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Long period gratings coated with ultrathin sensitive polymer films for opto chemical water monitoring

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Abstract

In this work, the numerical and experimental analysis of coated Long Period Gratings (LPGs) as high sensitivity opto-chemical sensor is presented. The proposed structure relies on LPGs coated with ultrathin high refractive index (HRI) overlays. When azimuthally symmetric ultrathin HRI coatings are deposited along LPGs devices, a significant modification of the distribution of the cladding modes occurs, depending on the HRI layer features (refractive index and thickness) and on the external refractive index. If these parameters are properly chosen, a strong field enhancement within the overlay occurs, leading to an excellent sensitivity to the coating properties. Here, the effects of the overlay thickness and the cladding mode order on sensor sensitivity and response time have been numerically and experimentally investigated. In order to provide a high sensitivity and species specific opto-chemical sensor, the LPGs were coated with ultrathin overlays of Syndiotactic Polystyrene (sPS) in the nanoporous crystalline δ form. The sensitive material was chosen in light of its selectivity and high sorption properties towards chlorinated and aromatic compounds. Sensor probes were prepared by using dip coating technique and a proprietary procedure to obtain the δ form sPS. Experimental demonstration of the sensor capability to perform sub ppm detection of chloroform in water at room temperature is also reported.

Keywords: Long Period Gratings (LPGs), Refractive Index Sensor, Syndiotactic Polystyrene, Chemical Sensors.

1 Introduction

In the past several years, great efforts have been dedicated to realize chemical sensors based on the integration of proper sensitive layers and suitable high sensitivity transducing mechanisms.

In this paper, an opto-chemical sensor employing long period gratings (LPGs) coated with ultrathin high refractive index (HRI) sensitive overlay is proposed. Here, LPGs were selected as high sensitivity refractive index transducers [1] and Syndiotactic Polystyrene (sPS) in the nanoporous crystalline δ form was used as HRI sensitive polymeric layer [2, 3, 4]. Due to its structure, the sPS δ form exhibits high sorption capability and an improved selectivity towards low molecular weight organic substances, mainly chlorinated and aromatic compounds. Hence, the sorption of the analyte would induce an increase of refractive index of the sPS layer leading to LPGs transmitted spectrum changes.

In the following, a comprehensive numerical and experimental analysis of the LPG cladding mode modification due to HRI overlays is presented, with particular regard to the sensitivity of the attenuation bands to the refractive index of the overlay itself. The theoretical analysis is confirmed by the experimental measurements obtained by coating the LPG with sPS overlays.

The performances of the proposed sensor have been tested by monitoring the attenuation bands related to different cladding modes orders and with different overlay thicknesses. In particular, resonance wavelength shift and amplitude changes of the attenuation bands have been monitored to detect chloroform in water in the range of 0-20ppm. The reversibility of the sensor was tested by monitoring the complete cycle of the sorption of the analytes followed by a washing with pure water flux.

The experimental results demonstrate the excellent performances of the proposed device, leading to the possibility to develop sensor networks.

2 Principle of Operation

LPGs are formed by inducing a spatial refractive index modulation in the core of germanosilicate fibers with periodicities typically of hundreds of

micrometers, typical modulation depth of 10^{-4} and length of 2-4 cm. The grating causes light to couple from the fundamental guided mode to discrete copropagating cladding modes. Because the cladding modes suffer from high attenuation, the transmission spectrum consists in a series of attenuation bands centered at resonant wavelengths given by [5]:

$$\frac{2\pi}{\lambda}\left(n_{eff,01}-n_{eff,0m}\right)+s_0\left(\zeta_{01,01}(\lambda)-\zeta_{0m,0m}(\lambda)\right)=\frac{2\pi}{\Lambda} \qquad (1)$$

where $n_{eff,01}$ is the effective refractive index of the core mode, $n_{eff,0m}$ is the effective refractive index of the m^{th} radial cladding mode, s_0 is the coefficient of the first Fourier component of the grating, $\zeta_{01,01}$ and $\zeta_{0m,0m}$ are the self-coupling coefficients of the core and the mth cladding mode, respectively, and Λ is the grating pitch.

