Characterization of zinc oxide coated optical fiber long period gratings with improved refractive index sensing properties

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Abstract

A fiber-optic refractive index (RI) sensor based on a long period fiber grating (LPFG) coated with a zinc oxide (ZnO) thin film was fabricated and characterized. A method to overcoat the LPFG's with a homogeneous ZnO thin films was developed.

Characterization of ZnO thin films, deposited simultaneously on silicon (Si) planar substrates, was performed using Scanning Electron Microscope, Energy Dispersive X-ray Spectroscopy and X-ray Photoelectron Spectroscopy. The LPFGs with ZnO coatings from 29 to 145 nm of thickness were characterized and compared in terms of the wavelength shift and the intensity of the attenuation bands changing the surrounding refractive index (SRI) from 1.300 to 1.600. An average wavelength sensitivity of ~ 7162 nm/RIU was achieved in the RI range from 1.440 to 1.456 and more than 12000 nm/RIU at 1.440 RI. Using a ZnO film thickness of 116 nm and in the RI region between 1.320 and 1.360 the average sensitivity of ~ 806 nm/RIU was measured for a 145 nm thick film. Working as an intensity sensing device, the 87 nm coated LPFG shows a linear sensitivity of 216.4 dB/RIU in a wide range of RI from 1.340 to 1.420.

Keywords:

Long period fiber gratings, Fiber sensors, Zinc oxide coated LPFG, Refractive index, Fiber optic refractometer

1. Introduction

Precise and real time determination of refractive index (RI) using optical fiber sensors based on long period fiber gratings (LPFGs) is an objective of ongoing research, covering a wide range of applications including, sensing of strain, bending and temperature [1], chemical and biochemical analysis [2], vapor detection [3], food quality control [4], recognition of bacteria [5] and a platform for DNA/Aptamer detection [6].

Sensors based on LPFGs rely on coupling light from the core mode of a single mode fiber into cladding modes and this is shown in transmission spectrum of the fiber as attenuation bands at specific wavelengths. The evanescent field of the cladding modes go beyond the cladding perimeter, thus making LPFGs sensitive to the optical properties of materials surrounding the fiber. This characteristic has led to studies of LPFGs coated with a number of materials, planned to change their optical properties in response to an external stimulation [7].

LPFGs are produced by introducing a periodic modulation in the RI of the fiber core, in the range 100 to 1000 μm and a length of a few centimeters. This RI modulation is obtained through UV laser irradiation, electric-arc discharge, periodic etching, CO₂ laser irradiation or mechanical processes [8]. The period of the RI modulation is such that phase matching condition between the core mode and a forward propagating cladding mode of an optical fiber occurs for a wavelength given by [9]:

$$\lambda = \left[n_{eff}(\lambda) - n_{clad}^i(\lambda) \right] \Lambda ,$$

where $n_{eff}(\lambda)$ is the effective RI of the core mode at wavelength λ , $n_{clad}^i(\lambda)$ is the effective RI of the i^{th} cladding mode and Λ is the period of the LPFG. Several attenuation bands are formed in the transmission spectrum of the fiber [10].

The sensitivity of the LPFG to the surrounding refractive index (SRI) can be explained by the dependence of the phase matching condition on the effective RI of the cladding modes, which in turn depend on the difference between cladding and the adjacent medium [11]. As the SRI changes from the

unit to near cladding refractive index (CRI), the main outcome is a blue-shift of the dip of the bands, mainly patent for higher order modes [8].

It is well known [12], that for this kind of structures the highest wavelength and transmission sensitivity to the refractive index of the external medium occurs for SRI values slightly lower than the CRI [11], and the sensitivity is higher for the higher order modes [12].

When the SRI is higher than the CRI all the attenuation bands show a considerable reduction in wavelength and transmission sensitivity [12]. An increase in sensitivity can be achieved by coating the LPFG with thin films with a RI higher than the CRI. It was calculated and experimentally demonstrated that high RI coatings induce strong changes on LPFG spectral properties [13, 14].

There are several theoretical and numerical investigations showing that high RI thin film coatings assist the transition between cladding guided modes in overlay guided modes, changing the wavelength and the minimum transmission value of the attenuation band [15-18]. The response of the LPFG is modified according to the RI and the thickness of the film.

