excite plasmons which can be an important issue when planar waveguides are being considered.

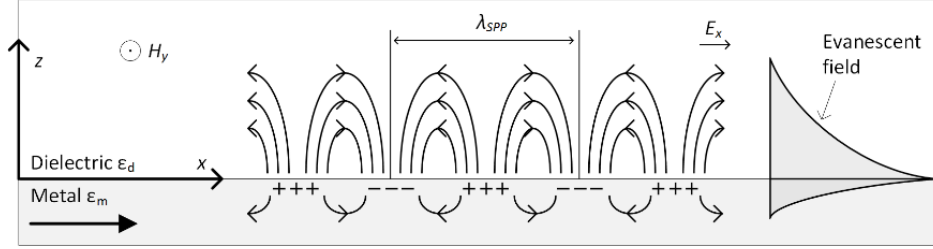


Figure 8.1 – Schematic representation of the electron charge-density wave propagating along the metal/dielectric interface of a planar waveguide.

The field distribution along the interface can be described as [289]:

$$E = E_0^\pm e^{i(k_x x \pm k_z z - \omega t)} \quad (8.1)$$

Being the sign ($\pm$) depending if z is positive or negative. The exponential decay of the field in the z direction is caused by the imaginary term k_z .

From Maxwell equations, the propagation constant of the surface plasmon wave (SPW) that propagates at the interface dielectric/metal is given by equation (3.10) [32]:

$$\beta = k_x = \frac{\omega}{c} \sqrt{\frac{\epsilon_m \epsilon_d}{\epsilon_m + \epsilon_d}} \quad (8.2)$$

where $k_x = 2\pi/\lambda$ is the free space wavenumber with λ the free space wavelength, ω is the frequency, ϵ_m the permittivity of the metal ($\epsilon_m = \epsilon'_m + i\epsilon''_m$) and ϵ_d the permittivity of the dielectric ($\epsilon_d = \epsilon'_d + i\epsilon''_d$) [290]. The dielectric constant of a metal, neglecting attenuation, can be calculated using the free electron model from the equation (8.3):

$$\epsilon_m(\omega) = 1 - \left(\frac{\omega_p}{\omega} \right)^2 \quad (8.3)$$

where ω_p is the Drude plasma frequency given by:

$$\omega_p = \sqrt{\frac{Ne^2}{\epsilon_0 m_e}} \quad (8.4)$$

where N , e and m_e the density, charge and effective mass of the electrons, respectively; ϵ_0 is the vacuum permittivity.

The plasma frequency ω_p defines a *cutoff* frequency above which the wave-vector becomes imaginary, indicating that the light cannot propagate in the medium.

The combination of a set of metal or dielectric layers would give rise to sensing sensitivity improvement, to tune the wavelength resonance position or to avoid chemical reactions of a specific metal with the analyte. In this case, a multilayer system is considered and the number of interfaces increases, each one with a different dispersion equation. An example of the dispersion relation of SPP at two different interfaces is shown in Figure 8.2. For this case, two dispersion equations for k_x can be found for $\omega = \omega_{SP1}$ and $\omega = \omega_{SP2}$ which depends on the dielectric constants of each interface.

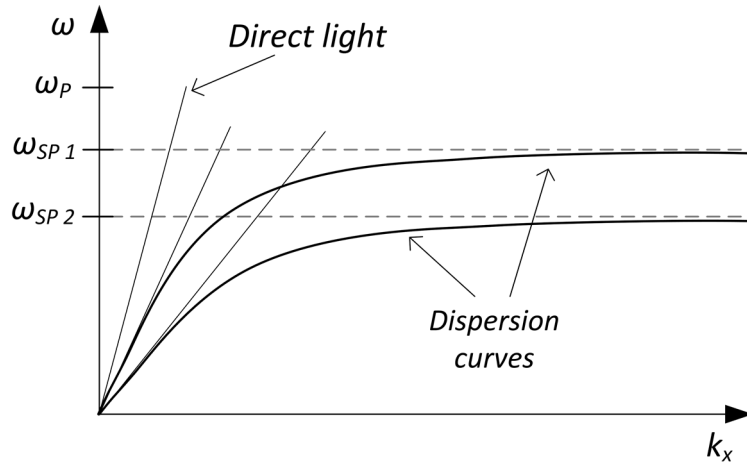


Figure 8.2 – Representation of two dispersion curves corresponding to the surface plasmon propagation at two different interfaces (adapted from [291]).

8.1.2 Excitation Configurations

The excitation of surface plasmons occurs when two propagation wave-vectors are equal. This is the reason why the direct light cannot excite surface plasmons at the interface metal-dielectric, because the dispersion curves of the direct light and the surface plasmon do not cross at any frequency. The surface plasmon waves are longitudinal waves and cannot be excited by a transverse wave as

electromagnetic. To excite surface plasmons the momentum and the wave-vector of the exciting light in external dielectric medium should be increased which can be achieved by the evanescent wave approach [7].

There are several configurations to excite surface plasmon waves, the Kretschmann and Otto configurations are the most used on bulk optics based SPR. There are, however, other interesting designs such as the grating coupling configuration and the waveguide coupling configuration [290].

The Kretschmann configuration is based on the prism coupling technique (PCT) [292] and employ the attenuated total reflection (ATR) [293]. The PCT involves the use of a high RI prism to couple light into the thin waveguide positioned at the base allowing the measurement of its thickness and refractive index [294]. At a single interface the ATR occurs when the incident light goes from a medium with high RI (n_2) to another with smaller RI (n_1) at a certain angle of incidence to the waveguide normal (θ_i) and depends on properties of both medium. The angle of the incident light above which ATR occurs is called the critical angle and is given by $\theta_c = \theta_i = \arcsin(n_2/n_1)$. Both Kretschmann and Otto configurations [295, 296] use the PCT and the ATR but they have different geometries.

In the Kretschmann configuration, [Figure 2.1-(b)], the base of the prism is coated with a metal and a dielectric with specific thicknesses, the incident p-polarized light is reflected back and part can propagate in the metal in the form of an electromagnetic wave [290]. This evanescent wave is characterized by a propagation constant along the interface and by an exponential decay in the direction perpendicular to the waveguide interface and can excite surface plasmon waves at the metal/dielectric boundary.

In the Otto geometry [Figure 2.1-(a)], a dielectric with a thickness q is placed between the prism base with RI n_p and the metal film with permittivity ϵ_m . The evanescent field at the prism/dielectric interface can excite surface plasmons at the dielectric/metal interface. The dielectric works as a spacer to allow the excitation of the SPW but is difficult to realize due to the small thickness required. The SPWs are excited at the metal/dielectric interface [33].

Another configuration to excite the surface plasmon waves is based on the diffraction of light on a diffraction grating. As represented in Figure 2.1-(c), the incident light from a dielectric medium on a grating coated with a metal layer gives rise to a series of diffracted waves.

Surface plasmon waves can also be induced by the propagating modes of a dielectric waveguide. Those modes when in contact with a thin metal film region penetrate through it and excite a surface plasmon wave at the outer boundary of the metal, as illustrated in Figure 2.1-(d).

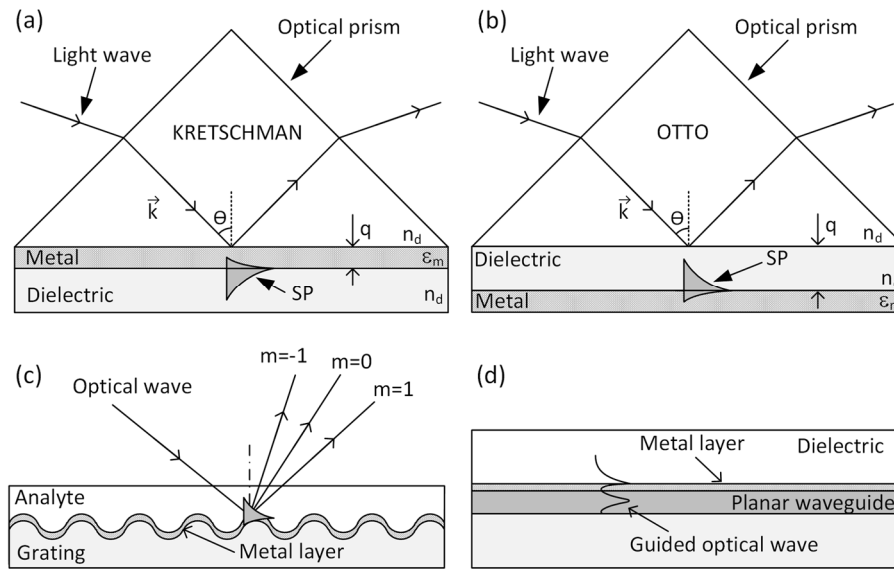


Figure 8.3 – Excitation of surface plasmon waves in different configurations: (a) Otto and (b) Kretschmann configurations; (c) the grating coupling; (d) the waveguide coupling.

The electromagnetic field of a SPW excited in the metal/dielectric boundary penetrates in both media but the decay in the metal is abrupt when compared to the field decay in the dielectric. An optical fibre can be coated with metals and dielectrics and the same concepts can be applied. In this case light travels in the core, so to excite the SPW the metal/dielectric coating needs to be as close as possible to the core.

8.1.3 Optical fibre SPR Probe Designs

In the past twenty years, much effort was focused on miniaturizing fibre optic SPR sensors in an endeavour which involved the use of different fibre types, including microstructured optical fibres, the application of different coatings coupled to nanotechnology developments, as well as the implementation of processes to perform side polishing of fibres, to obtain tapered and decladded fibre structures and, between others, the consideration of resonant devices such as Bragg and long period gratings to assist the SPR phenomenon.. Schemes of some configurations are shown in Figure 8.4.

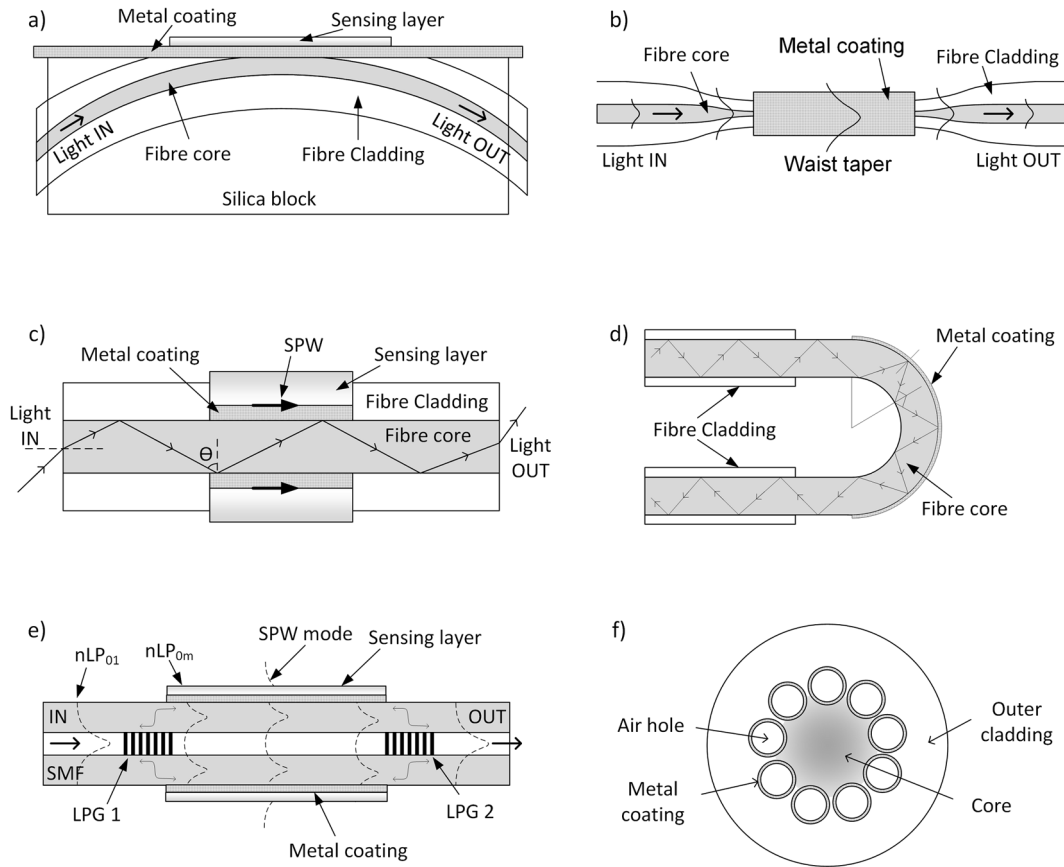


Figure 8.4 – Schematic operation principle of SPR sensors based on: (a) side polished or D-type shape fibre, (b) tapered fibre, (c) multimode decladded fibre, (d) U-bent shape fibre, (e) LPGs in a single mode fibre and (f) photonic crystal fibre.

The easiest way to reach the evanescent field to produce SPR is by side polishing single mode fibres in a D shape [297, 298], multimode fibres [299, 300] or even large core plastic optical fibres [301], Figure 8.4-(a). This usually involves the process of attach the fibre to a resin block and to perform the polishing with several grain size until the evanescent field is exposed. The concept is to polish the sensing region as a D-Type fibre [302] and coat the plane surface with metal and dielectric thin films using a Kretschmann's configuration.

Another well studied configuration is using adiabatic tapers implemented in single mode fibres [303] [304-307], Figure 8.4-(b). The tapers allows the direct interaction of the evanescent wave with the external medium because at the waist region the core light is coupled to the cladding modes which makes them good candidates to SPR excitation. The tapers are usually produced with a very smooth surface profile being very sensitive to the coating thickness. By introducing some roughness with

chemical etching technique asymmetry of the coating can be overlapped as reported [116, 308]. Multimode fibres were also studied in a multi-taper configuration to produce SPR sensors [309].

One of the first applications of fibre optic SPR based sensors was reported by Jorgenson *et al.* in 1993 [310] using a multimode plastic-clad silica-core fibre with a large core. The SPW excitation has been achieved in small length sections where the cladding was easily removed with a flame, Figure 8.4-(c). Since then, several works have been published using similar designs [92, 311-318]. Several other works have been theoretically studied using this configuration [319-322]. Bimetallic nanoparticle alloy combinations of Ag/Au were also a subject of study and can be found in [323, 324].

The above mentioned configurations with the exposed multimode core can be bent in a U-shape configuration inducing changes in the guiding properties and increasing the evanescent field [325, 326], Figure 8.4-(d).

LPFGs can be an alternative to the mechanical processes to expose the guided mode. A possible operation principle of a sensor with two LPFGs in the edges of the sensing length in a single mode fibre based on SPR is represented in Figure 8.4-(e). The metal layer is in this case deposited on the cladding around the fibre between the two LPGs and the SPW is excited in the metal/dielectric interface by a cladding mode as presented by He *et al.* in 2006 [327], Figure 8.4-(e).

Photonic crystal fibres (PCFs) are designed to have air holes inside and along the entire length becoming a potential configuration for chemical and biological sensing. With many specific architectures this type of fibres are also called microstructured optical fibres. The PCFs can be classified based on the light being guided in a solid core or in a hollow core relying on the modified effective RI distribution or on the existence of photonic band gaps. These characteristics depend of the shape, the size and the position of the holes being controlled during the fabrication process [28]. The PCFs are very interesting due to the position of the holes in the vicinity of the fibre core. If these holes are coated with a metal and a dielectric, the interface between them can, in specific situations, support a propagation of a SPW [328-333], Figure 8.4-(f).

Besides the features presented by PCFs, the above mentioned configurations also have been studied in retro-reflecting mode. This configuration is particularly useful when a tip probe is needed [297, 306, 334-337].

8.1.4 Interrogation System

The perturbation of the RI of the surrounding medium results in a modification of the properties of the SPW, thus making the SPR phenomenon interesting for sensing applications. In fact, SPR based sensors are refractometers with different RI sensitivities.

At resonance conditions energy is transferred from the incident photons to surface plasmons, which reduces the energy of the reflected light. The resonance can be interrogated by three different methods: angular, wavelength or intensity modulation [32].

When the output signal is measured as a function of the incident angle, maintaining all the other parameters unchanged, is observed a sharp dip in the reflected light. The angular interrogation is typically used in bulk systems and consists of varying the angle of the incident light while keeping the wavelength constant. Figure 8.5 shows the typical shape of a resonant dip which depends on the variation of the reflectance with the incident angle [33].

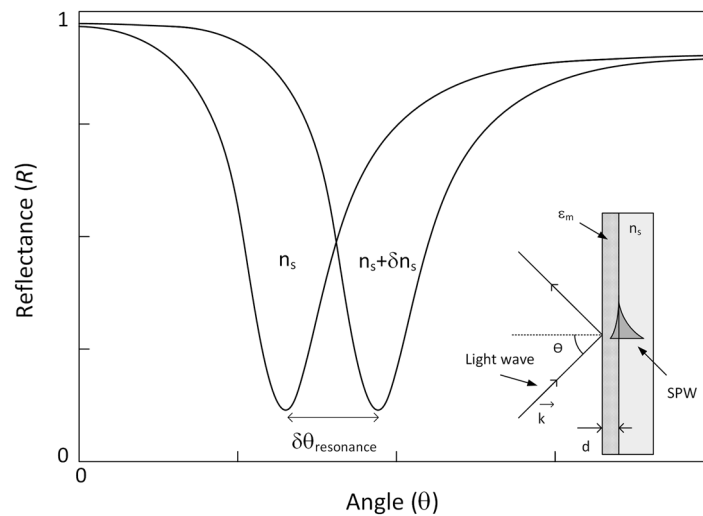


Figure 8.5 – Reflectance (R) as a function of the incident angle (θ). The observed shift ($\delta\theta_{\text{resonance}}$) is due to the change of the RI of the medium.

The wavelength modulation is used in optical fibres where the angle is kept constant while a broadband light source is used to excite the SPW. Here, a dip in the transmitted spectrum changes according to the RI of the dielectric medium [338]. The output signal comes out as a function of the wavelength and a shape similar to the angular interrogation is obtained. In the case of optical fibres the interrogation is made with a fixed angle distribution determined by the numerical aperture of the fibre, $NA = n \sin(\theta)$, where θ is the acceptance angle of the fibre.