The effective refractive indices of the cladding modes are strongly dependent on the refractive index of the surrounding medium. This means that also the resonant wavelengths will be modified as the refractive index of the surrounding medium changes.

The normalized transmitted power by the fundamental guided mode through the grating at the resonant wavelength regarding the m^{th} cladding mode can be approximately expressed as [5]:

$$T_0^m = \cos^2\left[\kappa_m L\right] \qquad (2)$$

where L represents the length of the LPG and κ_m is the coupling coefficient for the m^{th} cladding mode, which depends on the overlap integral of the core and cladding mode and on the photo-induced refractive index modulation.

When a HRI layer is deposited along the LPG, a strong modification of the distribution of the cladding modes occurs [5,6]. This leads to a decrease in the modes bounding and a consequent enhancement of the evanescent wave interaction with the surrounding medium. Differently for common LPGs, here, the sensing mechanism relies on the reflection-refraction regime at the cladding-overlay interface, where part of the optical power carried by the cladding modes is radiated within the overlay providing a strong interaction with the coating itself. The new cladding modes are now bounded within the structure comprising the core, the cladding and the sensitive overlay, and their distribution results strongly influenced by the refractive index changes induced in the overlay due to the chemical sorption.

As HRI sensitive layer, the δ form sPS (refractive index 1.5781) was used. The sPS in the semicrystalline δ form exhibits a nanoporous structure that is able to adsorb reversibly certain analytes whose size and shape fit the nanocavities well, establishing specific host–guest interactions when they are exposed to a vapor or liquid environment. This means that the sPS exhibits high sorption capability and an improved selectivity towards low molecular weight organic substances, mainly chlorinated and aromatic. Moreover, the sPS can operate in water environments [4].

The main effect of the sorption of the analyte is a strong increase in density and thus in refractive index of the sPS layer according to the Lorentz-Lorenz law [4]. In addition, since sorption occurs mainly in the crystalline nanocavities at low analyte concentration, it can be assumed that no volume change of polymer layer occurs, while the average refractive index dramatically increases of 10^{-2} at ppm concentration levels in the case of chloroform. In this conditions, the exposition of the sPS coated LPG would induce a consequent modification of the cladding modes distributions leading to a wavelength shift of the attenuation bands combined with amplitude changes. For higher analyte concentrations, the sorption occurs mainly in the amorphous phase leading to volume changes and different density variations.

2.1 HRI coating effects: Numerical analysis

In order to investigate the HRI coating effects on the distribution of the cladding mode, numerical analysis has been carried out. The analysis based on scalar approximation or LP modes of a four-layer cylindrical dielectric waveguide was used [7,8]. As efficient coupling is achieved only between core and cladding modes with similar electric field profiles, only the LP_{0m} cladding modes were considered. The analysis is referred to the standard Corning SMF-28 optical fiber parameters: numerical aperture 0.14, refractive index difference 0.36%, cladding and core diameter, 125μm and 8.3μm, respectively, and water as surrounding medium (n_{sur}=1.33). In addition, every mode was characterized by the same power P_0 and the transversal fields were normalized to the maximum amplitude of the core guided mode.

Figure 1.a shows the fields related to the cladding modes LP_{04} and LP_{08} as function of the radial co-ordinate within the transverse section of a HRI (1.58) coated fiber for different overlay thickness. As evident, the HRI overlay causes a spatial shift of the cladding modes field toward the HRI medium, and this effect is clearly evident for both modes and overlay thickness. In addition, for a given thickness, the field within the overlay of higher order modes is higher compared with low order modes as shown in figure 1.b. Finally, for the same cladding mode, the field enhancement in the overlay results more evident as the overlay thickness is increased as showed in figure 1.c.

A relevant component of the cladding modes field in the HRI coating is the direct responsible of the sensitivity of the attenuation bands to the overlay refractive index. This means that, as the refractive index of the overlay changes, strong modifications in

the distribution of the cladding modes occur that are able to influence the LPG transmitted spectrum. In particular, an increase of the overlay refractive index would induce a consequent increase in the effective refractive indices of the cladding modes combined with a spatial shift of the field content toward the HRI overlay, responsible of a decreasing of the integral overlap with the fundamental core mode. Thus, from equations (1) and (2), a blue wavelength shift of the attenuation bands and a diminution of the peak transmission loss are expected. Moreover, due to the field enhancement within the overlay, as the thickness and the mode order are increased, higher sensitivity is expected.