Metal oxides are known to undertake variations of their physical properties upon chemical adsorption, thus making themselves interesting solutions for chemical and biochemical sensing applications. Zinc oxide (ZnO) is an advantageous material for the implementation of chemical sensors [19], because of its optical and electrical properties and the variety of methods available for its synthesis [20], and the multiplicity of geometries that can be produced [21]. The refractive index of ZnO is 1.929 at 1450 nm [22], higher than the pure silica which would increase the sensitivity of the LPFGs.

Real time optical monitoring of the formation of a thin dielectric film of ZnO around a LPFG is presented together with material characterization techniques: Scanning Electron Microscope (SEM), Energy Dispersive X-ray Spectroscopy (EDS) and X-ray Photoelectron Spectroscopy (XPS). The same devices were experimentally characterized for different coating thickness with variations of the SRI greater and lesser than the CRI.

2. Material and methods

The LPFGs sensors were created by the electric arc technique [1] which consists on point-to-point short time discharges in uncoated ordinary single mode fiber (SMF28, Corning, Inc.). The fibers were positioned between two electrodes spaced by 1 mm, clamped in one end together with a translational stage and stretched in the other end with a mass of about 5 g to keep the tension constant and produce similar tapering regions. The electric arc is produced by applying to the electrodes a current of 9 mA with a time duration of 1 s. The translational stage is controlled by a computer and after each discharge it moves the fiber 387 μm with a precision of 0.1 μm . The process is repeated until the band reaches the maximum attenuation (>20 dB).

The period of the gratings was 387 μm , a value chosen to produce a resonance wavelength at 1.48 μm , matching to the antisymmetric 6th order cladding mode according to Ivanov and Rego [23]. The maximum LPFG attenuation value was reached for a sensor length of 40 ± 5 mm.

A Zn thin film was deposited around the grating region by thermal evaporation of pure Zn using an electron beam evaporator model Auto 306 (Edwards Ltd, U.K.) whose chamber was kept at $\sim 2 \times 10^{-6}$ mBar. The improvement of the adhesion between the fiber and the Zn was accomplished with a 3 nm layer of Chrome (Cr). The equipment is fitted with a home-produced rotary system placed inside the vacuum chamber in order to rotate the fibers. The rotation velocity was set to 5 rpm, a value which was found to produce homogeneous thin films around the cylindrical fibers, for the range of thicknesses of interest.

A set of Zn thin films were deposited simultaneously on silicon (Si) substrates for further SEM/EDS (model QUANTA 400 FEG, FEI, U.S.A./Pegasus X4M, EDAX, U.S.A.), XPS (model AXIS Ultra HAS, KRATOS, U.K.). A quartz micro balance model FTM5 (Edwards Ltd., U.K.), gives

112 the value of film thickness deposited on the stationary Si substrates. The step profile of each thin film
113 was measured with a surface profiler model DektakXT (Bruker Co., U.S.A.).

114 The homemade rotating system was calibrated with a set of thin films and a calibration curve
115 between the static substrate and the rotating substrate was achieved. The film thickness on the static
116 substrate was measured by the thickness monitor of the evaporation system with a resolution of 0.1 nm
117 and confirmed by profile measurements. With this data we can estimate and control the real thickness of
118 the metal phase around the cylindrical fiber.

119 A set of Zn thin films was deposited around the LPFGs in the range from 10 to 100 nm of thickness.
120 They were then placed in a set-up where one end was clamped with a magnet and at the other end a 5 g
121 magnetic weight kept the fiber stretched at a constant tension in the central region of a 20 cm long, 520 W
122 tubular furnace (Termolab, Portugal). Annealing was performed at 400 °C for 1 hour, following the
123 procedure described in [24]. Heating and cooling were maintained at an approximate rate of about ~4 °C
124 per minute. As the furnace had both ends open, Zn oxidation took place in an air atmosphere. Silicon
125 substrates coated with a patterned Zn film with the same thickness were placed simultaneously in the
126 furnace, which were then measured with the surface profiler in order to determine the final ZnO thickness.