In the intensity modulation approach the sensor output is associated with the intensity at a specific wavelength located in the region of the SPR resonance. When this signature changes due to a variation of the medium refractive index the optical power at the operation wavelength also changes, being this mechanism the base of the intensity interrogation.

It is worthwhile to indicate at this point that with a small thickness of metal, the backscattered wave and the incoming wave are out-of-phase and the two waves interfere destructively reducing the reflected intensity down to zero. On this situation, the whole radiation field is absorbed by the metal film. When the thickness of the metal film is large the radiation field is totally reflected and any light is absorbed [33].

8.1.5 Theoretical Study of SPR – Transfer Matrix Formalism

The transfer matrix formalism can be used to calculate the reflectance R using a slab multilayer system as an approximation to the optical fibre geometry. This methodology has already been reported by several authors [339, 340] [322]. This formalism is based on light propagation through a planar isotropic and homogeneous multilayer system defined by the thickness d_k , dielectric constant ϵ_k , permeability μ_k and the RI n_k .

A scheme of the multilayer system is presented in Figure 2.1 considering a four layer structure (optical fibre – metal – dielectric – analyte), and the electric field vector $\vec{E}$ and the magnetic field vector $\vec{H}$ at the launching surface.

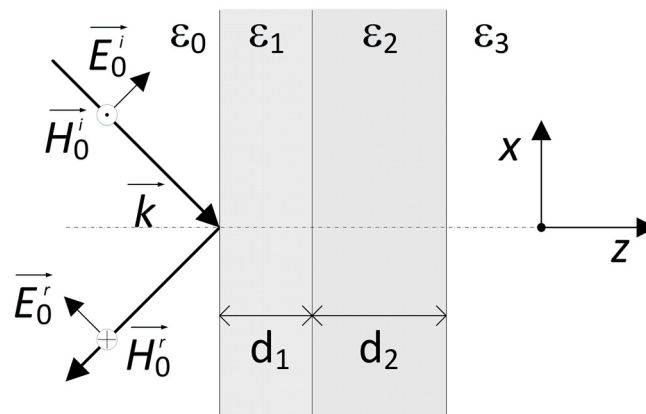


Figure 8.6 – Electric and magnetic field vectors of p wave at the first surface of the multilayer system (adapted from [322])

The amplitude of $\vec{E}$ and $\vec{H}$ of adjacent layers are related within the equation:

$$\begin{bmatrix} E_0 \\ H_0 \end{bmatrix} = [M] \times \begin{bmatrix} E_N \\ H_N \end{bmatrix} \quad (8.5)$$

with $N = 3$ and M is known as the characteristic matrix of the layer system considered above defined by [322] :

$$[M] = \begin{bmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{bmatrix} = \prod_{k=1}^{N-1} \left(\begin{bmatrix} \cos \delta_k & -i \sin \delta_k / q_k \\ -i q_k \sin \delta_k & \cos \delta_k \end{bmatrix} \right) \quad (8.6)$$

with

$$q_k = \left(\frac{\mu_k}{\epsilon_k} \right)^{1/2} \cos \theta_k = \frac{(\epsilon_k - n_0^2 \sin^2 \theta_0)^{1/2}}{\epsilon_k} \quad (8.7)$$

and

$$\delta_k = \frac{2\pi}{\lambda} n_k \cos \theta_k \times (z_k - z_{k-1}) = \frac{2\pi d_k}{\lambda} (\epsilon_k - n_0^2 \sin^2 \theta_0)^{1/2} \quad (8.8)$$

where $n_k = (\epsilon_k \mu_k)^{1/2}$ and $d_k = (z_k - z_{k-1})$ is the RI and the thickness of each layer, respectively. The θ_0 is the angle of incidence and λ the wavelength of the input light.

The reflectance R of the multilayer system can be defined in terms of the Fresnel reflection coefficients, r_s and r_p , considering the TE modes and TM modes, respectively. Once only TM modes can excite the surface plasmons only r_p is considered and the reflectance intensity for p-polarized light is:

$$R_p = |r_p|^2 = \left| \frac{(M_{11}^p + M_{12}^p \cdot \eta_N^p) \eta_0^p - (M_{21}^p + M_{22}^p \cdot \eta_N^p)}{(M_{11}^p + M_{12}^p \cdot \eta_N^p) \eta_0^p + (M_{21}^p + M_{22}^p \cdot \eta_N^p)} \right|^2 \quad (8.9)$$

The power, dP , that reaches the fibre end at the angular range $d\theta$ around θ is :

$$dP \propto \frac{n_0^2 \sin \theta \cos \theta}{(1 - n_0^2 \cos^2 \theta)^2} d\theta \quad (8.10)$$

Considering the contributions of all rays and multi-reflections the total power transmitted, P_T , through an optical fibre for a p-polarized light with an optical absorption-based SPR sensor is given by:

$$P_T = \frac{\int_{\theta_c}^{\pi/2} R_p^{N_{ref}(\theta)} (n_0^2 \sin \theta \cos \theta / (1 - n_0^1 \cos^2 \theta)^2) d\theta}{\int_{\theta_c}^{\pi/2} (n_0^2 \sin \theta \cos \theta / (1 - n_0^1 \cos^2 \theta)^2) d\theta} \quad (8.11)$$

with

$$N_{ref}(\theta) = \frac{L}{d \tan \theta} \quad (8.12)$$

where N_{ref} represents the number of reflections that each ray performs at an angle θ to the surface normal along a length L and for a fibre core with diameter d .

8.2 Sensing Structure Based on SPR in Chemically Etched Single Mode Optical Fibres

In this section the surface plasmon resonance concept is applied to a single mode fibre (SMF) working at the standard C-band telecom window (1530 nm-1565 nm). This wavelength region is widely used for communication systems due to the low losses of silica fibres and the availability of detectors and optical sources as the erbium-doped fibre amplifiers.

To achieve the plasmonic effect, the evanescent field from the core mode needs to reach the fibre surface, so a small section of the fibre was chemically etched and coated with a metal / dielectric combination which corresponds, with good approximation, to the Krestchman configuration. The sensing structure was fully characterized as a function of the RI of the external medium, in transmission and in reflection modes. Schemes of the two operation modes are presented in Figure 8.7 and Figure 8.8 with both metal/dielectric layers in the chemical etched region of the fibre.

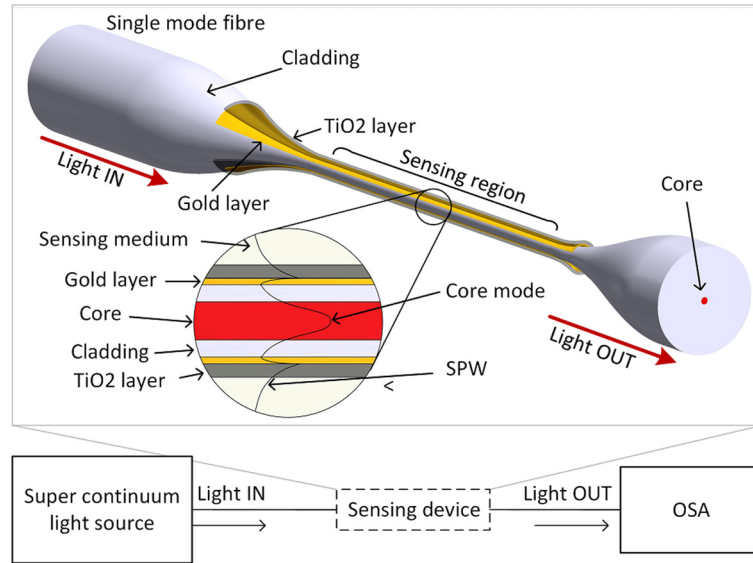


Figure 8.7 – Scheme of the sensing device (top) setup used in transmission mode (bottom).

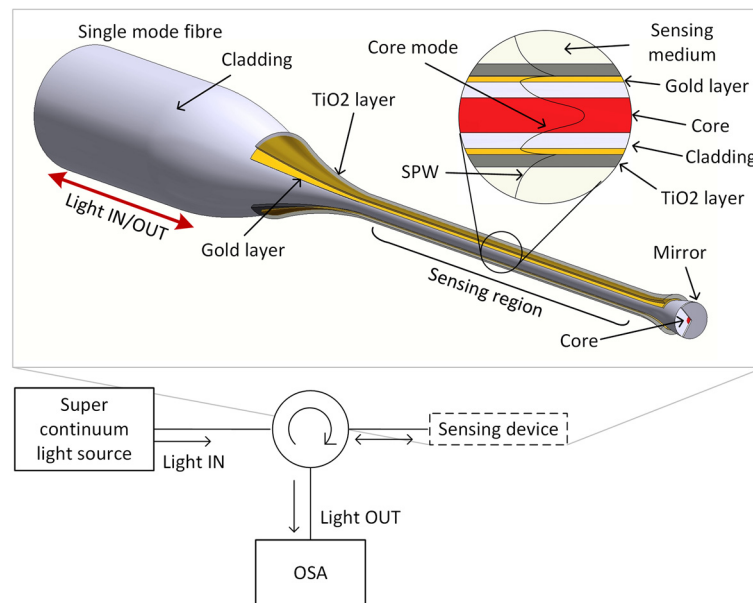


Figure 8.8 – Scheme of the sensing device (top) setup used in reflection mode (bottom).

8.2.1 Substrate Preparation and Coatings

The transmission mode operation sensing device was performed in a single mode fibre SMF28 (Corning) with a core diameter of 8.2 μm and a cladding diameter of 125 μm . The plastic protective jacket was removed and a section with 10 mm long of the fibre was chemically etched by following the procedure described in section 3.1.2.

For the reflection mode of operation, the same type of fibre was used but it was firstly cleaved and a titanium (Ti) thin film of 150 nm thick was deposited at the end in order to increase the reflectivity of the sensing tip. The mirror coating was then protected with negative photoresist S1818 (Shipley Company Inc., EUA). After the photoresist being dried in an oven for 2 h at 80 °C the tip was chemically etched. The tip was then immersed in pure acetone to dissolve the photoresist.

On both situations the small fibre section was placed in an aqueous solution with 10 ml of 48% HF during 38 minutes at 22 °C and 60 % of humidity until the etched region became approximately 13 μm in diameter.

The sensing region is located in the thinner section where the evanescent field is able to excite the plasmonic wave, for both modes of operation. First, the etched region was coated with 2 nm of pure chromium (Cr) to improve the adhesion of gold (Au). Then, a layer with 16 nm thick film of Au was deposited around the fibre followed by a 120 nm thick dielectric layer of titanium dioxide (TiO_2).

The metal/dielectric coatings were performed with the electron beam evaporator fitted with the rotary system by following the procedure described in section 3.1.3.

Previous measurements with the ellipsometry technique resulted in an estimation of the TiO_2 RI of around 2.2.

A SEM picture of the produced sensor is presented in Figure 8.9 being possible to see the smooth transition from the thick section to the thin section due to the etching procedure.

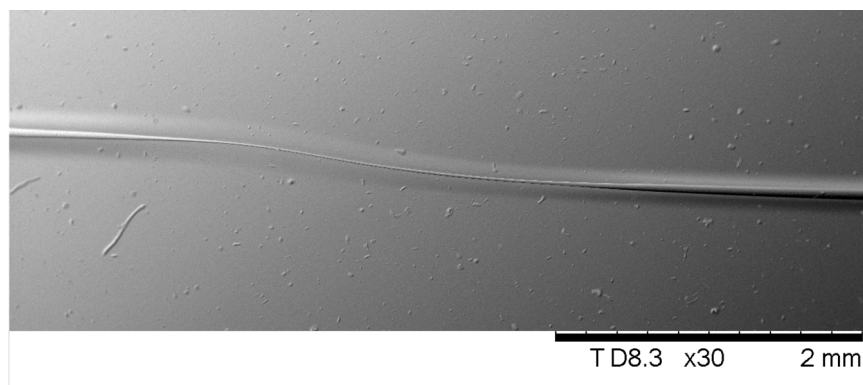


Figure 8.9 – SEM picture of the sensing region in the transmission configuration with a transition between diameters of 125 μm to 13 μm (30 times magnification).

The chemical analysis of the etched fibre region after coated with Cr, Au and TiO_2 is presented in Figure 8.10. The red line is the obtained spectra while the symbols with the droplines are the tabled

data for known transition lines from [124, 341]. The spectra looks very clean with low contaminants as sodium (Na $K\alpha$) and the usual carbon (C $K\alpha$), showing the well-defined peaks of Au (lines $L\alpha$ and $M\alpha_1$) and Ti (lines K) and the high intensity peak of the silica substrate from the $K\alpha_1$ and $K\beta_1$ lines. A very small peak can be identified corresponding to the adhesion layer of Cr (line K). Around 500 keV the big peak is a convolution of Cr, Ti (both with lines L), and O (line $K\alpha_1$). The inset is a SEM photograph of the fibre surface and the white square represents the region where the EDS spectra was acquired. Although all the fabrication steps and the manipulation processes from the chemical analysis and the SEM picture it is possible to attest the robustness over time of the thin coated structure.

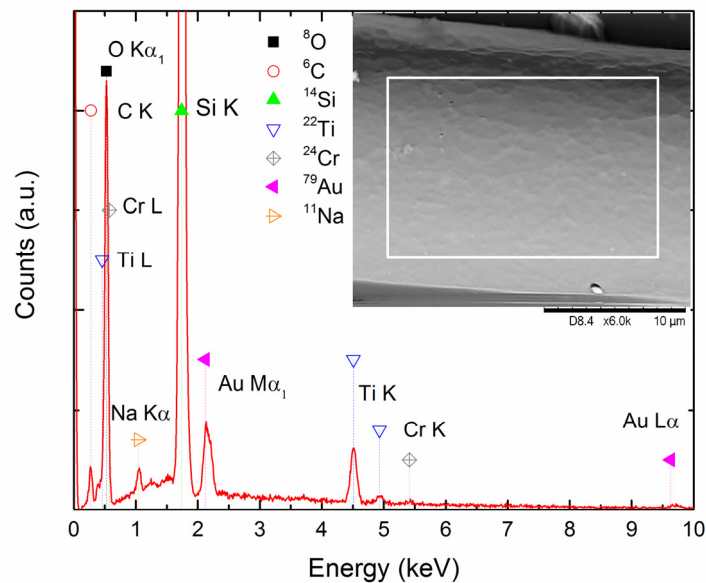


Figure 8.10 – EDS spectra of the sensing substrate coated with Au and TiO_2 . Inset is the SEM picture of the centre taper region (the white square shows the limits of the EDS measurement).

8.2.2 Sensor Interrogation

The interrogation setup was deployed into two different sensing configurations. In the transmission setup, the optical signal was analysed with an Optical Spectrum Analyser (OSA - model ANDO AQ-6315B with a range 350 nm to 1750 nm) as shown in Figure 8.7. In the reflection setup, the scheme is presented in Figure 8.8, where an optical circulator must be used to allow the reading of the reflected signal in the OSA. Due to the large spectral window (1100-1700 nm) both sensors have used a homemade super continuum light source with a laser centred at 1064 nm that excites a special Photonic Crystal Fibre in a range from 600 nm to 1800 nm.

8.2.3 Results and Discussion

– Simulation results

Changing the thickness of the metallic and mainly of the dielectric layer, the plasmon resonance can be tuned in wavelength. Considering the transmission mode of operation, numerical simulations were performed in order to determine the optimal thicknesses of each thin film to create a resonance dip in the C-band spectral range. This working wavelength range is highly desirable due to the large portfolio of fibre and optoelectronics components available from the optical fibre communication sector.

The simulations were performed using the transfer matrix formalism for a slab multilayer system described in the previous section. The shape of the resonant dip and the red shift obtained for increasing RI are presented in Figure 8.11-(a). The resonant dip appears at 1500 nm for a RI of 1.30 using thickness layers of 16 nm of Au and 120 nm of TiO₂. The results were obtained using RI steps of 0.005 from 1.335 to 1.375 in fibres with core diameter of 8.2 μm and the cladding diameter of 13 μm .

The sensitivity for an interval is calculated tracking the wavelength position of the resonance dip for different RI medium, with results shown in Figure 8.11-(b). This was achieved by fitting the SPR curves to a 3rd order polynomial trend being the most convenient and adequate procedure, as calculated by Boltovets et.al. [342]. The simulation results show an exponential dependency with the refractive index, nevertheless a rough linear fitting was calculated, leading to an average sensitivity higher than 5600 nm/RIU.

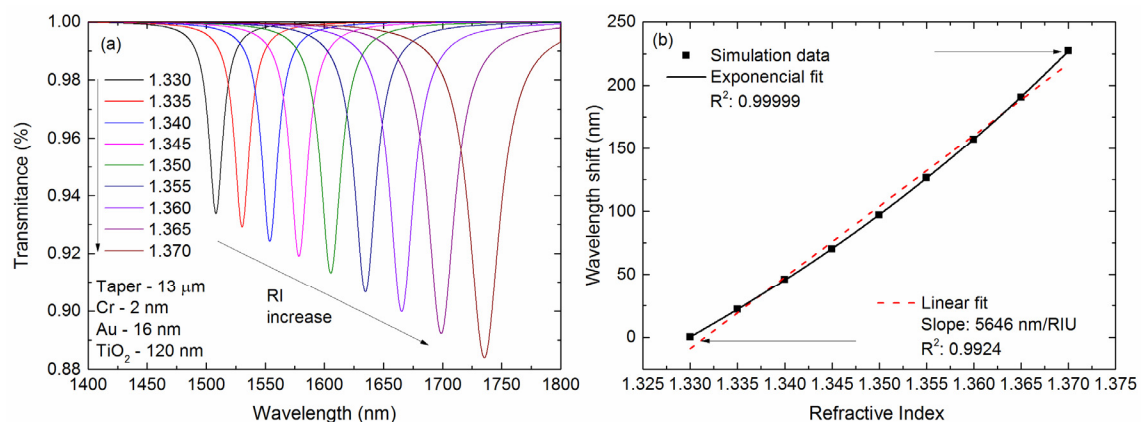


Figure 8.11 – Simulated results obtained for different external RI medium from 1.350 to 1.375: (a) optical spectra; (b) calculated sensitivity.