In order to clearly understand the effect of the HRI overlay thickness on the distribution of the cladding modes, the effective refractive indices of different cladding modes are reported in figure 2 as a function of the overlay thickness with water as surrounding medium. As observed, the effective refractive indices increase slightly along with the overlay thickness until a critical point is reached. At this point, a significant shift in the effective index of cladding modes occurs. In particular, the lowest order cladding mode (i.e. the one with higher effective index) starts to be guided within the overlay while the others cladding modes simultaneously shift to recover the original distribution [5,6]. The immediate consequence is a quasi simultaneous shift in the effective index of all cladding modes to recover the original distribution. The effective index of the m^{th} mode shifts to match the index of the $(m-1)^{th}$ mode, and so on.

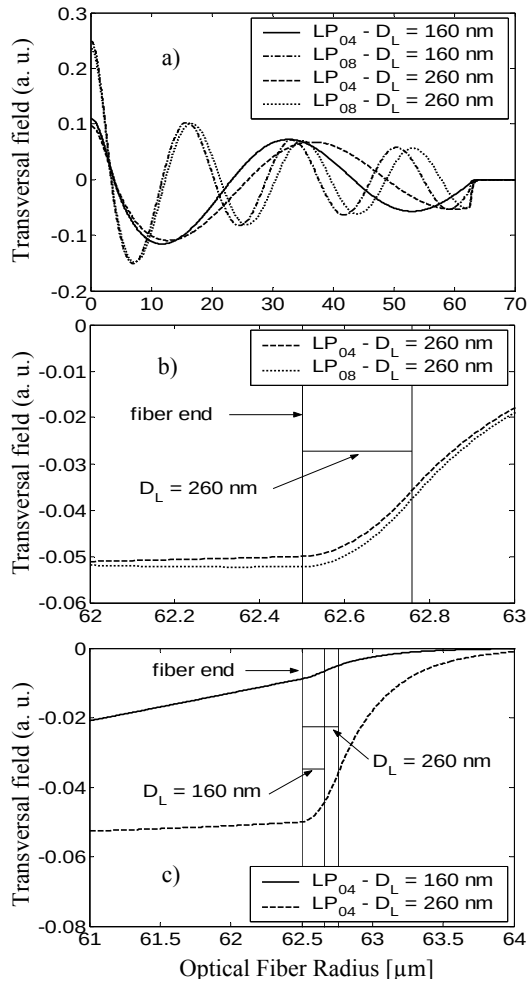

Figure 1: a) LP_{04} and LP_{08} cladding modes in coated fiber with D_L=160nm and D_L=260nm thin overlay; b) LP_{04} and LP_{08} modes in coated fiber with D_L=260nm; c) LP_{04} mode in coated fiber with D_L=160nm and D_L=260nm.

It is worth noting that the effective index difference between consecutive cladding modes increases with the mode order, as well as the spectral distance of the related attenuation bands. Thus, as the mode order increases, greater shift is required for the m^{th} mode to cover the position of the $(m-1)^{th}$ mode. From equation (1), similar behaviour is expected for the central wavelength of each attenuation band.

Figure 3 shows the effective refractive index sensitivity to the overlay refractive index as function of the thickness for different cladding modes with water as surrounding medium (n_{sur}=1.33). The highest sensitivity occurs in correspondence of the modes transition because of the strong field enhancement within the overlay. A similar effect was observed in HRI coated LPGs with regard to the sensitivity to the surrounding medium refractive index (SRI) [6].