127 For optical characterization, the LPFGs were placed in the setup illustrated in Fig. 1 using the same
128 holding magnets. Light from a super luminescent diode source (SLD) model S5FC1550S-A2 (Benchtop
129 SLD – Throlabs, Germany) was coupled to the fiber and the LPFGs characterized in transmission mode
130 with an optical spectrum analyzer (OSA) (ANDO, model AQ 6315B).

131 The refractive index of medium surrounding the sensing device was varied from 1.300 to 1.600
132 using a set of refractive index calibrated oils (Cargille-Sacher Laboratories Inc., U.S.A.). The oil sample
133 to be tested was placed in a glass V groove aligned with the sensing region in the fiber covering the entire
134 LPFG length. After each measurement both fiber and the V groove were flushed with acetone to avoid
135 contamination to the next oil sample.

136

3. Experimental results and discussion

3.1 Fabrication and characterization of ZnO thin films

A SEM photograph of a 67.5 nm thick Zn film, before and after annealing (ZnO), is presented in Fig. 2 a) and b), respectively. A high surface inhomogeneity is visually evident. For the sample before annealing, an average particle diameter of 157.9 ± 62.2 nm was calculated using the image software analysis ImageJ (National Institutes of Health, U.S.A.). After the annealing process the average particle diameter diminishes to 106.6 ± 38.7 nm.

The thickness of the Zn coated Si samples was measured before and after oxidation using the surface profiler, leading to an average factor of 2.9 for the thickness increase after oxidation.

The thermal process leading to oxidation of the Zn thin film gives rise to wavelength shift and attenuation variation of the resonant bands of the LPFG, as is illustrated in Fig. 3 for the LP₁₆ mode of a 40 nm thick Zn coated LPFG (the spectrum of a bare LPFG is also shown). The metal coating was enough to act as a mirror to the evanescent field, given that part of the light was recoupled to the fiber core mode. The result is a reduction of the attenuation band when compared to the bare LPFG. When the oxidation process starts, at 400 °C, the coating reflectivity diminishes and the attenuation band of the cladding mode increases.

Figure 4 and 5 illustrate the normalized wavelength shift and attenuation variation, respectively, of the LP₁₆ mode of a bare and of a 40 nm thick Zn coated LPFG as function of temperature from 25 to 600 °C.

For the bare LPFG there is a constant red-shift with temperature rise and corresponding blue-shift with cooling. Also, a variation of ~12 dB in the attenuation band during the heating-cooling cycle, can be observed. Coating the LPFG with Zn leads to a red-shift and to a reduction in the attenuation band. Increasing the temperature up to 400 °C has a similar red-shift effect as for the bare LPFG, while an additional, although small, reduction in attenuation takes place. When the temperature reaches 400 °C the oxidation reaction takes place. A blue-shift of ~5 nm and a sudden attenuation increase of about

~16 dB could be observed. During cooling the LP₁₆ cladding mode moves to shorter wavelengths, ending 4.5 nm and ~4 dB away relatively to the initial position of the bare LPFG. A blue-shift and a decrease of the attenuation were expected [15], and are consistent with the results reported for a LPFG coated with a Langmuir-Blodgett [25], and with TiO₂ [26], thin films.

The resonance wavelength depend on the effective RI of the cladding modes which in turn depend on the SRI. Even though the inscription of LPFGs in the turning points increases their sensitivity to changes in the SRI, it is known that the sensitivity is higher as the SRI approaches the CRI. The formation of the ZnO thin film on the LPFG induces a re-distribution of the cladding modes that leads to a wavelength and amplitude shift of the attenuation bands.

Zinc thin film samples deposited over Si substrates and annealed with the same conditions than the optical fibers were analyzed with XPS technique identifying each element over the surface due to the unique binding energy between the species and with SEM/EDS which provides information on the morphology, the distribution and the grain size and the local chemical composition.

Figure 6 a) shows the binding energy spectrum, from 1010 to 1060 eV, with two peaks that can be identified as Zn2p_{1/2} and Zn2p_{3/2} electrons with energies of 1044.36 and 1021.31 eV respectively [27]. The assessed difference between the two lines is ~23 eV which is in agreement with the standard reference value of ZnO [28].