Simulations of the propagating light in this type of structure were performed through beam propagation method (BPM) with the RSOFT (Synopsys Inc., CA, E.U.A.) software in order to understand how the fundamental mode is affected. The results are shown in Figure 8.12. The guiding structure becomes multimode in the sensing region affecting the evanescent field and the plasmon excitation. The existence of several modes combined with small variations on coating thickness may explain the large profile of the resonant dip obtained in the experimental results.

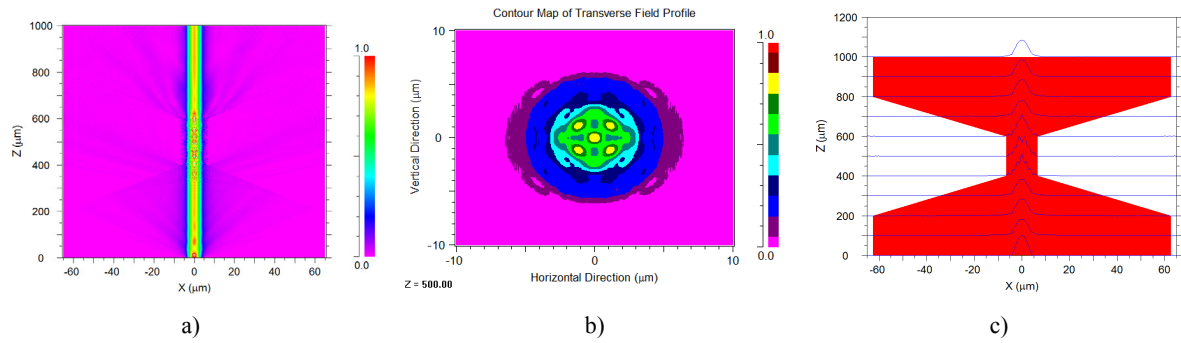


Figure 8.12 – Simulation of the electromagnetic radiation propagated in the fibre structure shown in Figure 8.7: (a) field amplitude as a function of x and z from $z=0$ to $z=1000$ μm ; (b) transverse field profile as a function of x and y at $Z=500$ μm ; (c) transverse profile at several positions along the propagation direction.

Figure 8.12-(a) shows the electric field amplitude as a function of x and z from $z = 0$ μm to $z = 1000$ μm , being visible the effect of the etched region from $z = 400$ μm to $z = 600$ μm . From Figure 8.12-(b) and Figure 8.12-(c) it is possible to see how the high reduction of the cladding diameter affects the fundamental mode, inducing the propagation of several modes in the sensing section.

– Experimental Results: Transmission Mode Operation

The scheme of the transmission mode operation is presented in Figure 8.8. Along with the optical source and the OSA, a simple setup is used maintaining the fibre stretched and fixed in two points away from the sensing region.

Several spectra were obtained considering different OSA resolutions (Figure 8.13) and due to the low power source the resolution chosen was 2 nm to increase the signal-noise-ratio. Once the resonance dip shape is very wide the changing in the OSA resolution does not affect significantly the wavelength position of the resonance.

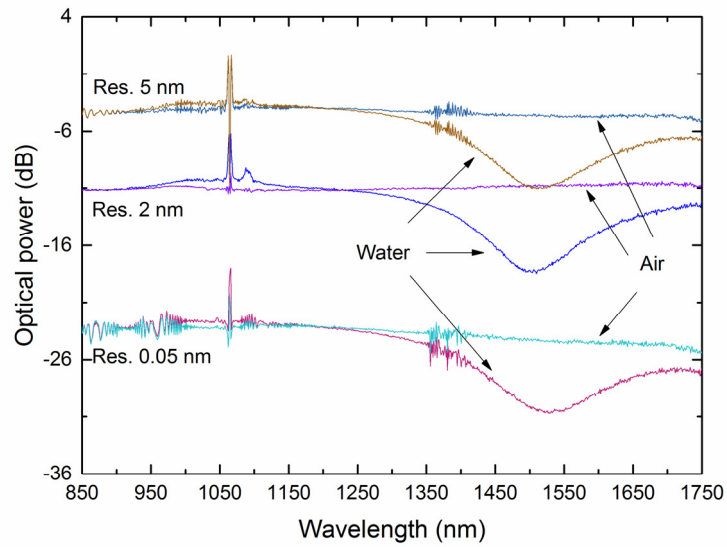


Figure 8.13 – Normalized spectra obtained for different resolution levels in water solution (RI = 1.335), being also shown the spectra when the environment is air.

The experiment was completed by adding ethylene glycol (RI = 1.430) to water (RI = 1.335) to obtain solutions with values of RI from 1.335 to 1.374 [343]. The RI of the solutions was measured with an Abbe Refractometer, model 2WAJ with accuracy of 0.00025 with a measurement range of $1.3 \approx 1.7$. Figure 8.14-(a) shows the SPR spectral position for the different RI solutions. The spectral data was subjected to a Fast Fourier Transform (FFT) smoothing filter to reduce the noise due to the low power level of the light that reaches the OSA.

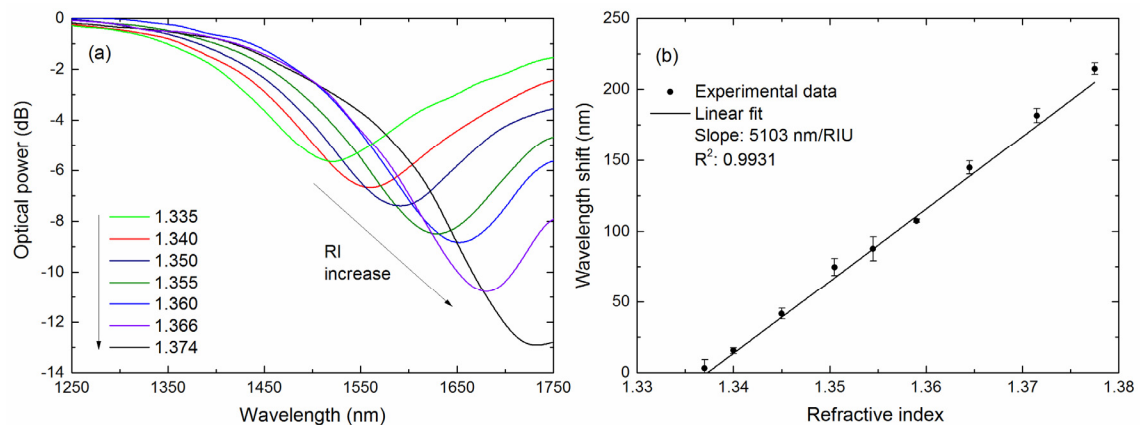


Figure 8.14 – Experimental results of the SPR spectral resonance for surrounding RI in the range from 1.335 to 1.374 when the sensing device is operating in transmission mode: (a) optical spectra; (b) calculated sensitivity.

The experimental dependence of the spectral position of the resonance dip with RI is shown in Figure 8.14-(b), indicating an average sensitivity higher than 5100 nm/RIU, a value similar to the obtained with the computational model described above.

To check the stability/repeatability of the process, the same ethylene glycol/water solutions were used to obtain several acquisitions, confirming the effectiveness of this sensing structure, Figure 8.15.

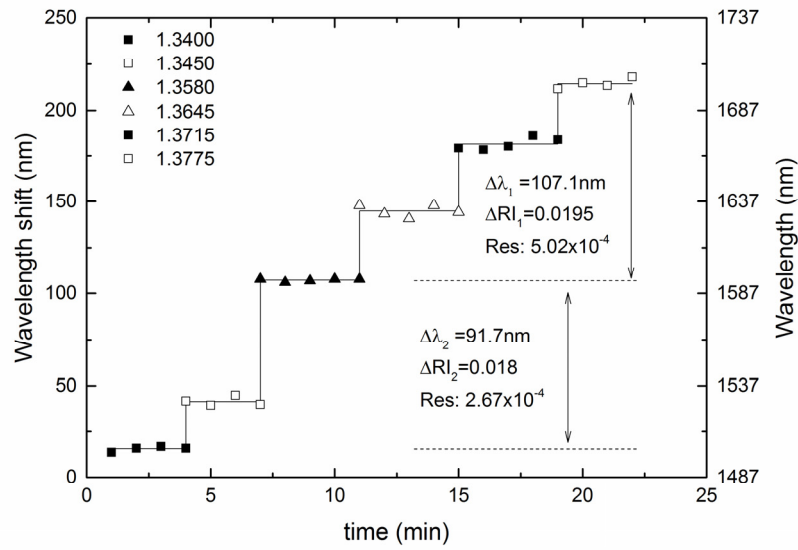


Figure 8.15 – Study of the stability/repeatability of the sensing device considering different values for the external RI

Considering the same method described in section 4.3.2, the spectral resolution R is calculated from two step measurements associated with two different values of the external RI, [161, 290, 344]. From the two steps, shown in Figure 8.15, a RI resolution better than 5.02×10^{-4} is obtained.

Figure 8.16 shows the dependence of the SPR dip with RI as obtained from the numerical simulation (—□—) and from the experimental data with RI values measured with the Abbe refractometer at 589.3 nm (o). Applying a correction to this value considering the dispersion function with wavelength, through the Sellmeier equation (3.10) the new experimental data (×) at 1550 nm can be compared with the simulation and the agreement is rather good.

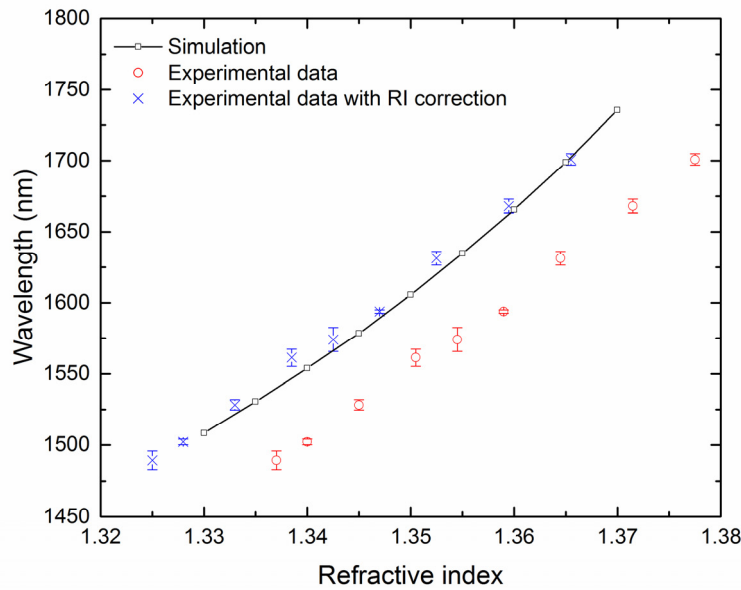


Figure 8.16 – Dependence of the SPR shift with external RI, in the range 1.3350 to 1.3775, as obtained by the numerical analysis and the experimental investigation.

– *Experimental Results: Reflection Mode Operation*

The reflection mode operation implies the introduction of an optical circulator, which reduces the light level at the output. The maximum transmission power of this device occurs in the range $1525 \approx 1625$ nm but it can be used in a wider range with higher losses. The same optical power and OSA as before have been used.

The full characterization was provided by changing the RI of the external medium from 1.300 to 1.360 using a set of RI calibrated oils (Cargille-Sacher Laboratories Inc., NJ. U.S.A.).

Figure 8.17 shows average plots of the evolution of the SPR for different RI values (the same FFT smoothing filter was used to reduce the noise due to the low power level of the light that reaches the OSA).

It is observed that the shape of each resonance dip appears slightly deformed and the optical power level is not constant when compared with the transmission setup. With this configuration, the light crosses the sensing region twice due to the mirror on the end of the fibre, inducing extra losses. Also, the fibre tip is suspended in air and quite susceptible to variable curvatures, which changes dynamically the plasmon coupling conditions. This effect induces variations in the shape/position of the SPR dip, visible in the plots of Figure 8.17-(a) by some oscillatory behaviour. For this configuration, Figure 8.17-(b) shows the variation of the resonance dip with the external RI.

8.2 - Sensing Structure Based on SPR in Chemically Etched Single Mode Optical Fibres

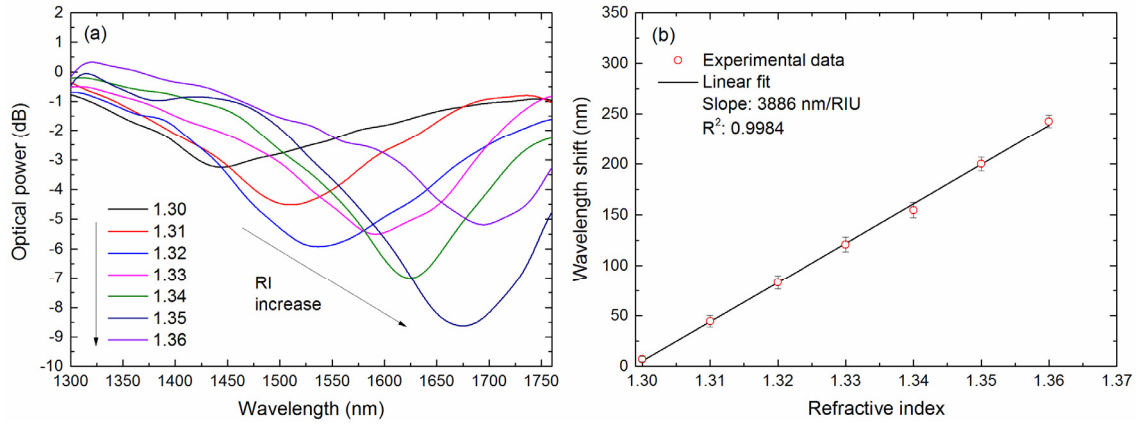


Figure 8.17 – Experimental results of the SPR spectral resonance for the surrounding RI in the range from 1.300 to 1.360 when the sensing device is operating in the reflection mode: (a) optical spectra; (b) calculated sensitivity.

Comparing with the transmission mode result (Figure 8.14), a smaller sensitivity was observed (<4000 nm/RIU against ≈ 5100 nm/RIU) but an improved linearity was obtained.

To assess the resolution Figure 8.18 shows the step change in the SPR associated with RI step variation 1.300 to 1.360.

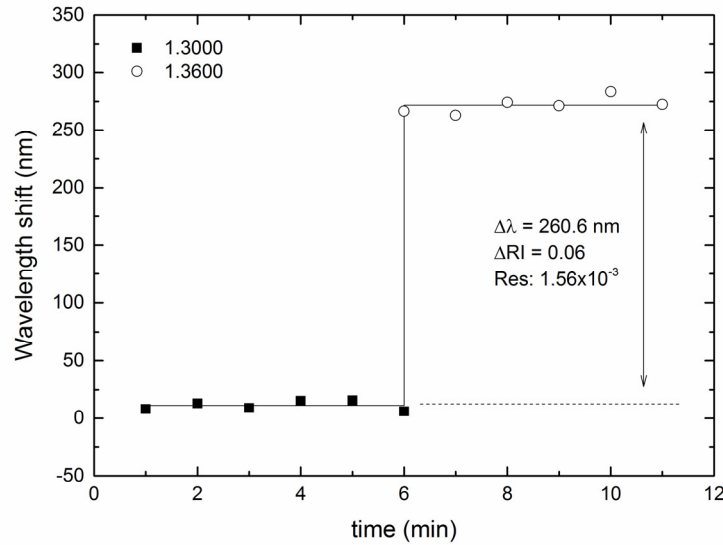


Figure 8.18 – Experimental results to determine the RI resolution of the sensing device operating in reflection.

Following a procedure similar to the one used in the context of Figure 8.15, it is obtained a RI resolution of $\approx 1.56 \times 10^{-3}$, a value worse than the one associated with the transmission mode configuration, as can be checked from the comparative data shown in Figure 8.19.

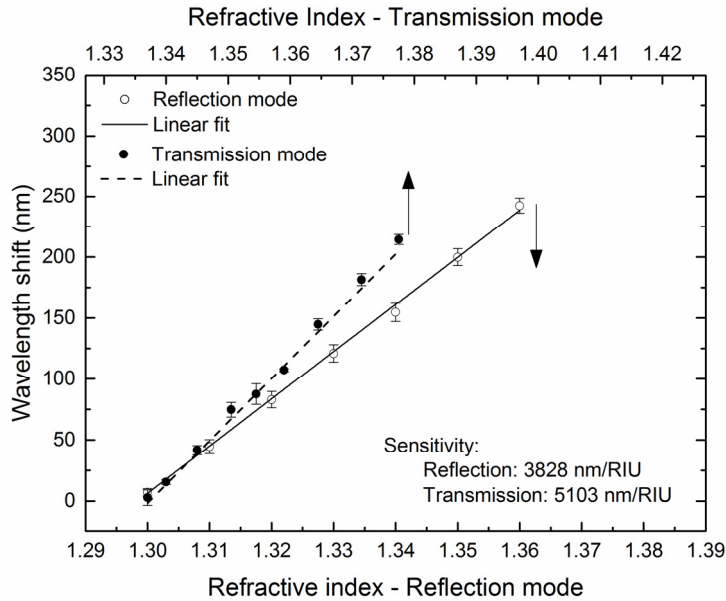


Figure 8.19 – Comparison of results obtained for the sensing structure operating in transmission and in reflection.

The reasons behind the worse resolution value obtained for the reflective configuration when compared with the one associated with the transmission mode layout may be grounded to the arguments expressed in the context of Figure 8.17. However, it is important to emphasize that the reflection mode layout is substantially more amenable to use in situations where a probe tip is on demand, being substantially more complex the arrangement to install in these cases the transmission mode device. Also, the problem of low power levels in the reflection mode configuration can be attenuated considering the use of higher power sources and/or optical amplification, with positive impact on the level of optical noise, therefore in the value attainable for the RI resolution. It was indicated, for the reflective layout, the oscillations in the shape of the resonance may derive from instability/oscillations of the fibre taper probe, with the negative consequences on the device RI resolution, factor that can be attenuated doing an adequate packaging of the fibre sensor. All of this point out to a possible margin of performance improvement for the fibre taper tip SPR sensor.