3 Experimental results

A commercial 30mm long LPG, with period of 340μm, written in standard boron-germania co-doped Corning single mode fiber was used for sensor fabrication. Since the LPGs are sensitive to strain and bending, a proper holder was designed and manufactured to fix the fiber without changing its tensional state, ensuring bending and strain free operation. The optoelectronic set-up, involved for both sensor fabrication monitoring and for further measurements, comprises two broadband superluminescent diodes (2mW) operating at 1310nm and 1550nm, respectively, an optical spectrum analyzer for transmitted spectrum monitoring with a resolution of 0.05 nm, and a white light source in 400-

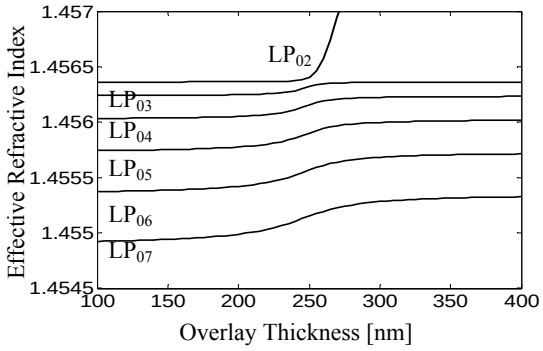

Figure 2: Effective refractive index of different cladding modes versus the overlay thickness with water as surrounding medium.

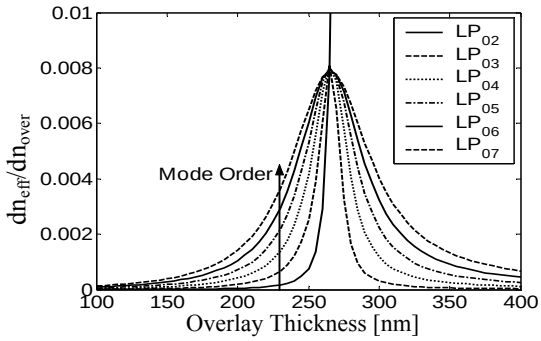

Figure 3: Effective refractive index sensitivity to overlay refractive index versus overlay thickness for different cladding modes with water as surrounding medium.

1800nm wavelength range for transition characterization. AFM and SEM analysis were performed for overlay thickness estimation. The temperature was held constant at 20°C.

The bare LPG was preliminarily characterized. The LP_{06} cladding mode exhibits a sensitivity to SRI of -5.06nm and 3.59dB in terms of wavelength shift and amplitude changes, respectively, referred to the distilled water as surrounding medium.

3.1 Far from the transition

The dip-coating method was used to deposit the δ form sPS layer on the LPG. This assures the formation of an azimuthally symmetric overlay with low cost equipment. The optical fiber with the LPG was arranged in the holder and a sPS chloroform solution (2%b.w.) was added. A first overlay was then deposited emptying out the test chamber in about 3 seconds. When sPS is cast from solution it can clathrate the used solvent molecules, housing them between helical chains, and releasing them during a subsequent desorption that lead to the empty δ form. The clathrate formed was finally exposed to air, for about 15 hours at temperature of about 35°C, in order to extract chloroform and obtain the empty nanoporous δ form crystalline layer. The final transmission spectrum demonstrated a final blue wavelength shift of 1.8 nm and a decrease of the peak transmission loss of 0.8dB compared with the bare one. The overlay thickness was measured and found to be approximately 160nm (d_1). For this thickness value, the cladding modes are far from the transition region as it can be clearly inferred from the figure 4 where the LP_{06} mode wavelength shift is reported in function of the SRI for a 150 nm sPS coated LPG [6]. This experimental result confirms how predicted by the numerical analysis.

In order to test the sensor response to overlay refractive index changes induced by species-specific chemical sorption, chloroform was used as analyte. Measurements consisted in recording the transmission spectra of the sensing grating as the sorption of the analyte in the nanocavities promotes an increase of the polymeric layer refractive index. The spectra were recorded every 40 seconds. The holder, with the sPS coated LPG, was connected with a thermostated beaker (20°C), containing initially 1 liter of pure distilled water. Chloroform was then added by successive steps of 10ppm (μl/l). The solutions were always magnetically stirred in order to ensure the maximum dispersion of the analyte in water and then added to the sensor holder.