The spectrum of O-1s was deconvoluted into three peaks, as shown in Fig. 6 b). The lower binding energy component peak corresponding to 530.20 eV is related to the wurtzite structure of the O²⁻ ion in the Zn-O bounding in the lattice and to the typical ZnO structure [29] 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 [30] [31].

Figure 7 shows the EDS analysis of the Zn sample as deposited compared to the same after annealing. It shows a very clean substrate without impurities and after the annealing process three peaks are shown with energies of 514.48, 1014.45 and 1739.31 eV corresponding to O_K, Zn_L and Si_K lines

respectively which is in a good agreement with the literature [32]. The EDS analysis is able to confirm the presence of high quantities of oxygen and it can be used to give semi-quantitative analysis of the elements showing atomic percentage of Zn and O around 41.45 and 58.55 % respectively. The ratio Zn/O 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.

3.2 Optical characterization of ZnO coated LPFG

Figure 8 presents the measured transmission spectra, from 1350 to 1600 nm, corresponding to 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 fiber.

For SRI higher than the CRI a shift for higher wavelengths is observed together with a substantial reduction in the attenuation bands. Even if this behavior is similar for 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 Fig. 9 a) and b) for a LPFG without coating and for LPFGs with several values of ZnO thickness between 58 and 145 nm. For easiness of analysis, plots for some ZnO thicknesses are not shown. For SRI values from 1.300 to 1.400, typical of certain chemical and biological systems - a region where a bare LPFG is useless - the wavelength shift increased for all the film thicknesses considered. 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 806.3nm/RIU for a 145 nm thick ZnO coated LPFG. It must be noticed that for SRI smaller than the CRI the LPFG high wavelength sensitivity feature moves left to smaller RI values as the ZnO thickness increases, Fig. 9 a).

211 With the increasing of the coating thickness the range of SRI decreases since the attenuation band
212 disappears. This can be explained by an eventual complex refractive index of the ZnO coatings that
213 would give rise to vanishing of modes, as it was observed previously, experimental and theoretically [13,
214 33].

215 For SRI higher than the CRI an increase of the wavelength shift with the thin film thickness was
216 measured, while for the bare LPFG there is no wavelength shift. For instance, in the RI region between
217 1.450 and 1.470, characteristic of most mineral and edible oils for example, the average sensitivity is
218 about 3433 nm/RIU, for a 58 nm thick film. Assuming a linear approximation, from Fig 9 b) an average
219 wavelength shift sensitivity of 5925 nm/RIU was calculated in a broad range of RI values, from 1.440 to
220 1.460, for a 116 nm thick film.

221 With the objective to enlighten the sensitivity level for several coating thickness and for the 1.300
222 to 1.600 RI range, the 1st derivative of the data plotted in Fig. 9 a) and b) is shown in figure 10 a) and b).
223 It can be easily observed that the sensitivity increases with the ZnO coating being possible to choose the
224 correct film thickness depending on the SRI that needs to be measured. The sensitivity can be as high as
225 ~1400 nm/RIU at 1.360 RI, a region characteristic of volatile organic compounds (VOC) such as ethanol
226 and acetone.

227 Without any coating only the surrounding medium influences the effective index of the cladding
228 mode. Increasing the film thickness both, film and external medium, influence the cladding mode
229 increasing the external average refractive index. Above a certain thickness the average refractive index
230 is equal to that of cladding and no guided modes are supported by the cladding and no attenuation bands
231 are observed [14]. For higher film thicknesses the attenuation bands can be explained by the existence of
232 leaky modes due to the refractive index profile. Increasing de external refractive index the leaky mode
233 became better confined with additional attenuation [11].

The spectral resolution, R , can be estimated considering the values obtained from two measurement linked with two different values of the external RI, obtained from the following expression [34]:

$$R = \frac{\sigma}{S_{RI}} = \frac{\delta n}{\delta \lambda} \sigma$$

where δn is the amplitude of the RI step variation, 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 between the two steps. To check the stability/repeatability of the process, the calibrated oils were used to obtain several acquisitions, confirming the effectiveness of this sensing structure. From the data shown in Fig. 11 a spectral resolution better than 2.4×10^{-4} RI 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 Fig. 12 for the particular case of 87 nm coated LPFG. The sensitivity is larger for higher order modes, as observed in [35]. The LPFG of Fig. 12 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 ($R^2=0.994$). An intensity resolution better than 1.55×10^{-3} dB was calculated.

