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pH sensor based on tilted fiber Bragg gratings covered by a sol-gel

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Abstract

This paper presents the development of a *pH sensor* based on a Tilted Fiber Bragg Grating (*TFBG*) covered with a microporous coating consisting of bromophenol blue (pH indicator) encapsulated in a *silica sol-gel* matrix. The covered TFBG shows important modifications of its transmission amplitude spectrum in the range of 1510-1590 nm as a function of the pH. All the cladding mode resonances show a peak-to-peak amplitude decrease with increasing pH according to a sigmoidal evolution. The response, defined as the change in amplitude of a resonance peak as a function of the pH, is fast (<10s) and reversible. The amplitude change between acidic and basic forms is about 4 dB at 1550 nm. This kind of sensor could be of interest for practical applications such as corrosion monitoring.

Key words: pH sensor, sol-gel, optical fiber, TFBG, Tilted Bragg Gratings.

Introduction

During the last decades, there has been a rising interest in the development of sensors based on optical fibers for many different applications, including chemical and gas sensing [1,2]. Numerous transduction techniques were studied and fiber Bragg gratings (FBGs) appeared to be very attractive candidates [3-5]. An FBG is a periodic and permanent modulation of the core refractive index of an optical fiber along the propagation axis. It is generally obtained by exposing a photosensitive optical fiber to an intense UV interference pattern. A fiber Bragg grating acts as a wavelength selective filter around the so-called Bragg wavelength [6]. The period Λ is usely around 500 nm and the Bragg wavelength is around 1550 nm.

Tilted Fiber Bragg Gratings (TFBG) present a refractive index modulation angled by a few degrees relative to the perpendicular to the optical fiber axis. They couple light between the core and the cladding. As a result, they present a comb-like transmission amplitude spectrum comprising several tens of resonances, each one characterized by its own sensitivity to the surrounding refractive index. The important point is that the position and the amplitude of these peaks depend on the refractive index of the surrounding medium. When immersed in a medium with a refractive index that matches the effective refractive index of some cladding modes, these modes become weakly guided, and the narrow resonance peaks are replaced by a smooth loss continuum.

TFBGs naturally yield refractometers accurate to 10^{-4} RIU (refractive index unit) [7-10]. More recently, TFBGs were used for sensing chemical or biochemical quantities [11].

TFBGs used as sensors present decisive advantages like small size (which is compatible with the use of tiny sample volumes), electromagnetic interferences immunity and high accuracy. To achieve these performances, various demodulating methods have been reported, based on whole spectrum analysis [7, 8], on single resonance tracking [12] or transmission power measurement [13]. Using wavelength encryption of the signal allows temperature-insensitive measurements [14].

Specific chemical sensors can be built by using TFBGs covered with a dedicated coating that changes its refractive index when in contact with target chemical species. Doing so, the sensors inherit the above-mentioned advantages of the optical fiber sensors.

This study demonstrates the possibility to sense pH variations with the help of a microporous

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sol-gel coating encapsulating a pH indicator whose refractive index changes due to the modification of the indicator state. Silica sol-gel was chosen because of its refractive index close to that of the fiber, enhancing in turn the response. Bromophenol blue was used due to its high Kreft's dichromaticity index and its convenient pKa.

In comparison to other existing optical sensors [15, 16], using TFBGs brings several benefits. They preserve the fiber integrity while offering intrinsic temperature insensitivity. Also, measurements can be operated at standard telecommunication wavelengths.

Sample preparation

Experiments were carried out on TFBGs classically manufactured into hydrogen-loaded single mode optical fiber (germanium doped core) by means of a 1095 nm uniform phase mask and a frequency-doubled Argon-ion laser emitting at 244 nm. The phase mask was tilted in the plane perpendicular to the incident beam. An external tilt angle of 6° was chosen. The protection coating was mechanically removed before inscription. After that, and before coating, gratings were annealed at 80 °C during 12 hours in air to remove the hydrogen and stabilize their physical properties.

The sensitive sol-gel coating was obtained by incorporation of the pH indicator, here bromophenol blue, in an alcoholic solution (15 ml) containing TEOS as precursor (15ml), water (3 ml) and HCl as catalyst (2M 0.25 ml). The solution was heated at 60 °C (reflux) for 1h and aged for 1 week before use.

The sensitive layer was deposited on the fiber by dip coating in one step and annealed at 80 °C for 1 hour, yielding a 5 µm thick transparent yellowish layer.