8.3 Multiplexing of SPR Sensing Devices on Etched Single Mode Fibre

Besides the considerations about the need of reliable sensing technologies when addressing complex systems, another core characteristic comes out associated with the demand of spatially distributed multipoint measurement layouts. Their relevance is well illustrated looking closely to a biological

sensing system, for example the tactile system in human hands [345, 346]. In addition to the high level processing of the information collected in the network, this sensing functionality relies on three basic processes: the way the individual sensing elements are integrated in the array (network topology), the form how the central unit selects the raw data from a specific sensor of the array (sensor addressing), and the approach followed to obtain from the measurand action on a particular sensor a signal in a format appropriated for further processing (sensor interrogation) [347]. These processes and the requirements involved impose strict constraints on the adaptability of sensor technologies to work out high density and spatially extended measurement networks, which are even strengthened if the sensors demand powering, as happens with many electrical based sensors. It is in this domain where the optical fibre sensor concept shows its uniqueness. In addition to the always relevant features of immunity to electromagnetic interference, the robustness of operation in chemical and radiation hazard environments and the substantial minimization of optical alignment issues, the simultaneously sensing element and communication channel is a remarkable characteristic of the fibre. This feature brings the intrinsic suitability of optical fibre sensing to handle dense and vast sensor networks, pointing out the appropriateness of this technology to deal with the monitoring needs of complex systems, reason why it has been widely considered in the context of many areas addressed by optical fibre sensing [348].

The reported R&D activity oriented to multiplexing of SPR sensors has been residual, although some efforts done on that direction in prism based sensors, as is the case of the work described by Hooper *et al* where a dual-channel configuration was proposed [349]. This reality derives from the recognition that prism coupling systems are not amenable to incorporate the multiplexing functionality, contrary to what happens when optical fibre is considered. Therefore, multiplexing of fibre optic SPR sensors has the potential to spread over a large sensing network the performance provided by a single localized SPR sensor, with the obvious benefits that may result from this scaling, for example when considering distributed biochemical monitoring. Being so, it is somehow surprising to observe that residual R&D have been undertaken on this subject, circumstance eventually routed to the paths historically followed by the R&D community involved in the development of SPR sensing.

In this section is described a technique to multiplex optical fibre SPR sensors based on wavelength addressing using FBGs. A ladder topology is considered and sensor interrogation is performed in the intensity domain. The sensor platform is an etched single mode fibre coupled to a combination of metal and dielectric layers to achieve plasmonic resonance at the 1550 nm spectral region.

8.3.1 Sensor Multiplexing

The multiplexing approach considered here is illustrated in Figure 8.20 for the case of three sensors in a ladder topology (equivalent to a tree arrangement when only two sensors are considered).

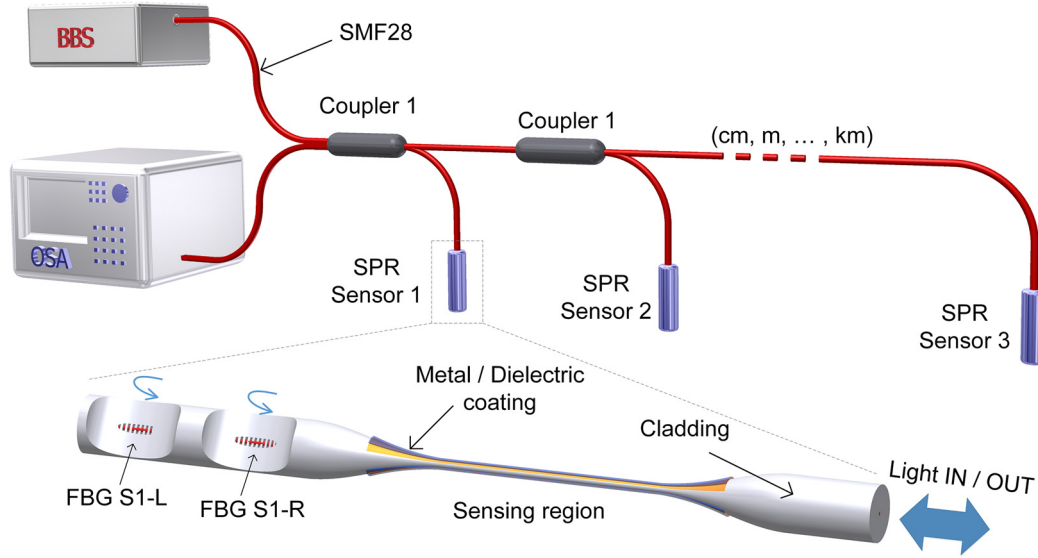


Figure 8.20 – Illustration of the sensor multiplexing layout for the case of three sensors in a ladder configuration.

The SPR spectral shape is very wide and is not possible to have several in a narrow range of wavelengths. To solve this issue, for each sensor, two FBGs are included in the fibre after the SPR structure. These FBGs have spectral signatures located at each side of the surface plasmon resonance. Therefore, each sensor is associated to a pair of FBGs with specific Bragg wavelengths, which means the sensors are addressed in wavelength (Figure 8.21). The sensing device operates in reflection, which means that due to the double pass in the measurement region the readout sensitivity is increased. Also, the sensing device can be deployed close or far away from the optoelectronics unit. The peak optical power returned from the gratings is detected and processed as

$$S_{out|S_i} = \frac{P_{FBG_i-L} - P_{FBG_i-R}}{P_{FBG_i-L} + P_{FBG_i-R}} = k(\lambda_{SPR_i}) \quad (8.13)$$

where k is a constant and, for the configuration illustrated, $i = 1, 2, 3$. P_{FBG} refers to FBG peak power and the indexes FBG_i-L , FBG_i-R are associated, respectively, to the left and right spectrally located FBGs relative to the resonance curve of sensor i (Figure 8.21). Therefore, the output signal of this sensor, $S_{out|S_i}$, is dependent on the spectral position of the surface plasmon resonance of this

sensor and determined by λ_{SPR_i} , meaning that a measurand induced change of this wavelength translates into a change in $S_{\text{out}|S_i}$.

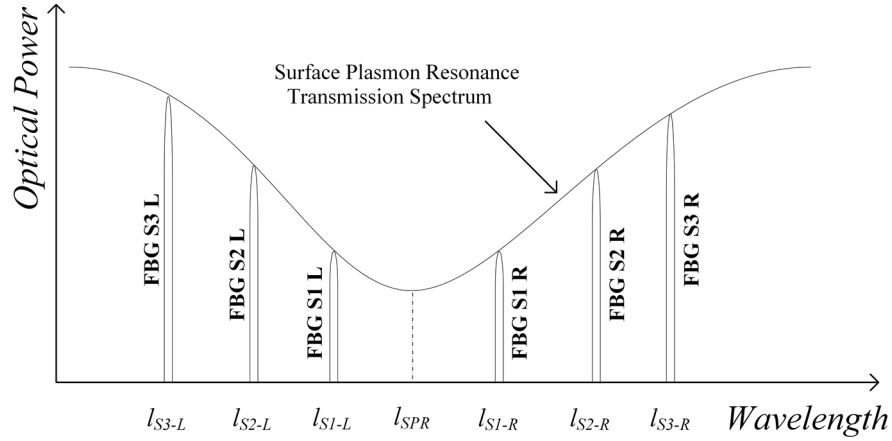


Figure 8.21 – Relative spectral position of the FBG pairs associated to the sensors and the plasmonic resonance.

This approach also provides intrinsic immunity to optical power fluctuations along the optical system, i.e., it exhibits self-referencing properties. When this functionality can be relaxed, which may happen in some applications, then only one FBG per sensor is required, located in one of the side-bands of the sensor spectral resonance. In this case $S_{\text{out}|S_i}$ is directly proportional to the peak power of the FBG_i , associated to sensor i . To experimentally validate this FBG based SPR multiplexing concept proposed here this simpler approach was considered.

It is relevant to emphasize that the multiplexing concept illustrated in Figure 8.20 is compatible with all sensors being equal, i.e., with the same plasmonic resonance (therefore $\lambda_{\text{SPR}_i} = \lambda_{\text{SPR}}$ independent of i).

8.3.2 Experimental Procedures

– Sensing Device

The multiplexing configuration presented above was experimentally tested and presented by using two SPR sensing devices similar to those studied in section 8.2 in transmission mode operation (Figure 8.22). Coupling each SPR sensor to an FBG from a special set with reflection peaks separated by few nanometres it is possible to relate all the reflected peaks to the associated SPR device.

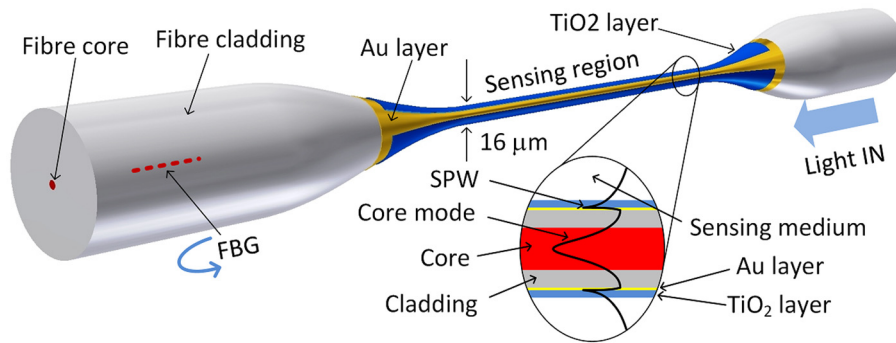


Figure 8.22 – Scheme of the SPR sensing device coupled to an FBG.

– *Substrate preparation*

The SPR sensing device was produced by following the procedure described in section 8.2.1 with few changes to tune the SPR position to lower wavelengths. This time the 10 mm fibre length section was chemical etched until the diameter was $\sim 16 \mu\text{m}$. It was then coated with $\sim 2 \text{ nm}$ of Cr, 16 nm of Au and with 100 nm of TiO_2 . The main difference in the fabrication process is the TiO_2 thickness leading to a different measurement range for the external refractive index.

– *Sensor Network and Interrogation*

For demonstration purposes, the sensing network was formed only by two sensors, situation in which a ladder topology is equivalent to a tree layout. First, each SPR sensing device was characterized in transmission mode, without the FBG structure, to map the profile of the resonance in a wide wavelength range for a series of RI samples. The setup used for this characterization is illustrated in Figure 8.23.

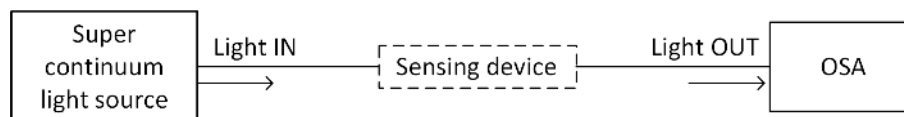


Figure 8.23 – Setup used in transmission mode for characterizing the optical fibre SPR.

The wide resonance dip observed was illuminated with the super continuum light source and collected with the OSA. Figure 8.24 shows the transmission spectrum of each SPR sensor for external media with RI of 1 and 1.36.

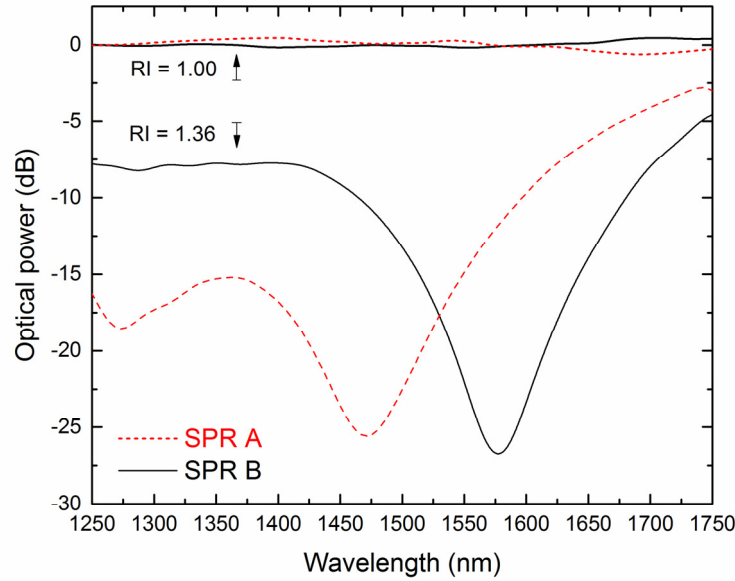


Figure 8.24 – Transmission spectrum of each SPR sensor for RI of the external medium of 1.00 and 1.36 in a wide wavelength band.

The visible differences in the resonances are justifiable with the uncertain in the fabrication processes chemical etching and coating thicknesses.

After this preliminary characterization the sensing device was coupled to a FBG. The power level of the reflected light at the peak wavelength of the grating is proportional to the wavelength position of the plasmon resonance in a certain RI range. The two-sensor multiplexing set-up is shown in Figure 8.25, where the two SPR sensors are located in the output arms of a 2x2 fibre coupler. The super continuum light source has low power level and the OSA was used with 5 nm resolution, enough to monitor the wide resonant dip. For readout of the FBG signatures, the light source can be commuted to an Amplified Spontaneous Emission Broadband light source combining the C-band with the L-band spectral range (1565-1625 nm), enabling larger power levels at the grating wavelength regions. The OSA resolution was changed to 1 nm to allow the reading of the narrow FBG bands.

The light reaches the sensing device inducing the plasmon waves with a specific resonance wavelength that depends on the external medium refractive index. The remaining light continues until is lost in the index matching gel but a narrow selected band is reflected by the FBG, crossing again the sensing device being afterwards collected in the OSA. As indicated before, the detected optical power derived from this reflected narrow band depends on the relative wavelength position of the SPR resonance spectrum and the FBG signature.

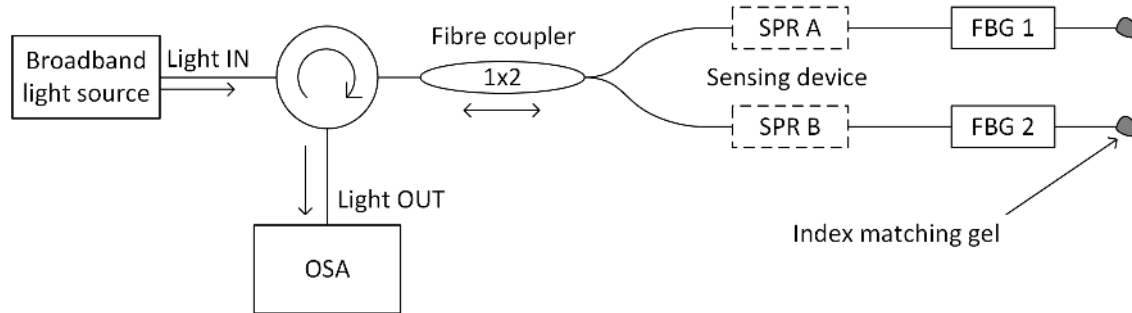


Figure 8.25 – Experimental setup for the characterization of the multiplexing layout with two SPR/FBG fibre sensors.

8.3.3 Results and Discussion

The transmission wavelength spectra of two sensing devices, SPR A and SPR B, obtained by using the setup in Figure 8.23, are shown in Figure 8.26 and Figure 8.27, respectively, for the cases where the external medium was air (RI ~ 1.00) and a liquid in which it was possible to change the RI from 1.300 to 1.380.

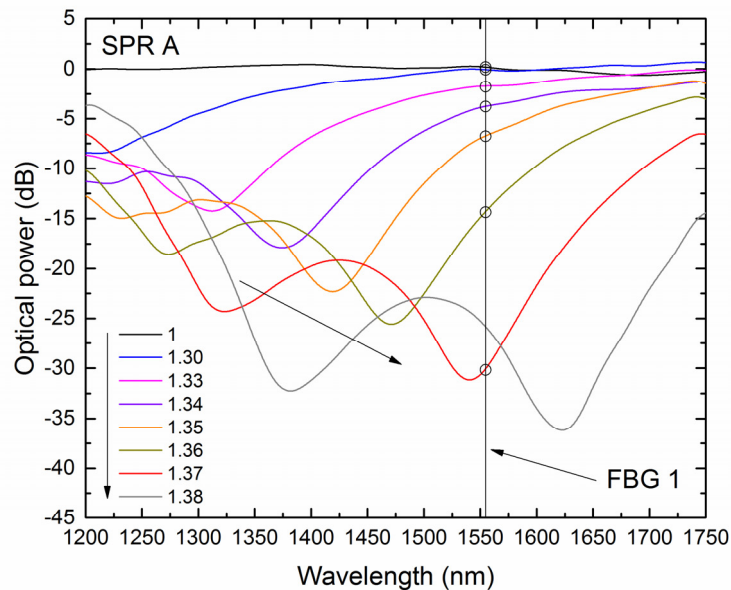


Figure 8.26 – Transmission spectra obtained with SPR A when the external medium is air and liquids with refractive indexes from 1.30 to 1.38.

The SPR A shows two resonances which is a result of two different plasmon excitations and is inherent to the fabrication process. Although both devices were fabricated at the same time, uncertainties related with the etching and coating deposition originates these differences. Taking this into account and regarding the interrogation system, the fact of having different resonances is not an

issue. In fact, other metal/dielectric combinations, which originate different type of resonances, could be used simultaneously. All the measurements were performed at a room temperature of 27.3 ± 0.5 °C.

The SPR B shows a well-defined resonance although a smaller one is detected for lower wavelengths. For both sensors the right side of the resonance dip is the one showing better characteristics for the interrogation approach proposed here, so it was selected for sensor operation considering the RI range from 1.300 to 1.350.

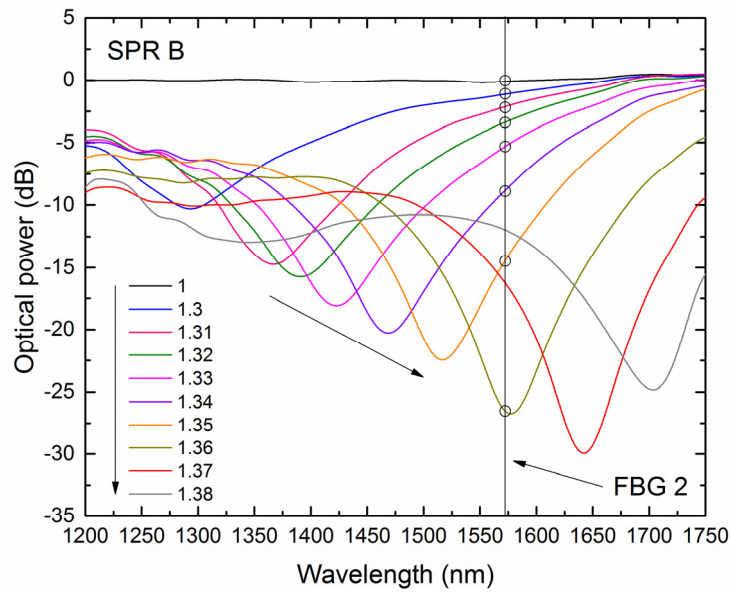


Figure 8.27 – Transmission spectra obtained with SPR B when the external medium is air and liquids with refractive indexes from 1.30 to 1.38.