4. Conclusions

Optical fiber sensors with increased sensitivity based on LPFGs coated with homogeneous ZnO thin films were fabricated and characterized.

The samples of Zn after annealing were analyzed with Energy Dispersive X-ray Spectroscopy and X-ray Photoelectron Spectroscopy techniques showing good indicators of full oxidation into ZnO in air atmosphere when heated up to 400 °C.

It was demonstrated that using a single LPFG coated with a thin film of Zn is possible to estimate the oxidation state by measuring the intensity of attenuation band during the process, which can be used to monitor specific Zn coatings in industrial processes.

Measurement of the transmission spectrum allowed the calculation of the wavelength and attenuation sensitivity as a function of the film thickness (from 29 to 145 nm) and of the refractive index of the surrounding 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 analyze 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.

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347

348 **Figure captions**

349
350 Figure 1. Measurement setup for optical characterization comprising a broadband source (BBS),
351 an optical spectrum analyzer (OSA) and the grating sensor.

352
353 Figure 2. Scanning Electron Microscope (SEM) photograph of a 40 nm thick Zn film: a) as
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357 function of temperature, from 25 to 400 °C. Also shown, for comparison, the spectrum of the LP₁₆
358 mode of a bare LPFG (uncoated).

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361 LPFG as function of temperature from 25 to 600 °C.

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Figure 6. X-ray Photoelectron (XPS) spectrum of an 87 nm thick ZnO film on silicon; a) binding energy spectrum, from 1010 to 1060 eV, with two peaks that can be identified as Zn2p_{1/2} and Zn2p_{3/2}, b) spectrum corresponding to O1s.

Figure 7. Energy-dispersive X-ray spectroscopy spectrum of the Zn sample as deposited and after annealing in air.

Figure 8. Transmission spectra corresponding to the LP₁₆ mode of a LPFG with an 87 nm thick ZnO coating, for several surrounding refractive index values between 1.300 and 1.600.

Figure 9. Normalized wavelength shift as a function of the surrounding refractive index for a bare LPFG and for LPFGs coated with 58 to 145 nm of ZnO in the RI range of: a) 1.300 to 1.460, b) 1.420 to 1.600.

Figure 10. Wavelength sensitivity as a function of the surrounding refractive index for a bare LPFG and for LPFGs coated with 58 to 145 nm of ZnO in the RI range of: a) 1.300 to 1.460, b) 1.420 to 1.600.

Figure 11. Normalized wavelength shift of the dip of the LPFG when the surrounding refractive index undertakes step variations.

Figure 12. Attenuation of the LP₁₆ mode of a LPFG with an 87 nm thick ZnO coating, for several surrounding refractive index values between 1.300 and 1.600.

Figure 1

Figure 2a

Figure 2b

Figure 3

Figure 4

Figure 5

Figure 6a

Figure 6b

Figure 7

Figure 8

Figure 9a

Figure 9b

Figure 10a

Figure 10b

Figure 11

Figure 12

Figure captions

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Figure 7. Energy-dispersive X-ray spectroscopy spectrum of the Zn sample as deposited and after annealing in air.

Figure 8. Transmission spectra corresponding to the LP_{16} mode of a LPFG with an 87 nm thick ZnO coating, for several surrounding refractive index values between 1.300 and 1.600.

Figure 9. Normalized wavelength shift as a function of the surrounding refractive index for a bare LPFG and for LPFGs coated with 58 to 145 nm of ZnO in the RI range of: a) 1.300 to 1.460, b) 1.420 to 1.600.

Figure 10. Wavelength sensitivity as a function of the surrounding refractive index for a bare LPFG and for LPFGs coated with 58 to 145 nm of ZnO in the RI range of: a) 1.300 to 1.460, b) 1.420 to 1.600.

Figure 11. Normalized wavelength shift of the dip of the LPFG when the surrounding refractive index undertakes step variations.

Figure 12. Attenuation of the LP_{16} mode of a LPFG with an 87 nm thick ZnO coating, for several surrounding refractive index values between 1.300 and 1.600.

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