Experimental setup

The amplitude transmission spectra were measured using an ASE (amplified stimulated emission) optical source (Ammonics) and an optical spectrum analyzer Ando AQ6317C (figure 1). The fibers were immersed in a 1M NaCl solution and the pH was adjusted by adding 1 M HCl and NaOH solution drops. The pH was controlled with a glass electrode pHmeter (Metrohm). NaCl is introduced to ensure that the refractive index of the solution is constant.

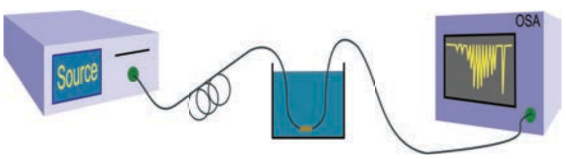

Fig. 1: Experimental setup.

The sweeping time for 10 pm resolution in the whole range (1520-1590 nm) is about 40 s.

Results and discussion

Figure 2 displays, with an offset in the vertical axis, the TFBG transmitted amplitude spectra for various pH values. The resonance modes are drastically affected by the pH variations (figure 3). This results from the fact that, for solutions having pH lower than 5 (acidic form of the indicator), the coating containing the indicator is yellow and for pH>6 (basic form), it becomes dark blue. For a free indicator, this color change is observed in the pH range 3-4.6. In addition, the refractive index of the coating increases when the indicator is in its blue form.

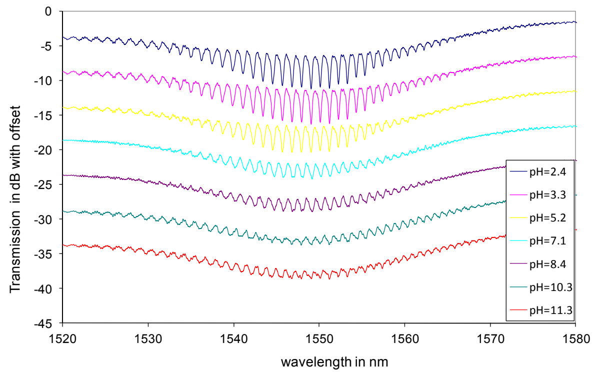

Fig. 2: Transmission spectrum of the TFBG at different pH values.

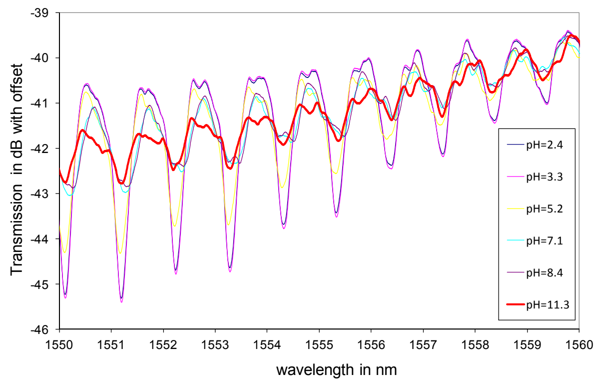

Fig. 3: Transmission spectrum of the TFBG at different pH values. Zoom around 1555 nm.

A simple way of demodulating the amplitude spectrum is to track the peak-to-peak amplitude of a given cladding mode resonance as a function of the pH. Figure 4 shows the amplitude evolution versus pH for the peak centered around 1550 nm.

As could be expected, the response of the sensor presents a reversible sigmoidal shape.

When following one given peak, the scan can be refreshed each second allowing to measure the response time. The response time is evaluated to about 10s when going from pH 3 to pH 10 or vice versa.

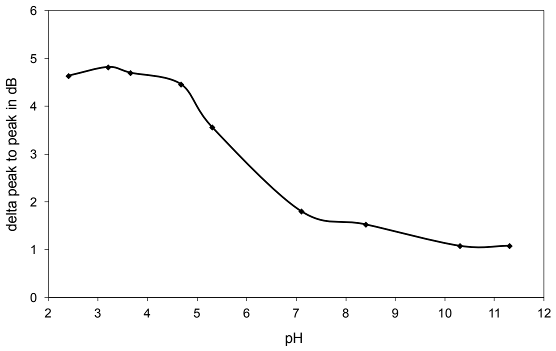

Fig. 4: Peak-to-peak amplitude of the cladding mode resonance near 1550 nm at different pH values.

Conclusions

TFBGs covered by a sol-gel layer show important modifications of their transmission amplitude spectrum in the range 1510-1590 nm as a function of the pH. All the cladding mode resonances present a peak-to-peak amplitude decrease with increasing pH values, according to a sigmoidal evolution. The amplitude change between acidic and basic forms is about 4 dB at 1550 nm. The response, defined as the change in the amplitude of a resonance peak, is fast (~10s) and reversible.

This kind of sensor could be of interest for practical applications such as corrosion monitoring.

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