Figure 5 shows the time responses of the sensor in terms of wavelength shift and amplitude changes due to two successive 10ppm chloroform exposures. At these concentration levels, negligible effects on the SRI occur, thus changes in the attenuation bands here reported can be attributable only to the chemical sorption within the sensitive overlay. The 10ppm and 20ppm chloroform concentrations induced a blue wavelength shift of 0.96nm and 1.26nm, respectively, and a reduction of the peak transmission loss of 1.20dB and 1.57dB, respectively. Here, a response time (10%-90%) of about 21 minutes (t_1) for 10ppm chloroform concentration was measured. Since chemical sorption dynamics rely on the diffusion of the analyte within the sensitive overlay, thinner is the thickness faster would be the sensor response. Moreover, the dependence of the response times on the analyte concentrations can be attributed to the dependence of the diffusivity on the concentration of investigated analyte. When the chloroform is added, the equilibrium response of the sensor progressively decreases. This is probably related to the combination of the non linear behaviour of the effective refractive index of the coupled cladding mode on the overlay refractive index with the non linear relationship between adsorbed mass of chloroform and its concentration in the liquid phase. Non linear sorption equilibrium was, in fact, reported in literature for sorption in the vapour and liquid phase [3, 4].

3.2 Within the transition region

To the aim to verify the sensitivity enhancement when the transition region is approached, as predicted by

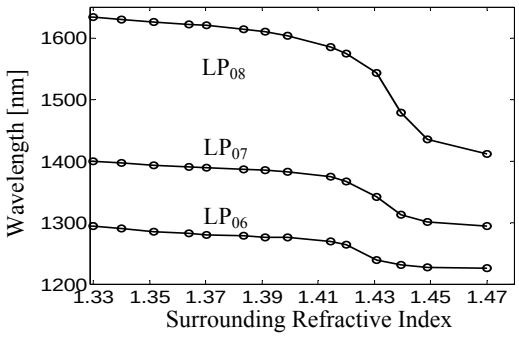

Figure 4: Wavelength shift of different cladding modes for the LPG coated with a 150nm sPS overlay versus SRI.

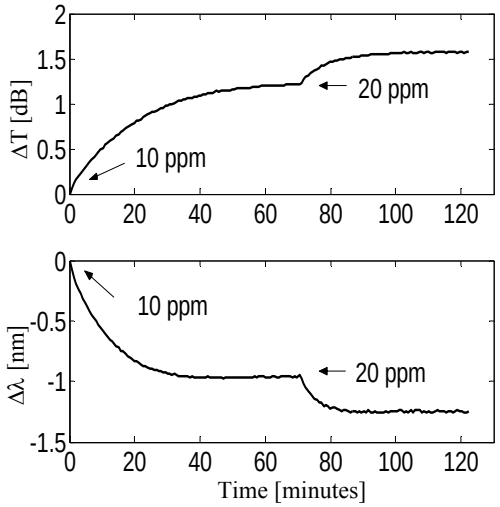

Figure 5: Time Response related to LP_{06} of the coated LPG (overlay thickness of about 160nm) exposed to chloroform.

the numerical analysis, the first overlay was removed and a new thicker overlay was deposited using the same technique.

Here, the measured thickness was of approximately 260nm (d_2) and LP_{08} mode attenuation band was observed in the 1550nm spectral region by using chloroform exposure in water at room temperature. This attenuation band was located at approximately 1700nm in the case of the 160nm coated LPG. Based on this line of argument, it is reasonable to assume that the overlay thickness is higher enough to force the transition also for lower SRI values. This assumption was consistent with the plot of figure 6.a, where the wavelength shift of the considered attenuation band is reported as function of the SRI for a 180 nm sPS coated LPG [6].

In order to prove the sensor performance a similar procedure by using chloroform exposure in water at room temperature was carried out. Figures 6.b and 6.c show the time responses of the sensor in terms of wavelength shift and peak loss changes, respectively, due to four successive 5ppm chloroform exposures. A blue wavelength shift of 3.95nm, 6.45nm, 8.03nm, 8.79nm and a decrease of the transmission peak loss of 1.20dB, 1.91dB, 2.34dB, 2.53dB, were measured. In this case, the response time (10%-90%) was estimated to be about 62 minutes (t_2) for 10ppm chloroform exposure. When chloroform was removed by enabling a continuous flux of distilled water, an excellent recovery was observed demonstrating the reversibility of the proposed configuration.