The vertical lines on Figure 8.26 and Figure 8.27 represent the Bragg wavelengths that will be used for the multiplexing configuration. The reflected FBG 1 band associated to the SPR A is centred at 1554 nm, while the reflected FBG 2 band associated to the SPR B is located at 1574 nm for a room temperature of 27.3 ± 0.2 °C. The spectral bandwidth of the gratings is ~ 3 nm.

The wavelength shift and the normalized optical power of the minimum resonant dip are represented in Figure 8.28 as a function of the external refractive index. This was obtained by tracking the wavelength position and the optical power of the resonance minimum for different external RI.

The wavelength sensitivity (filled symbols) follows the same exponential behaviour as obtained by simulation in section 8.2.3. A linear fitting was calculated, leading to a rough average sensitivity of 5312 and 4967 nm/RIU for SPR A and SPR B, respectively. Although the position of the resonant

dip is different for the same value of the external RI, both devices presents approximately the same behaviour.

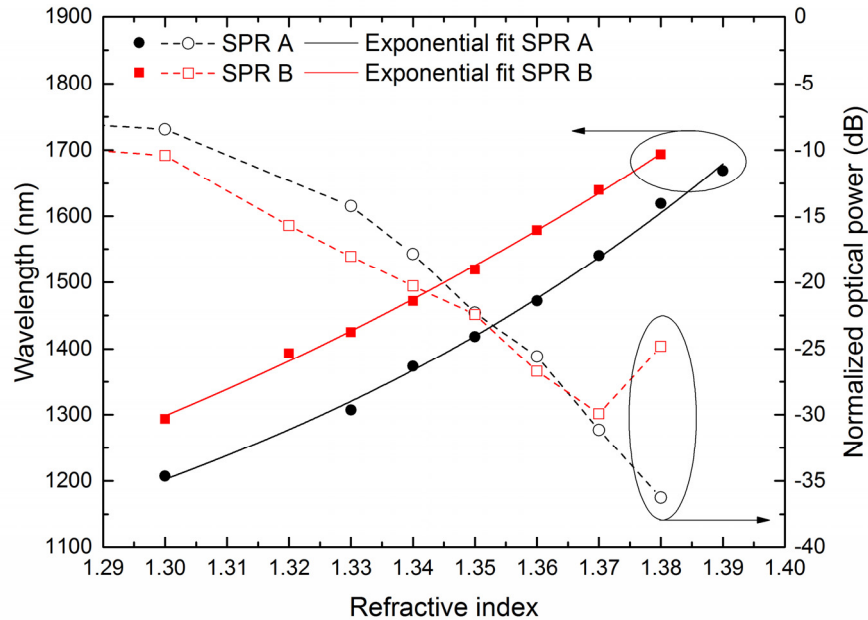


Figure 8.28 – Variation of the wavelength shift with the external RI (filled symbols) and the minimum optical power (open symbols) of both SPR devices.

In order to test this configuration, the single SPR B sensor combined with the respective FBG 2 was immersed in media with different refractive indexes. The response is presented in Figure 8.29.

The open circles show the variation of the reflected optical power from FBG 2 while the RI changes. It is visible a high sensitivity to the external refractive index. The optical power variation of FBG 2 suffers a reduction while the external RI increases as expected and predicted in Figure 8.27. In fact, it has changed more than 20 dB with a RI variation of ~ 0.05 .

The thermal sensitivity was tested by using the same liquid solution with different controlled temperatures. The sensing region was then placed into a glass container filled with water with 1.3325 at 24.8 ± 0.1 °C while the FBG 2 was kept in air. The water was heated with a hot plate in several steps until 52 °C. The filled red circles show a linear effect of the temperature in the FBG 2 optical power.

The RI of water depends of the temperature and it was calculated for the range between 25 and 52 °C by using tabled values [196]. These results were then compared with the calibration curve from the open black circles and a very good agreement is observed.

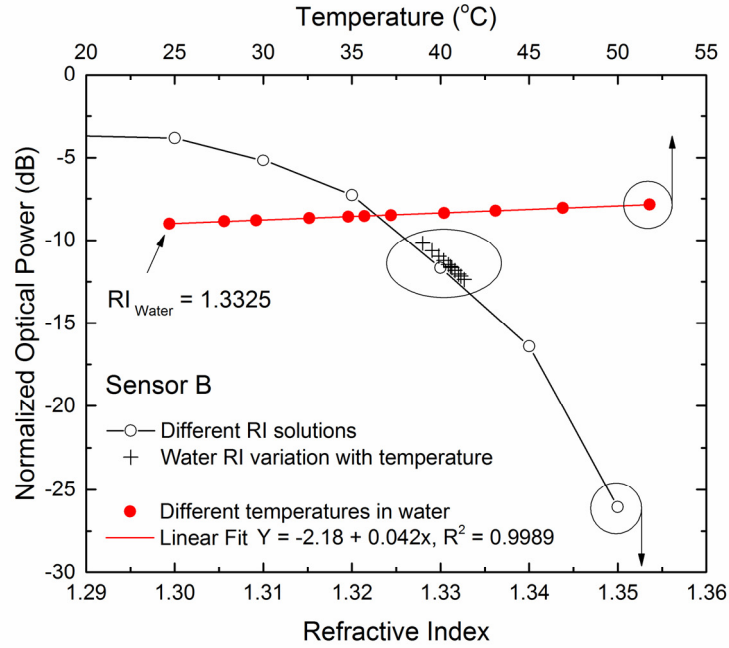


Figure 8.29 – Variation of the reflected output power with the external RI for the FBG 2 combined with SPR B (-o-); optical power level variation increasing the temperature of liquid water (-●-); optical power level considering the water RI variation when the same temperature range is applied (+).

It may be concluded that the reflected optical power of FBG 2 changes not because the physical properties of the sensing device but because of the changes in the RI of the liquid itself. In fact, the sensing device appears to be insensitive to temperature but it can be estimated indirectly by the changes in the RI for the same liquid solution. This is valid for the tested range of temperatures, the thermal expansion of silica, metals and dielectric should in principle affect the sensing response.

The multiplexing approach was characterized in two steps; first the SPR A was tested with different RI liquid samples while SPR B was maintained in air. The second step is the other way around, i.e., to keep the SPR A in air and change the RI solution around SPR B. The FBGs 1 and 2 were located together outside the liquid region to create the same environment conditions. The results are shown in Figure 8.30, clearly indicating the absence of crosstalk between the sensors, an expected result considering that the detection and processing unit of the two sensors operate in different spectral regions due to the wavelength selectivity provided by the FBGs.

It can also be observed for the solution with RI of 1.350 the light signal is very close to the noise level, particularly for FBG 1, indicating the need to tailor the position of each FBG relative to the SPR spectral curve so for the measurement range that needs to be covered this situation does not occur.

The maximum RI sensitivity was achieved for the interval between 1.330 and 1.350 where the resonance is thinner, therefore originating a larger optical power variation for the same RI change. The average sensitivity obtained for this RI interval was 490 and 829 dB/RIU for SPR A and SPR B respectively.

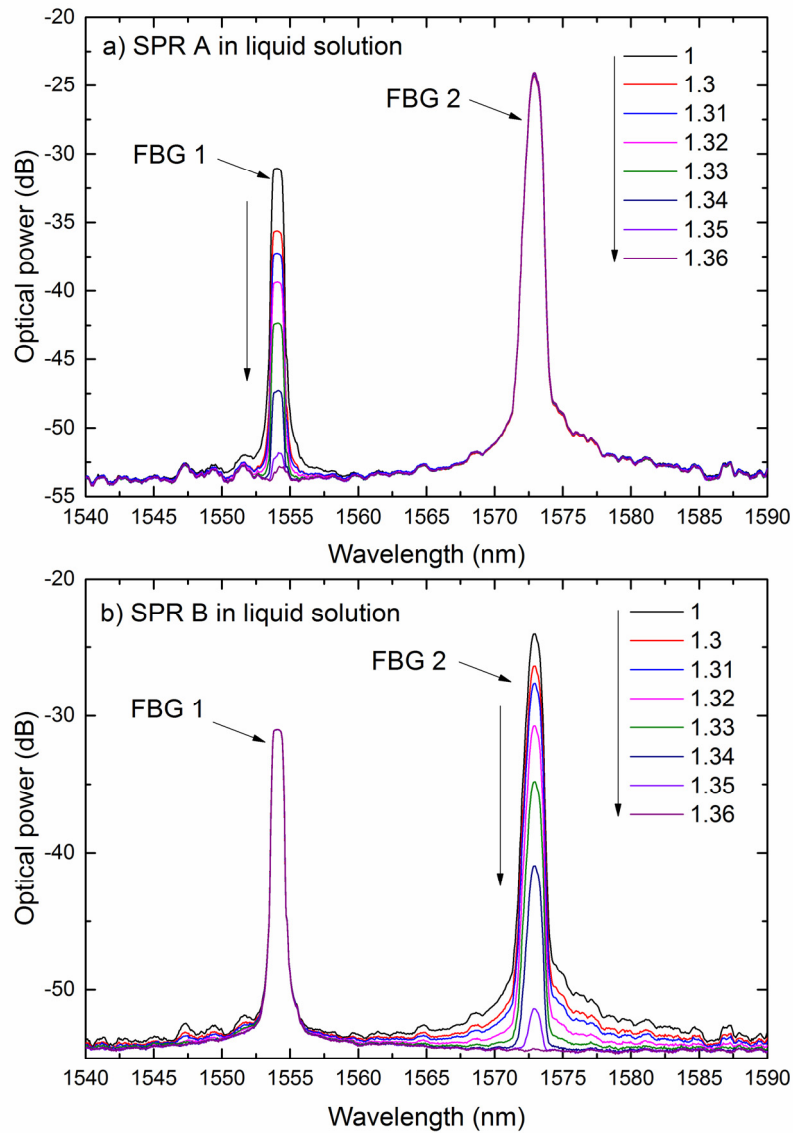


Figure 8.30 – Optical response of both sensing devices in the configuration illustrated in Figure 8.25; sensor A experiences RI changes of the surrounding medium while sensor B is kept in air (a) and the other way around (b).

From the data given in Figure 8.30, the variations in the optical power of each reflected signal are shown in Figure 8.31.

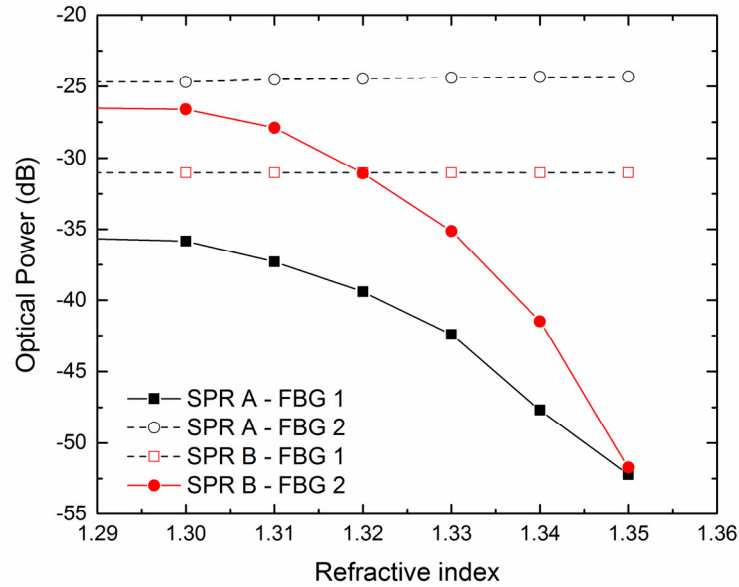


Figure 8.31 – Optical power level returned from the FBGs when the associated SPR sensors are kept in the air and experience liquids with different refractive indexes.

The open symbols represent the reflected optical power of the sensing device that is not in presence of any liquid, therefore maintaining the same optical level. The filled symbols show the variation of the optical power level generated in each FBG when the associated sensor experiences an external medium with different refractive indexes. What turns out from this figure is the non-linear dependence with the RI of the signal generated in each sensing device, as well as the already identified absence of sensor crosstalk.

The measured optical power level depends on the reflectivity of each FBG but the sensitivity to external RI after normalization doesn't depend. Figure 8.30 and Figure 8.31 are not normalized to emphasize that the FBGs and SPR devices could be different as long they are well identified and characterized.

The resolution was estimated with a series of measurements for each RI sample. The process is illustrated in Figure 8.32, that shows the output of the system for sensor A and for sensor B when step RI changes are applied to the sensors. From the sensor response and the noise level present, it was estimated a RI resolution by using the calculation method described in section 4.3.2 of $\sim 2 \times 10^{-4}$ which is an average resolution value for this RI range. It has been demonstrated that the SPR prism technique can achieve RI resolutions down to 10^{-7} [350], with fibre configurations not reaching yet these values but on their way [351]. It is recognized that the value obtained with this setup could be improved by optimizing the relative spectral position of the SPR and FBG devices, as well as looking

for narrower spectral signatures for these structures. The focus here was the demonstration of the multiplexing principles applied to SPR sensors. The potential of wavelength addressing is manifest by observing Figure 8.30.

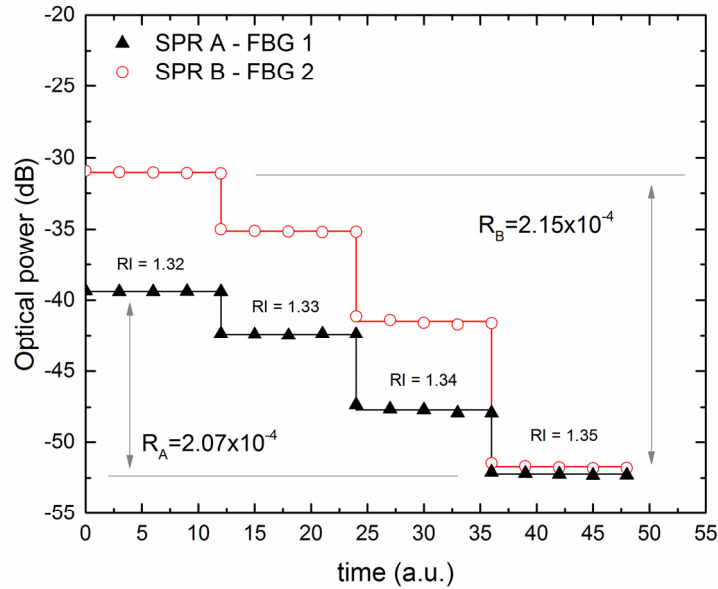


Figure 8.32 – Variation of the sensor's signal output when the surrounding medium undertakes step variations of their RI.

The ability to multiplex a number of SPR sensors is essentially dependent on the number of FBGs with spectral signatures that can be packed in a certain wavelength range, dependent on the spectral response of the SPR sensor structure. Looking into the SPR and FBG spectra shown in Figure 8.24 and Figure 8.30, a number of 10 multiplexed sensors can be considered conservative, anyway indicating the huge increase of measurement capacity based on SPR sensors when the multiplexing approach here described is considered.

As indicate before, when a single FBG is allocated to a SPR sensor, the performance of the proposed interrogation technique is prone to be affected by random intensity fluctuations that can occur in the optical system and not attributed to measurand variations. However, this drawback is overcome by fully applying the methodology described in section 8.3.1 of considering a pair of FBGs for each sensor. Additional attention needs to be delivered for temperature effects. Indeed, when the temperature changes, the Bragg wavelength of the FBGs shifts, therefore inducing a relative variation of the FBGs and SPR spectral signature, that translates into a measurement not related with variation of the medium. This means the need to monitor the temperature changes in each sensing device location, which by itself can be favourable because, with adequate calibration, it permits to separate

the medium RI variations originated by temperature changes. This monitoring can be performed by adding a third FBG to each sensor, located before the SPR structure and with a spectral signature that does not conflict with those that perform wavelength multiplexing of the SPR sensors. The tracking of the Bragg wavelength of this third grating will provide the continuous temperature monitoring of the sensing device, allowing the implementation of compensation procedures.

8.4 Conclusions

In this chapter two works were presented involving surface plasmon resonance phenomena combined with modified optical fibres structures, both presenting high sensitivity to the refractive index of the external medium.

A novel configuration of a surface plasmon resonance sensor in a single mode fibre section chemically etched was presented. The theoretical simulation described accurately the obtained experimental results concerning the sensor sensitivity. The single path in the sensing region (transmission mode) presents better results comparing to the double path when a mirror is produced at the end of the fibre (reflective mode). The wider resonant dips obtained experimentally could be explained with the multimode excitation in the sensing region and the small different thicknesses of the films in the coated region. Sensitivities to RI variations higher than 3800 and 5100 nm/RIU were attained considering the reflection and the transmission modes respectively. It was pointed out that the reflective configuration has potential to show a substantial better sensing performance in what respects RI readout resolution, which adds to its intrinsic favourable geometric characteristics for operation as a remote point sensor.

It was demonstrated that SPR fibre optic sensors are intrinsically compatible with the multiplexing functionality, in the case with the sensors addressed in wavelength and interrogated in intensity. Sensor addressing is achieved by considering for each sensor a pair of FBGs with unique spectral signatures located in the sides of the SPR spectral response. The topological arrangement considered for the sensors was the ladder structure (equivalent to a tree topology for the case of two sensors), with the addressing principle amenable to integration with other topological layouts. The performance of the two-sensor system was characterized, resulting into RI sensor resolution in the order of $\sim 2 \times 10^{-4}$ with sensitivities up to 829 dB/RIU and the observation of negligible sensor crosstalk. Considerations on the dimension of the sensor array based on the proposed multiplexing approach and on the effect of temperature were also delivered.

Chapter 9

Fibre Sensors for Thrombin Detection

Optical fibre sensing devices for the detection of thrombin based on surface plasmon resonance and long period fibre gratings coated with an oxide layer are studied. They are based on the functionalization of the sensing surface of the structure with an aptamer to allow the binding of the target molecule leading to optical variations detectable in the transmission spectrum of the refractometric system.

9.1 Introduction

One of the main objectives of the sensing technology is the development of devices capable to be applied on the recognition of specific target molecules. In this work, the previous developed refractometric platforms were validated as biosensors. For this purpose, the detection of thrombin using an aptamer based probe was used as a model system for protein detection. Thrombin is a key protein involved in the blood coagulation cascade. This enzyme enable blood clotting by cleaving the soluble fibrinogen into the insoluble fibrin strands [352, 353] and plays an important role in thrombosis and hemostasis [352, 354]. The concentration of thrombin in blood is quite variable and several clotting factors, such as fibrinogen, factor V and VIII and platelets are affected by thrombin

concentrations [355]. It is therefore important to monitor the concentration of thrombin in blood in real time. The use of aptamer-based assays for thrombin detection and quantification are interesting diagnostic tools because aptamers can interact with high specificity and affinity to their targets [356, 357], due to its ability to fold into numerous tertiary conformations. Furthermore, they can be generated by a combinatorial procedure called systematic evolution of ligands by exponential enrichment - SELEX [358] and synthesized in a large quantity in vitro in a very reproducible way [359, 360]. They are also thermally and chemically very stable, which increases its use in time without losing its ability to bind specifically to their target [361, 362].

Surface Plasmon Resonance (SPR) is the base for some of the most sensitive label free optical fibre biosensors. However, most solutions presented to date require the use of fragile fibre optic structures. On the other hand, long period fibre gratings (LPFGs) are an interesting solution to attain an evanescent wave refractive index (RI) sensor platform while preserving the optical fibre integrity. The combination of these two approaches was recently demonstrated by detailed theoretical study [33, 363].

In the present work, different approaches with LPFGs and SPR aptamer based devices were tested in order to obtain a reliable study to the thrombin detection being then validated as a biosensor. First, a LPFG-SPR platform is explored in two different configurations (symmetric and asymmetric metal coatings between the two cylindrical shape LPFGs). The purpose is to have maximum coupling of energy from the core mode to cladding modes in order to obtain a strong interaction of the electromagnetic field with the SPR structure which will be then coupled back to the core mode with a minimum of interference.

The Mach-Zehnder based configuration was adopted using two identical inline LPFGs and attenuation bands intensities of more than 20 dB. Then, the single LPFG and SPR structures studied in sections 4.3.1 and 8.2, respectively, are presented after functionalization leading to the binding of thrombin target molecule. Those two sensing structures are compared using thrombin concentrations from 10 nM to 100 nM.

9.2 Materials and Methods

9.2.1 Reagents and Solutions

The procedure for the detection and quantification of thrombin involves the combination of a set of reagents and solutions: the thrombin binding aptamer (TBA), a 15 mer DNA oligonucleotide (5'-amine-GGTTGGTGTGGTTGG-3') with a synthesis scale of 0.2 μ M, HPLC purification, 5' amine modification, purchased from Sigma-Aldrich (Spain). Human- α -thrombin was obtained from Haematologic Technologies in a concentration of 1 mg mL⁻¹ (50 mM sodium phosphate, 150 mM sodium chloride, pH 6.5, 3757 U mg⁻¹). The solutions of thrombin used in each assay were prepared by dilution in 10 mM of phosphate buffered saline (PBS) from Sigma-Aldrich (Spain) in Eppendorf's blocked with 1 % bovine serum albumin (BSA), from Merck, aliquoted and stored at -80 °C. Salts for buffer solutions were prepared in ultra-pure water, <15 M Ω .cm at 25 °C. Hydrochloric acid (HCl), isopropyl alcohol (IPA), sodium hypochlorite, ethanol (EtOH) and magnesium chloride was purchased from Panreac (Spain), tris(hydroxymethyl)aminomethane (Tris), 0.1 % (w/v) poly-L-lysine (PLL), potassium chloride (KCl), sodium chloride (NaCl), SSPE buffer 20X concentrate (1X = 0.150 M sodium chloride, 0.010 M sodium phosphate, 0.001 M EDTA) and Tris-EDTA (TE) were obtained from Sigma (Germany). The buffers used in this work were: aptamer resuspension buffer: TE (10 mM Tris pH 7.5-8.0; 1 mM EDTA); aptamer immobilization buffer: SSPE (1:10), (diluted from 20X SSPE); affinity buffer (50 mM Tris-HCl pH 7.4, 250 mM NaCl, 5 mM MgCl₂) and measurement buffer (10 mM Tris-HCl pH 7.4, 100 mM KCl). All the reagents were of analytical grade.

9.2.2 Sensing Probe Assembly and Thrombin Detection

Both sensing surfaces were functionalized with PLL, followed by the immobilization of the DNA probe, TBA, for the specific recognition of thrombin. The detailed biosensor principle is illustrated in Figure 9.1. First, the sensing surface (a) was cleaned with IPA and then rinsed with ultra-pure water and dried with N₂. Then, the surface was functionalized with PLL (b) for 60 min. at room temperature. The polycationic nature of the PLL leads to its electrostatic attraction onto the fibre negatively charged surface, in an aqueous environment at neutral pH (7.4). The 5'-amine modified TBA (500 nM) was then incubated during 60 minutes at room temperature to enable covalent attachment to PLL backbone (c). In the absence of thrombin, the TBA remains at its secondary

conformation. In the presence of thrombin, the TBA folds around the protein and forms a TBA/thrombin complex, acquiring the G-quarter (tertiary) conformation (d). The formation of this complex causes an increase in the effective RI which change the optical properties of the guided light.

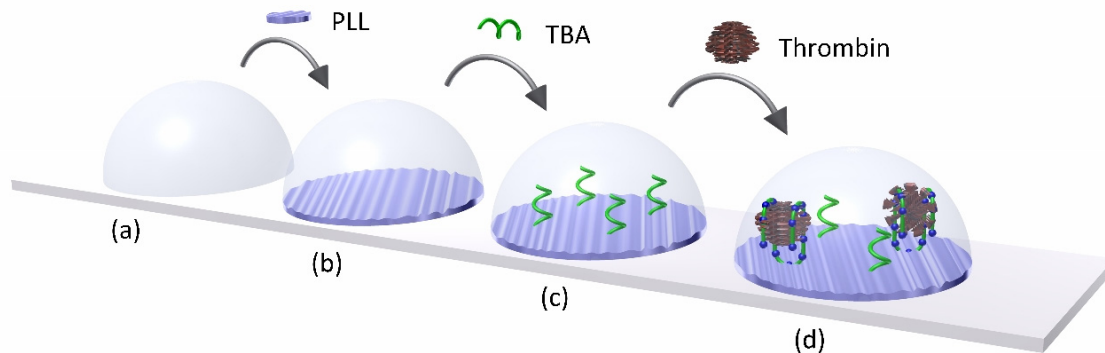


Figure 9.1 – Detailed scheme of the biosensor binding principle.

The sensing devices were incubated with several varying concentrations of thrombin, in the affinity buffer for 1h. The sensor response was measured in the concentration range from 10 to 100 nM. Between all concentrations steps the sensing device surfaces were washed with Tris–HCl buffer and the transmission spectra was recorded with the Bragg meter in the measurement buffer. After a complete assay the sensing probe was washed with a hypochlorite solution for 30 minutes, to regenerate the fibre sensor surface for re-use.

9.2.3 Sensing Structures

Taking advantage of the characterizations fulfilled in the previous chapters the detection of thrombin is achieved in this section based on two configurations, LPFG and SPR-based fibre. First, two LPFGs were used in series as a medium to the evanescent field of the guided light interact to the fibre surface and excite the plasmon wave leading to the SPR effect aiming the detection of thrombin. Second, the two configurations are explored independently. The sensing properties of the LPFG coated with titanium dioxide (TiO_2) thin film and the SPR-based taper configuration for thrombin detection are analysed and compared. The LPFGs and the SPR-based devices were fabricated according to the procedures described in section 3.1.

The configuration LPFG-SPR-LPFG is illustrated in Figure 9.2 (scheme 1) were a section of fibre containing a metal/dielectric coatings was fusion spliced between two LPFGs working in

transmission mode. The LPFGs were fabricated with the same characteristics and spectral properties as wavelength position and maximum attenuation. It is important to obtain these characteristics in order to minimize the interference among them. Due to the LPFG structure the light traveling in the core mode is coupled to cladding modes. The evanescent wave in the higher cladding modes reaches the surface interacting with the external medium. The optical setup included a broadband light source (BBS), an optical spectrum analyser (OSA - model ANDO AQ-6315B) and a fluidic system where the fibre is fixed maintaining the coated fibre section in contact with the sample while the LPFGs are free.

The coating region is formed by 2 nm of chromium (Cr), 16 nm of gold (Au) and 100 nm of TiO_2 and is less than 1 cm long. The evanescent wave excite surface plasmonic waves in the metal/dielectric interface, decaying exponentially into both medium, being highly sensitivity to the external RI variations. When the light crosses the second LPFG, two centimetres ahead, a substantial fraction is coupled back to the core mode and interfere with the remaining light of the core. This interference has a minimum visibility when the spectral features of the LPFGs are identical with a maximum of attenuation. The fibre was properly fixed with a fibre clamp in one end and a mass in the other, applying a small and constant strain to avoid strain/curvature cross sensitivity. Two types of coatings were performed, one homogeneous around the cylindrical fibre obtained by rotation (sensor A) while the other is fixed being the film deposited only in one side of the fibre (sensor B).

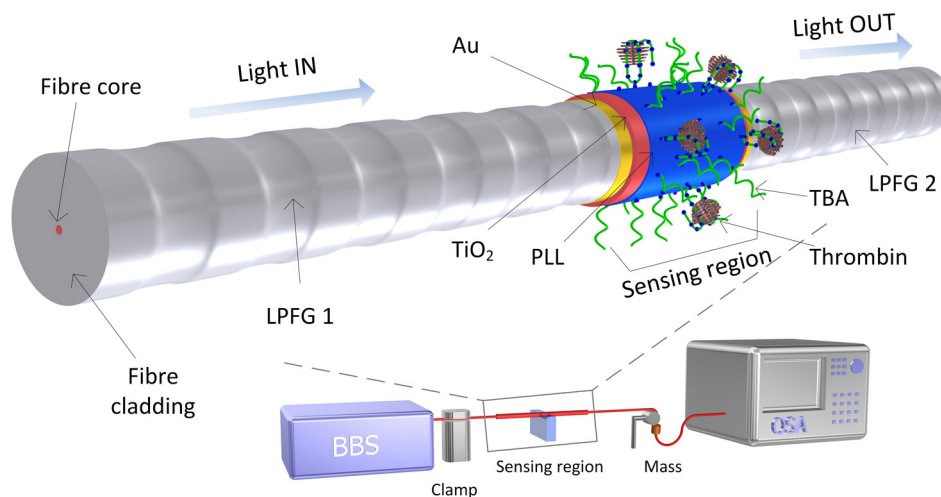


Figure 9.2 – Scheme of the LPFG-SPR-LPFG configuration (Scheme 1).

The independent configurations using the LPFG and the SPR are depicted in Figure 9.3. The coated LPFG, as studied in section 4.3.1, is used in this study to attest the improvement of the sensitivity to

external RI medium and shown in Figure 9.3-(a), (scheme 2). It was coated with 2 nm of Cr and 30 nm of TiO_2 which improves the sensitivity to the external RI around 1.335. The LPFG is sensitive to thermal variations so, in order to compensate this effect, a fibre Bragg grating (FBG) which is insensitive to RI variations was produced next to it. The characterization setup for the LPFG (a) includes a FS2200 Bragg Meter from FiberSensing, SA (Portugal), a fluidic system containing a reaction chamber with capacity of 750 μL and a laptop (not shown) with LabVIEW software that receives and processes the readout information. The sensing elements LPFG and FBG were characterized using the FS2200 Braggmeter (working in the 1500–1600 nm range with 2.5 pm of resolution) and modified to measure signals in both modes, reflection and transmission.

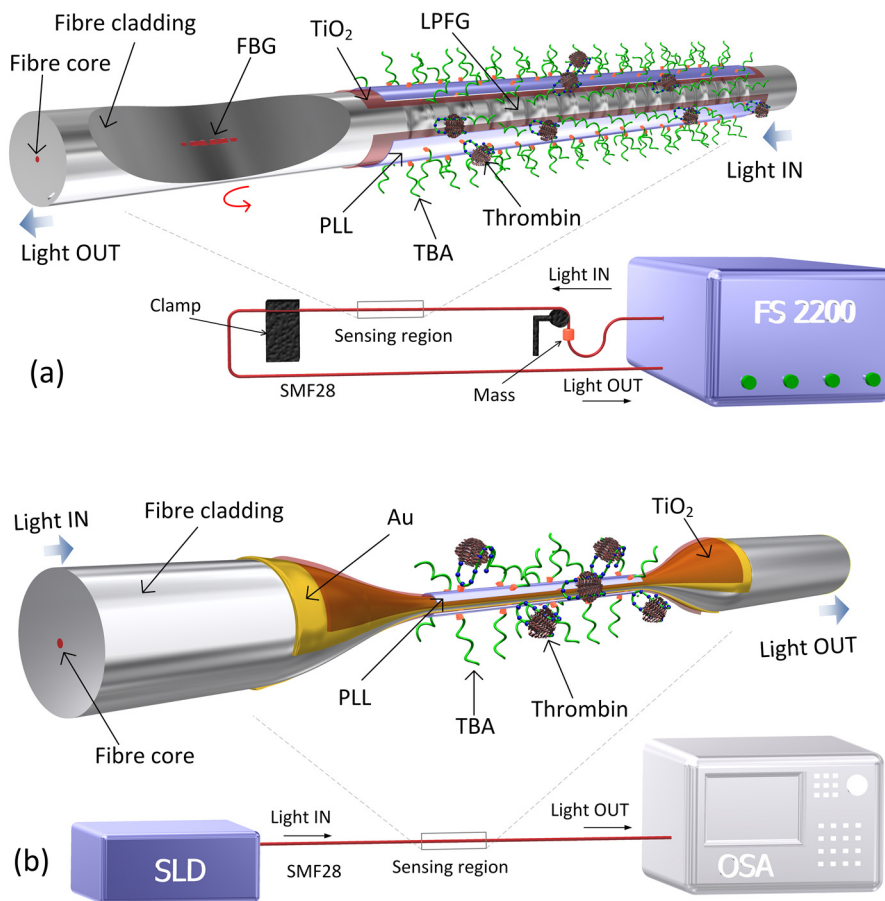


Figure 9.3 – Schemes of the independent configurations for the thrombin detection: (a) LPFG (Scheme 2); (b) SPR (Scheme 3).

The SPR configuration adopted was already studied in section 8.2 with an etched section of a single mode fibre to monitor the external RI [shown in Figure 9.3-(b), scheme 3]. The sensing region, located in the thinner region of the etched section where the evanescent field is able to excite the

plasmonic wave, has approximately 16 μm of diameter. It is coated with 2 nm of Cr, 16 nm of Au and 100 nm of TiO_2 .

The characterization setup for the SPR sensor (b) includes a super luminescent diode source (SLD) model S5FC1550S-A2 (Benchtop SLD – Thorlabs, Germany), a fluidic system where the fibre is fixed and the OSA (ANDO, model AQ 6315B). The two different setups are needed for simultaneous measurements. Although the FS2200 Braggmeter is capable to monitor two sets of sensors, the spectral window is limited to a region away from the SPR spectral response when low RI values are considered.

9.3 Results and Discussion

9.3.1 LPFG-SPR-LPFG configuration (Scheme 1)

This configuration implies two identical LPFGs in order to diminish the optical interference. The individual transmission spectra of the four LPFGs used in the sensors A and B are plotted in Figure 9.4. Although the fabrication of LPFGs based on the electric arc technique has many variables the attenuation bands are quite similar.

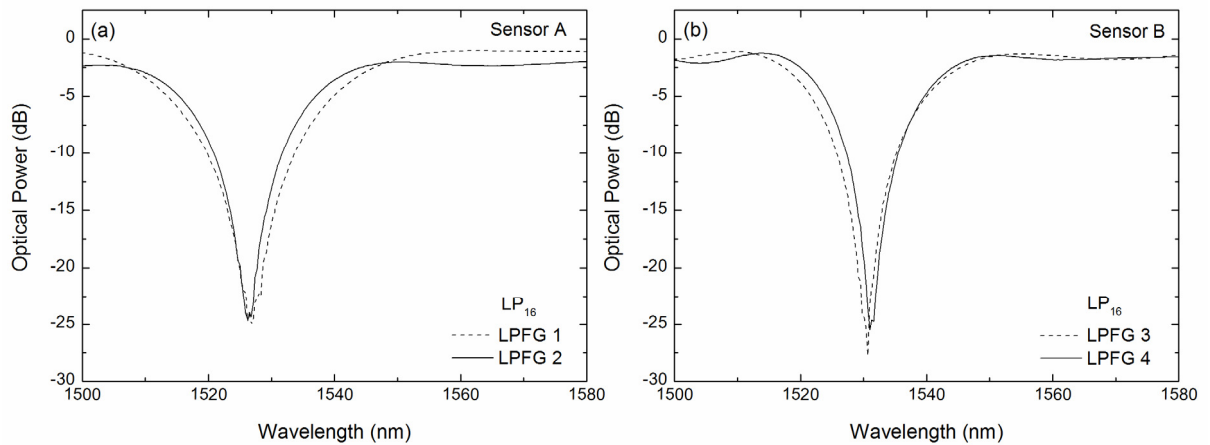


Figure 9.4 – Transmission spectra of each independent LPFG used in the scheme 1: (a) sensor A; (b) sensor B.

– Refractive index characterization

The sensors A and B, corresponding to the different coating type between the LPFGs, were characterized as a function of the surround refractive index (SRI) with the same set of RI calibration

liquids (Cargille-Sacher Laboratories Inc., NJ. U.S.A.). Figure 9.5 shows the spectra obtained for each device for a set of RI from 1.00 to 1.42 at 589.3 nm.