3.3 Discussion

In this section, the experimental results are resumed and the sensor performances outlined. With regard to the response times, according to the diffusion theory and with experimental results previously reported a quadratic rule can be assumed [3, 4]. This means that the thickness ratio matches the square root of the response time ratio:

$$d_1/d_2 = (t_1/t_2)^{0.5} \quad (3)$$

where d_1 and d_2 are overlay thicknesses and t_1 and t_2 are response times. In our case, with $d_1 \approx 160$nm $d_2 \approx 260$nm, $t_1=21$ minutes and $t_2=62$ minutes, we obtain 0.615 for the left side and 0.586 for the right one demonstrating good agreement with the data previously reported.

With regard to sensor sensitivity, without the sensing overlay negligible variations have been observed in term of the wavelength shift and amplitude changes. Sensitivities of -0.130nm/ppm and 0.163dB/ppm were observed for the thinner overlay, in the range 0-10ppm.

Sensitivities of -0.85 nm/ppm and 0.26 dB/ppm were measured for the thicker overlay, in the same range.

Based on this results, it is evident how the presence of the polymer layer is the unique responsible of the significant changes observed in the attenuation band due to the addition of few ppm in water. Moreover a

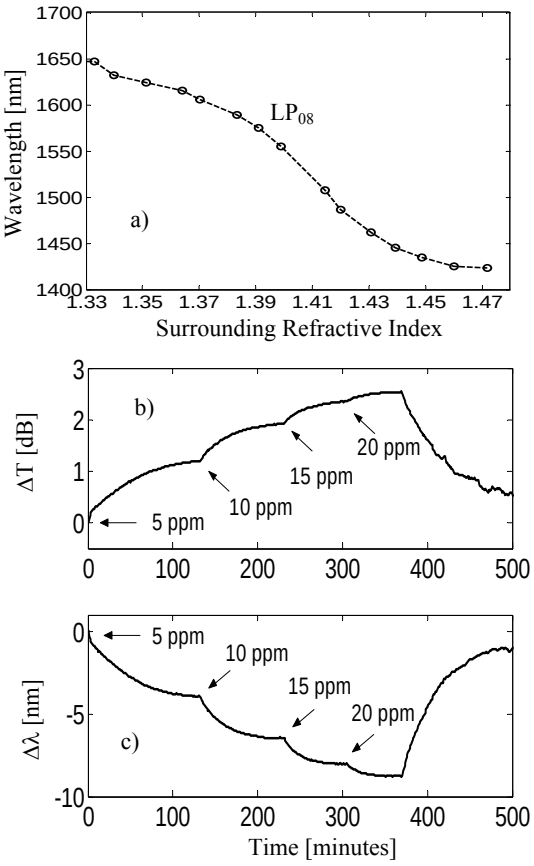

Figure 6: a) Wavelength shift of LP_{08} cladding mode, for the LPG coated with an 180nm sPS overlay, versus SRI; b) peak loss changes and c) wavelength shift related to the LP_{08} mode of a coated LPG exposed to chloroform. Versus the response time.

sensitivity improvement of more than six times in terms of wavelength shift was obtained in the range 0-10 ppm by considering an overlay with higher thickness and higher order cladding mode. This latter result is in good agreement with the numerical analysis previously reported.

4 Conclusions

In conclusions, in this work, HRI coated LPGs were proposed as excellent opto-chemical sensors. It was theoretically and experimentally proved that ultrathin HRI coating promotes a significant modification of the distribution of the cladding mode, depending on the overlay features and on the surrounding refractive index. When the transition region is approached, the lowest order mode would be guided within the overlay forcing the higher order mode to shift in order to recover the original configuration. In these conditions, a strong field enhancement occurs within the overlay leading to a dramatic increasing in the sensitivity to the overlay and surrounding medium refractive index. If a sensitive material is selected the proposed configuration offers the ideal solution for advanced chemical sensing in light of the wavelength encoded measurements, high sensitivity and easy multiplexing. Here, the proposed mechanism was experimentally proved by the integration with nanoscale overlay of syndiotactic polystyrene as species-specific sensitive material. Low cost fabrication steps were carried out for the sensor realization. Sub ppm detection of chloroform in water at room temperature was demonstrated by using different overlay thickness and mode orders. Improved performances were demonstrated if the transition region is approached by increasing the overlay thickness.

In addition, the multi-feature nature of LPG based sensors allows the manipulation of the coupled mode order and overlay coating thickness to satisfy stringent constraints in terms of sensitivity and response time.

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