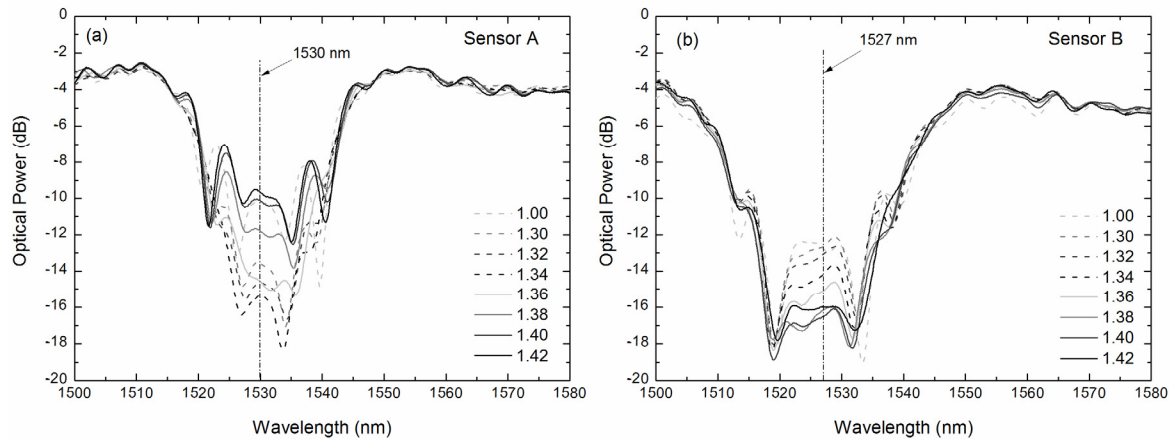


Figure 9.5 –Spectra obtained with different SRI from 1.00 to 1.42: (a) sensor A; (b) sensor B.

The variations in the optical power at the LPFGs region are visible and are related to the overlapping of the SPR phenomenon which causes losses in the recoupling at the second LPFG.

Considering, for example, a fixed wavelength at the central region of both sensors, A (1530 nm) and B (1527 nm), the variation in the optical power is recorded and correlated to the external RI. The Figure 9.6 shows the response of both cases (a) and (b) respectively, where the curves suggest the shape of the SPR resonance. The first (a) appears to be narrower than the second one (b) due to the full overcoat of the fibre. In this case the film is produced with the rotary system and the film thickness may change slightly which causes an enlargement of the typical SPR spectral shape due to the integration of all resonances that appears for each film thickness. For sensor B, the same effect is observed but the dip looks wider due to the presence of regions where the thickness goes down to zero.

To detect small changes in the effective RI the slope of the sensitivity curves needs to be higher as possible and it depends of the SPR position and attenuation. This can be optimized by changing the physical properties of the coating.

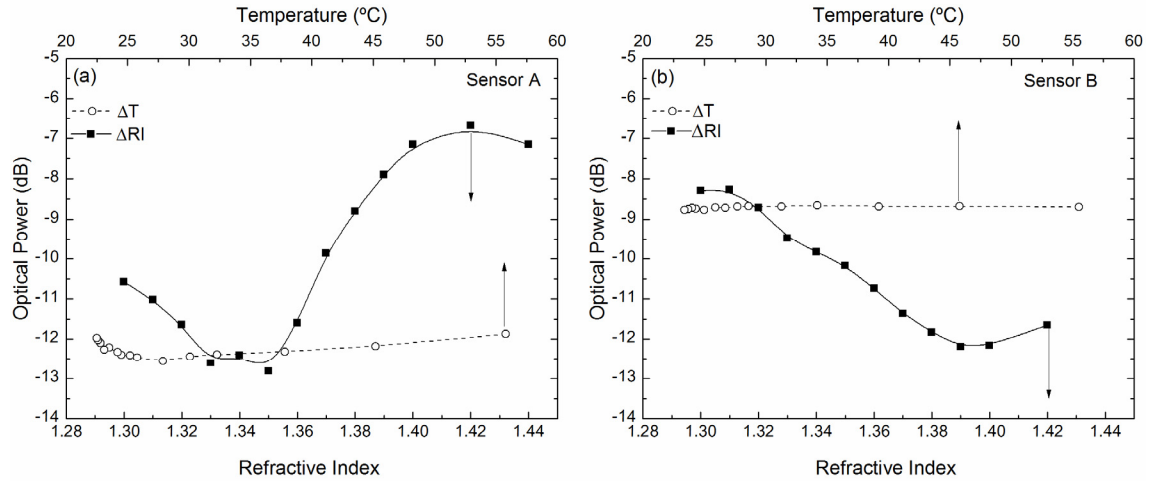


Figure 9.6 – Calibration of the sensors A and B to the SRI changes considering a specific wavelength: (a) 1530 nm (sensor A) and (b) 1527 nm (sensor B).

The results of Figure 9.6 also show that the sensor structures are essentially not affected by temperature variations, an important characteristic considering their application in field environments.

– Sensor performance

The sensing performance of the LPFG-SPR-LPFG (Scheme 1) configuration was tested to 100 nM of thrombin concentration in the measuring buffer solution.

The preliminary results with sensor A are shown in Figure 9.7-(a) and it is possible to observe that after the binding of the thrombin to the TBA the signal shifts 0.5 dB, returning to the initial position when regenerated. The thrombin molecule binds to the aptamer origin a variation in the effective RI. The plasmon resonance shifts in wavelength causing a variation in optical power in the LPFGs region. When the coating surface is exposed, the signal returns to the same level suggesting the total regeneration.

The results achieved with sensor B show smaller sensitivity to the presence of thrombin [Figure 9.7-(b)] but still can be observed that the molecule is attached to the fibre. The thickness profile of the coating, due to the geometry, shows that only a small region of the coating has approximately the desired value. The remaining coating excites plasmons in different wavelengths which do not interfere in the LPFGs region. The small area of interaction decreases the sensitivity to the thrombin detection. The regeneration in this case wasn't observed. It may be concluded that the deposition of thin films around the fibre improves the sensitivity of the sensor.

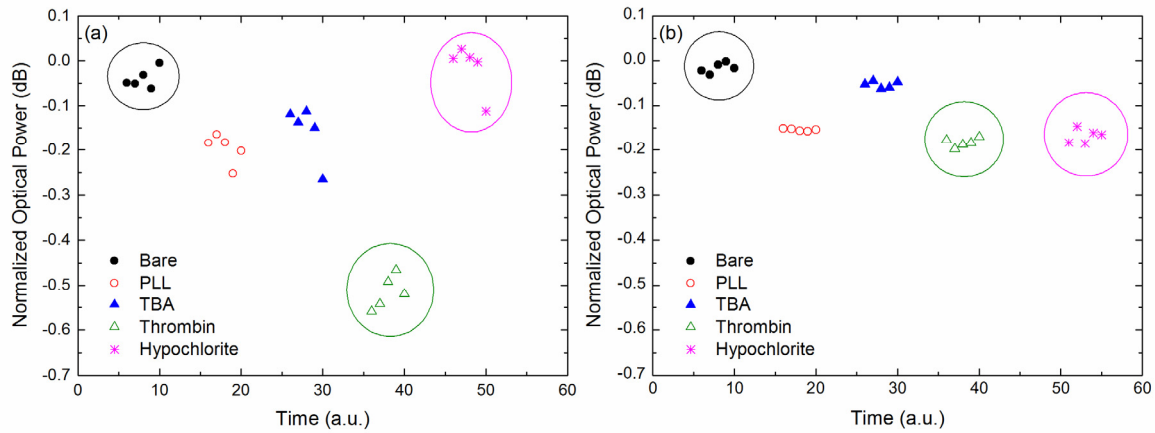


Figure 9.7 – Normalized optical power for both sensors at the same specific wavelengths: a) 1530 nm (Sensor A) and b) 1527 nm (Sensor B).

9.3.2 Independent LPFG and SPR Fibre Based Thrombin Detection (Schemes 2 and 3)

– Refractive index characterization

Both sensing devices were characterized in terms of the SRI changes. Solutions with different RI values were prepared by adding ethylene glycol to ultra-pure water. This method allows the possibility to create solutions with RI from 1.335 (water) to 1.430 (ethylene glycol) [343] varying the concentration of the mixture. In order to accomplish homogeneous solutions, a magnetic stirrer was used and the measurements were accomplished within the minimum time. The solution concentration was changed by adding 10 ml of ethylene glycol on each step starting with 100 ml of ultra-pure water. In parallel to the optical characterization of the fibre sensing devices the RI of the samples was measured at room temperature (26 ± 1 °C) using an Abbe refractometer (A. Kruss, Optronic, Germany) with a RI resolution of 2.5×10^{-4} . Solutions with RI in the range from 1.3350 to 1.3725 were attained.

After each measurement the sensing device was flushed with 20 ml of ethanol and dried with filtered air to avoid contamination to the next sample. Then the spectrum of each sensor was monitored to ensure that the initial spectral conditions was verified.

The importance on this optical characterization of the sensors relies on the expected increase of the effective SRI after the PLL layer coating as well as with the immobilization of the TBA and the binding of thrombin.

The wavelength dependence with the external refractive index of the LPFG and the SPR are presented in Figure 9.8 (Scheme 2) and Figure 9.9 (Scheme 3), respectively.

The dependence of the wavelength with the RI is not linear as was discussed in the previous chapters and confirmed here, nevertheless, a rough linear fitting can be made in the RI range from 1.335 to 1.355 where the corresponding changes induced by the thrombin detection are expected.

a) Scheme 2

Figure 9.8-(a) shows the spectra of the LPFG when placed in different RI solutions allowing to trace the spectral sensitivity to the SRI wavelength shift presented in Figure 9.8-(b).

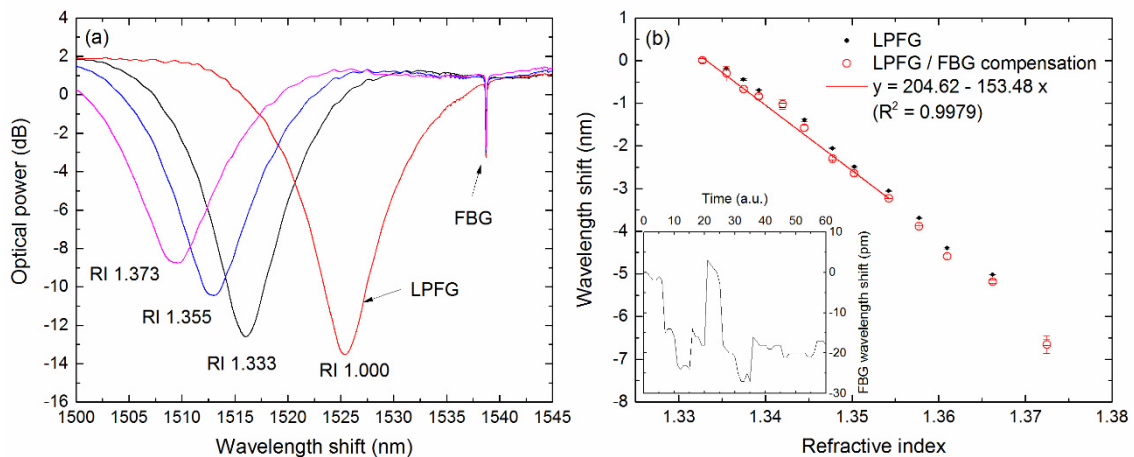


Figure 9.8 – (a) Spectra of the LPFG at different SRI, the FBG located at higher wavelength (b) LPFG wavelength shift to SRI between 1.335 and 1.375 with thermal compensation and with a linear fit up to 1.355. Inset: FBG spectral response due to thermal variations.

The LPFGs are sensitive to temperature as well but coupled to the FBG which is insensitive to the SRI these variations can be compensated [282]. Inset is the wavelength shift of the FBG transmission peak showing the thermal variation of each measuring point, which is used to calibrate the LPFG data points leading to a sensitivity to the SRI of 153.5 nm/RIU, which is slightly higher than the bare LPFG as reported in section 4.3.1.

b) Scheme 3

In Figure 9.9-(a) the spectra obtained with the SPR are presented. It is visible the wider shape of the attenuation band, nevertheless the wavelength shift attained for the same RI samples is extremely higher comparing to the LPFG. The data points corresponding to the SPR sensor presented in Figure 9.9-(b) were fitted to a linear trend in the range from 1.335 to 1.355 range, which leads to a calculated sensitivity higher than 3000 nm/RIU.

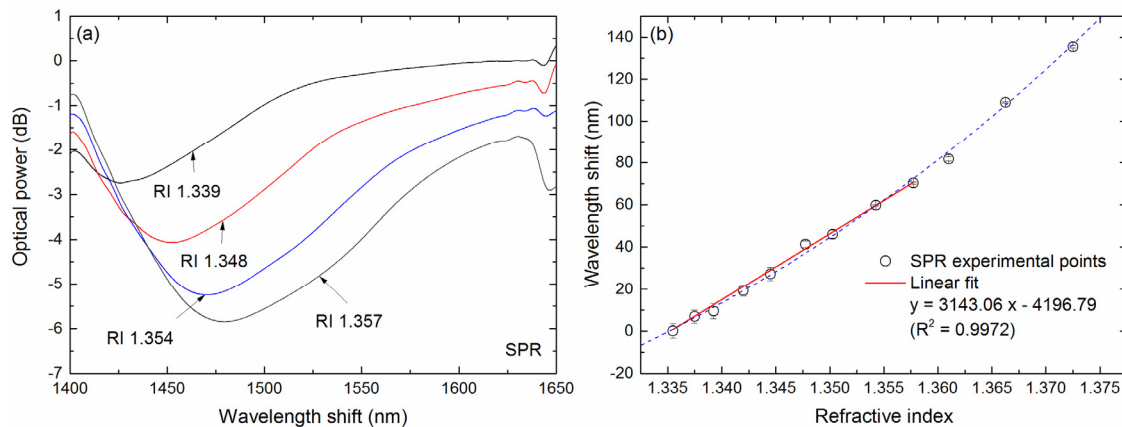


Figure 9.9 – (a) spectra of the SPR at different SRI, (b) SPR wavelength shift to SRI between 1.335 and 1.375 with a linear fit to lower RIs .

The low temperature variations are not an issue when the SPR device is considered, as discussed in section 8.3.3. Despite the material properties of the SPR layers being affected by temperature, as thermal expansion, it is not reflected in the optical properties when low variations are considered. In addition, it is known [196] that the RI of liquids changes with temperature with a factor of $\sim 1.73 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$, which can be neglected for this working range.

– *Sensor performance to 100 nM of thrombin*

The sensor performance was tested against varying concentration of thrombin (10 – 100 nM) in the measuring buffer solution, using both sensing systems, LPFG and SPR-based.

a) Scheme 2

Figure 9.10 shows the spectral results of the LPFG coated with 30 nm of TiO_2 in series with a FBG across the functionalization procedure with PLL, the immobilization of the DNA probe, the thrombin detection with a concentration of 100 nM and the regeneration using hypochlorite. In Figure 9.10-(a) the raw spectra of the LPFG is shown and slight changes are observed for the different conditions.

The LPFG response to the surface functionalization and thrombin detection measured in buffer solution is shown in Figure 9.10-(b). Well defined steps, corresponding to the different layers attached to the LPFG surface, were attained after the thermal effect correction calculated with the FBG from Figure 9.10-(c) and Figure 9.10-(d). Although the small variations observed in the FBG transmitted spectra in Figure 9.10-(c), due to thermal oscillations along the functionalization and detection procedure, the FBG wavelength shift in Figure 9.10-(d) is used for the LPFG calibration considering the well-known intrinsic temperature sensitivities of each structure.

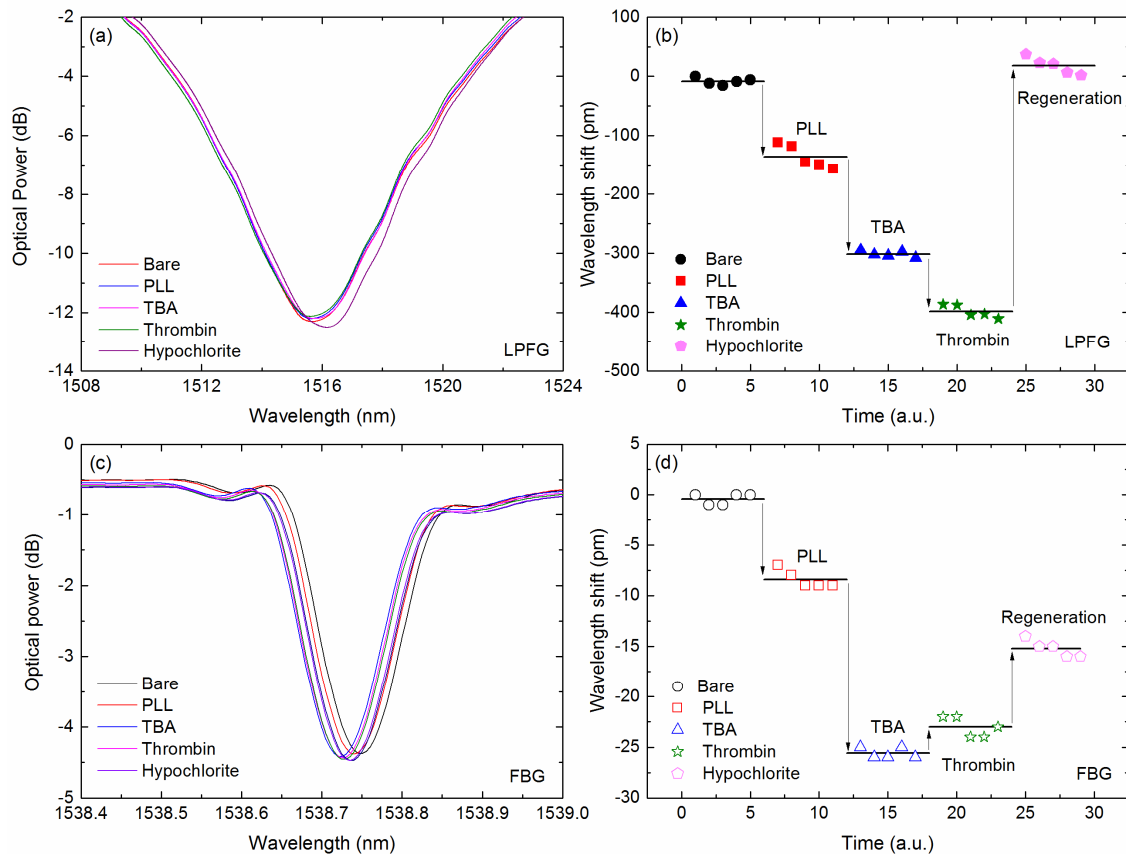


Figure 9.10 – Results in Tris-HCl buffer solution after each procedure step (PLL, TBA, thrombin and hypochlorite) at room temperature with $n=5$: (a) Spectra of the LPFG coated with 30 nm of TiO_2 , (b) Wavelength shift of the LPFG after temperature correction, (c) Transmission FBG spectra (d) FBG wavelength shift behaviour.

The negative wavelength shift of about 128 pm observed, reflects an increase of the effective RI, which is a result of the PLL coating (as reported by [364]). The immobilization of the DNA probe – TBA cause a resonance peak shift of 165 pm. The aptamer binding to thrombin results in a wavelength shift of about 100 pm. The resolution for the thrombin detection was calculated using the TBA / thrombin step as 10.4 nM for a concentration of 100 nM. It is visible in the last step

(regeneration with hypochlorite) that the sensor surface was completely regenerated and ready for a new functionalization and detection procedure.

b) Scheme 3

The SPR spectra obtained at each step of the thrombin detection (for a concentration of 100 nM) is shown in Figure 9.11. The shape is wider with lower attenuation when compared to the LPFG therefore the sensitivity to the SRI is more than 20 times higher. In addition to the wavelength sensitivity to the SRI, this particular sensor presents an intensity sensitivity which can be exploited.

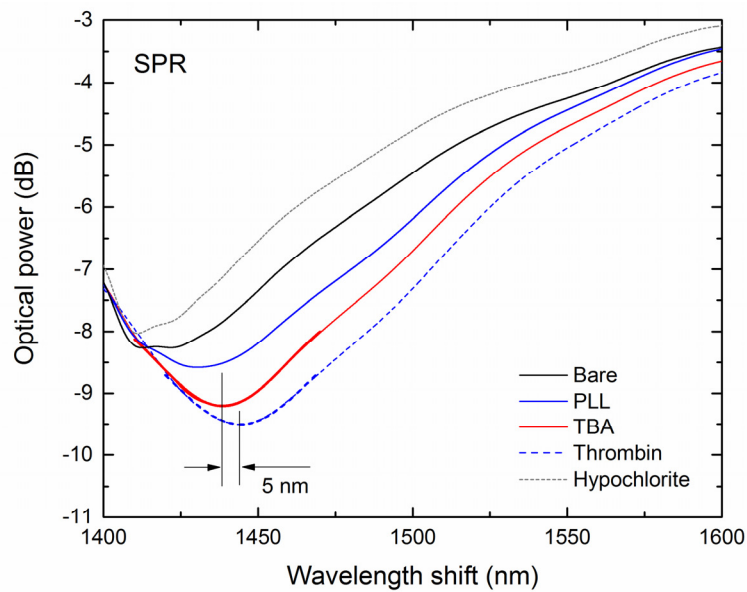


Figure 9.11 – Average spectra of the SPR with Au and TiO₂ at each procedure step.

The spectral features of the SPR in transmission mode are illustrated in Figure 9.12 in terms of the wavelength shift (a) and the optical power shift (b) considering the functionalization steps, the thrombin detection and the regeneration of the sensor. Wavelength shifts of 10.3 and 8.2 nm for the PLL coating and the TBA immobilization, respectively, were achieved. The step corresponding to the 100 nM thrombin detection shows a variation of 4.94 nm, a considerable improvement when compared to ~100 pm from the LPFG results (Scheme 2).

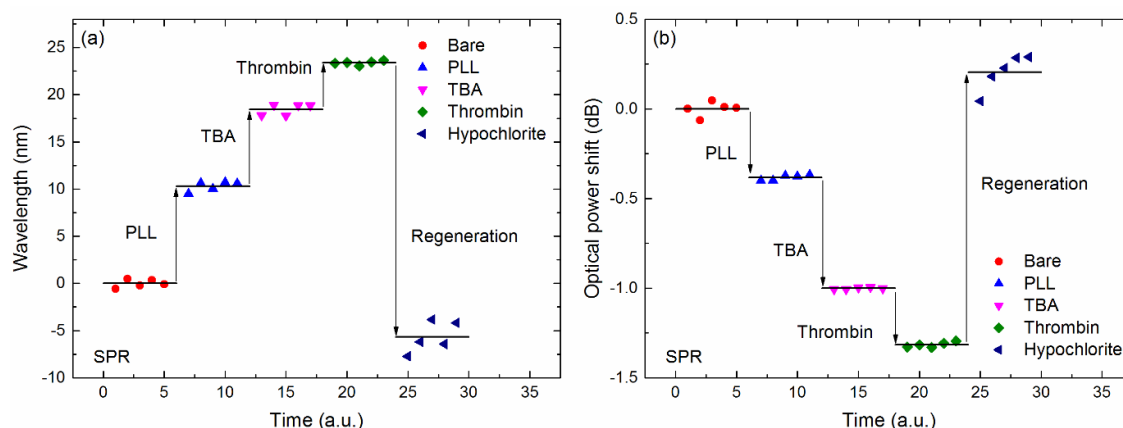


Figure 9.12 – Results of the SPR in buffer solution after each procedure step (PLL, TBA, thrombin and hypochlorite): (a) wavelength shift; (b) optical power shift.

The optical power shift follows the same behaviour with well-defined steps allowing the sensor to be used in intensity modulation mode. In both modes the functionalization layers are completely removed from the surface in the regeneration step allowing new measurement cycles.

The thrombin detection resolutions using the SPR sensor for the wavelength and intensity modulations was calculated as 1.08 nM and 0.13 nM, respectively.

– Sensor performance in the range 10 to 100 nM of thrombin (Schemes 2 and 3)

Concerning the feasibility of the sensing devices to the thrombin detection to 100 nM of concentration, new functionalization cycles using the same sensing devices were processed aiming the detection of thrombin with concentrations of 10, 50 and 100 nM.

The results of the wavelength shift for both concentrations normalized to the TBA are shown in Figure 9.13. The SPR results (Scheme 3) are represented with empty symbols. In the presence of 10 nM of thrombin, the resonance shifts ~ 3.5 nm with a resolution of 0.54 nM. Increasing the concentration to 50 nM leads to new shift of the resonance of about 1.5 nm with a total 5 nm shift after the TBA immobilization, which corresponds to the previous results using 100 nM. A new increase of the concentration to 100 nM using an incremental procedure returned the same resonance position. The unexpected absence of wavelength shift between 50 and 100 nM and considering the ~ 5 nm obtained between 0 and 100 nM of thrombin concentration in different trials, suggests that this concentration level is out of range. While the concentrations of 50 and 100 nM of thrombin have returned “virtual” results, the measurement of 10 nM appears to be far from a saturation limit, thus far from a detection limit with a shift of 3.5 nm.

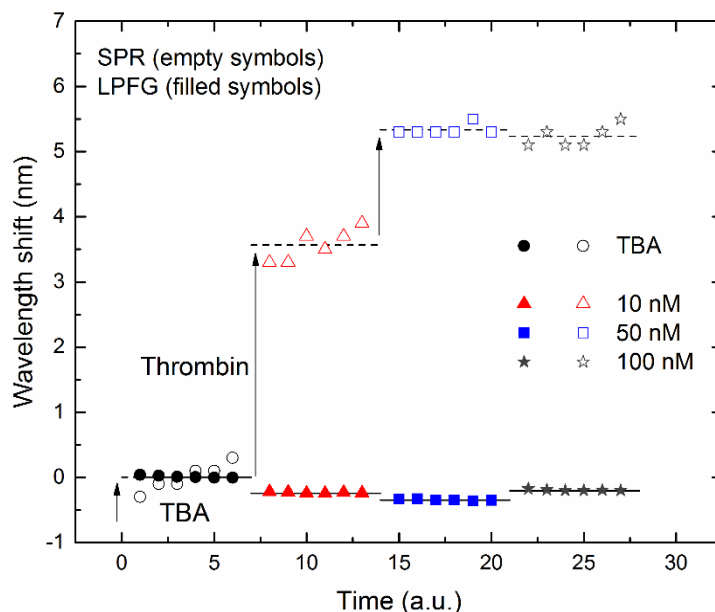


Figure 9.13 – Wavelength shift of the LPFG (filled symbols) and for the SPR (empty symbols) in Tris buffer solution after the TBA immobilization and after the thrombin concentrations 10, 50 and 100 nM.

The LPFG (Scheme 2) have returned wavelength shifts between 200 and 300 pm for the increasing thrombin concentrations. The lower sensitivity to the external RI is a barrier to quantify the thrombin concentrations with accuracy, nevertheless in can be used to act only for presence/absence detection.

9.4 Conclusions

The detection of thrombin was studied using three sensing schemes based on two different sensing configurations, LPFGs and SPR fibre based, where the sensing region is functionalized with the same cationic polymer PLL. The results indicate the viability of the Fibre-Aptamer as a flexible platform to point of care biosensors for diagnostic purposes.

Preliminary results of combined LPFG-SPR-LPFG structures show that the thrombin molecule is immobilized on the surface changing the optical properties of the sensing device. The functionalization over the homogeneous coating around the cylindrical fibre was found to be the best approach. However, this structure presents high dependence to a considerable number of parameters as strain, curvature and temperature. The study of independent structures as LPFGs and SPRs have returned more promising results. LPFGs with oxide coatings improves the sensitivity to external refractive indices and have proven the feasibility of thrombin detection and quantification. Although the dependence to temperature, the robustness and the narrow bands leads to possible applications

with multiplexing capabilities. The coupling to FBGs allows the post processing corrections to thermal variations. The higher RI sensitivity of the SPR, combined with the low sensitivity to thermal variations, have shown detection levels (with reproducibility) of thrombin in solution with concentrations down to 10 nM. The regeneration of the surface was attained in both configurations allowing new functionalization procedure using the same sensing device. Both refractometric platforms allows to use the external RI variations to calculate the thrombin concentration in the buffer solution, therefore, the same concept could, in principle, be applied to estimate the RI/thickness of the PLL layer or even the DNA immobilization.

Chapter 10

Final Conclusions and Future Work

The work presented in this dissertation has as core element the expertise and competences acquired in thin films coating technology associated to the conception, development and characterization of optical structures in fibre optic for sensing purposes. The coated induced enhancement of optical properties of sensing structures relying on Bragg gratings, long period gratings and surface plasmon resonance in standard optical fibres, all operating in the at 1500 nm wavelength window, enable new possibilities in fibre optic sensing technology which have been started to be explored in recent years.

The deposition of metal and oxide thin films around silica optical fibres with cylindrical shape have been accomplished. It was found that the spectral behaviour of long period gratings changed according to the coating properties. Studies of LPFG coated with metal oxides as titanium oxide (TiO_2) and zinc oxide (ZnO) have been developed, showing a considerable sensitivity improvement in a wide refractive index range, in particular from 1.450 to 1.470, above the refractive index of the cladding. The performance of such structures enabled to analyse the optical properties of edible oils when thermally deteriorated and when contaminated with organic solvents as hexane. It was verified that in both situations the refractive index changes, allowing the quantification of the deterioration and contamination based on the variations in the spectral features of the attenuation band of the LPFGs. The combination with fibre Bragg gratings leads to a thermal compensation of the LPFG

and could be used to provide an indirect measurement of the LPFG wavelength position through the optical power variations in the reflected narrow band which is easier to characterize.

The features of the spectral attenuation band of metal coated LPFGs allow the real time monitoring of the process of oxidation when placed in an oxygen environment, which is depending on time and temperature. It was observed that the registration of the dynamics of the features of the LPFG attenuation band when combined with the chemical and morphological analysis would lead to the identification of specific oxide states for a metal coating. The optical characterization of LPFGs with 60 ± 10 nm metal oxide coatings for changes in the surrounding refractive index (SRI) from 1.300 to 1.600 have returned sensitivities up to 2000 nm/RIU and 20000 nm/RIU for 67 nm of Cu_2O at 1.420 and 50 nm of Al_2O_3 at 1.442, respectively.

Detection of hydrogen was attained by coating the chemical etched surface of fibre Bragg gratings with palladium metal. With changes in the palladium coating thickness up to 150 nm and with a reduction in the fibre diameter was possible to increase the sensitivity up to 20 pm/% v/v of hydrogen at atmospheric pressure. The systematic study performed has shown that humidity has destructive effect onto the palladium coating. A cheap solution with a sealed layer of Teflon around the sensing region was presented and tested. Moreover, thick layers of ZnO around LPFGs would lead to the detection of vapours with combinations of wavelength position and intensity of the attenuation band. For the case of ethanol and hexane in the gas phase, nonlinear response was obtained in the range up to 174 g/m^3 and 1989 g/m^3 respectively, with resolutions of 3.2 g/m^3 and 220 g/m^3 .

A novel configuration of a surface plasmon resonance sensor in a single mode fibre section chemically etched was presented. The theoretical simulation described accurately the obtained experimental results concerning the sensor sensitivity. The single path in the sensing region (transmission mode) presents better results when compared to the double path when a mirror is produced at the end of the fibre (reflective mode). The wider resonant dips obtained experimentally could be explained with the multimode excitation in the sensing region and the small different thicknesses of the films in the coated region. Sensitivities to refractive index variations higher than 3800 and 5100 nm/RIU were attained considering the reflection and the transmission modes, respectively. It was pointed out that the reflective configuration has potential to show a substantial better sensing performance in what respects refractive index readout resolution, which adds to its intrinsic favourable geometric characteristics for operation as a remote point sensor.

The applicability of the LPFGs and the SPR structures in optical fibres by using thin film coatings was attested in the biosensing field with the detection of thrombin. Three different configurations were compared based on aptamers binding mechanism to attach the specific thrombin protein. The attachment of a molecule on the fibre sensor leads to changes in effective refractive index. Systems with higher sensitivities will provide more efficient results which was obtained for the thrombin detection. The sensitivity of a SPR sensor above 3000 nm/RIU enable detection of the presence of 10 nM with a resolution of 0.62 nM. Although the LPFG have been coated with TiO₂ to improve the sensitivity up to three times more for refractive index in the range 1.330 to 1.350, was not enough to detect these kind of variations. However, the LPFGs was capable to detect the presence/absence of thrombin.

SPR based refractometric platforms in optical fibres have shown several advantages and also some disadvantages over coated LPFGs. The SPR-based devices present sensitivities to SRI above 5000 nm/RIU in the wide refractive index range from 1.300 up to 1.450 with low sensitivity to thermal variations, however, the need of a high wavelength bandwidth with high power are constraints which need to be taken into account.

On the other hand, the LPFGs have narrower attenuation band which turns the interrogation easier and allows the use of light sources and detectors with reduced wavelength window range. In addition, the LPFGs are capable to work with external RI in the vicinity of the cladding RI, in particular above 1.457. As a recognized drawback stands the length of the LPFGs, turning the sensing heads based on these devices more susceptible to bending and strain gradients.

The research undertaken along this PhD path pointed out topics that need further investigation and opened windows for new ones. Two of them are highlighted in the following.

- High sensitivity to refractive index variations of the surrounding medium is achieved through the conception of sensing devices based on FBG, LPFG and SPR. Concerning LPFGs, when these gratings are combined with proper coatings it is possible to measure a wide range of refractive indices, a feature important in the monitoring of the quality of high refractive index liquids such as mineral and edible oils and the concentration of hexane or other organic solvents in storage tanks and processing reactors in edible oils extraction or refining plants, when the LPFG is coated with titanium oxide. In addition, the LPFG coated with thick ZnO would allow to evaluate the solvent vapour concentration or pressure in the gas phase. The combination of two or more LPFGs, each one with the appropriate coating, could allow the complete characterization of the

dynamics of sealed systems. Furthermore, the proper design of coated LPFG sensing systems may enable the detection of biochemical changes in foodstuff, the characterization of pharmaceutical products and, more broadly, the development of optical sensing approaches to be applied with advantage in the wide biochemical field.

- The SPR is a well-known technique in bulk waveguides, nevertheless the consideration of optical fibre based SPR structures for sensing is more on the table. Due also to a much wide freedom design, this sensing approach will certainly expand rapidly in the future, with some domains closer of the application phase. It is the case of high sensitivity detection of refractive index variations in mediums with refractive indices in the range of 1.300 to 1.400, an ideal region for the detection of specific bio targets after proper surface functionalization with aptamer based DNA. Further work would pass by the functionalization of the surface of such devices aiming highly selective detection of a variety of targets. In addition, the taper structure developed and coated with metal/dielectric may be efficiently used in new applications as a tip enhanced Raman spectroscopy.

Fibre optic sensing has evolved along the years into a wide variety of concepts, technologies, methodologies and applications, benefiting from the remarkable characteristics of light, in particular the freedom it provides to register the fingerprint of a phenomenon, a parameter, a measurand. Indeed, the interaction can be recorded on the intensity of light, on its wavelength, on its frequency, on its phase, on its polarization and even, in some cases, on the light wavefront. In each of these processes many factors are involved which opens the sensor design possibilities into a huge space.

This broad world shares a common feature which is, in most of the situations, the light be guided in the optical fibre. Therefore, when the propagation characteristics are modified the same happens with the interaction conditions of the guided light with the targeted measurand and, in principle, this interaction can be adjusted to achieve optimum performance. This means coating the optical fibre in the sensing region with proper materials (including metamaterials) with tailored geometric characteristics opens a new dimension into the optical fibre sensing field. This door has been guessed since the outcome of fibre optic sensing but technological limitations constrained its development until few years ago. Since then the situation is changing quickly and the worldwide level of research in coated based fibre optic sensing has been increasing significantly. The work reported in this thesis is just a contribution for this fast expanding field which offers the promise of novel fibre optic sensors with outstanding characteristics.

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