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SPR Fiber Based Sensor for Long-term Monitoring of Aqueous Media

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***Abstract*—The paper presents results obtained by experimentally testing fiber optic based SPR (Surface Plasmon Resonance) sensors for quality monitoring of aqueous media. The research focuses on the direct impact of the temperature in such measurements for certain applications, being introduced as a parasitic effect . A novel and cost effective configuration for a fiber optic based SPR sensor system, exploiting a compensation method of the thermo-optic effect, is also presented. Its working principle is already proven based on previous results and performances obtained from experimental work, and it is ready to be implemented. The sensor is basically a refracto-meter in the range of 1.33-1.37 RI (Refractive index), thus for aqueous media, intended to be used as a long-term monitoring device for the quality of the swimming pool water (real time chlorine concentration analysis) compensating the parasitic effect of temperature.**

***Index Terms*—Optical fiber sensors, Plasmons, Refractive index, Optical sensors, Optical devices**

I. INTRODUCTION

Surface Plasmon Resonance (SPR) sensors have gained attention by the research community because of their high sensitivity as refractive index (RI) sensors for liquid media. In metal-coated optical fibers, the SPR occurs at the interface between the dielectric surrounding the fiber and the metal layer, when the evanescent field of a light beam polarized parallel to the interface (TM-polarized), propagates along the fiber undergoing total internal reflection (TIR). Small size, low cost, real-time monitoring and capability of in-vivo and in-vitro applications, make optical fiber-based SPR sensors excellent candidates in bio-medical and industrial sensing applications. Different methods have been developed to enhance the performance of SPR sensors and several review articles have been written on the topic [1]–[4]. Both single-mode (SM) [5] and multi-mode (MM) fibers [6] have been used; Mono-chromatic [7] and broadband sources [8], [9] have been used to interrogate the sensors. Engineering of the fiber such as bending [10], tapering [11], U-shaping [12] and coating with extra layers [13]–[15] have been investigated. These researches have highlighted limits and trade-off among sensing performances, functionality and cost effectiveness. This paper consolidates the previous investigations by proposing a cost-effective configuration of an optical fiber-based SPR sensing system that exploits a differential measurement to compensate thermal effects during the measurement of refractive index of aqueous media. The devised application is monitoring of chlorine concentration in water of swimming pools, where the thermal variation of refractive index is known to be remarkable, in the order of $1 \times 10^{-4} RIU/°C$ [16] in the range of $20 - 40°C$. The sensors hereby presented exhibit a sensitivity down to $1 \times 10^{-4} RIU$ in the full refractive index range of 1.33-1.37 and even better performance for smaller ranges.

Chlorine (calcium hypochlorite) is required to be in a specified range (above 1 ppm up to several ppm, according to the specific standards), meaning that the water refractive index needs to be maintained in the corresponding range to satisfy the health and safety requirements for the swimmers. Knowing the relationship between chlorine concentration and refractive index, being in the order of $4 \times 10^{-4} RI/ppm$ [17], it is possible to monitor the chlorine concentration through direct refractive index analysis.

Since chlorine concentration and thermo-optic effect have similar contribution to the refractive index of water, an effective thermal compensation of the sensor reading is necessary. The system hereby presented can be constructed using a laser source, two SPR fiber optics sensors, and two photo-detectors. Two identical optical fibers (MM), uncladded and coated with a gold (Au) nano-layer are used as the sensitive part of the device. One sensor is surrounded with a solid resin layer with a known RI , then used as a temperature sensor, exploiting the change in the refractive index (δRI) of the resin with respect to the temperature of the medium. Simultaneously the other sensor is used as a refracto-meter in the required range of RIU (Refractive Index Unit) with the water flowing directly above the gold nano-layer. The results of the experiments regarding the stability of the sensors and the direct impact of the temperature are then presented.

A. Short Theoretical Background

A short theoretical background based on [18], [19] will be introduced in this section. A plasmon is defined as the quantum particle of the plasma oscillation, as a photon stands for light wave and a phonon stands for sound wave. Plasma oscillation is considered to be the rapid oscillation of the free electron gas of conductive materials such as plasma or metals. This oscillation occurring at the surface of the metal is called surface plasmon (SP) wave and its particle a surface plasmon. The interaction between a surface plasma wave (plasmon) and a light wave (photon) in certain conditions gives rise to the surface plasmon resonance (SPR) phenomenon and its respective particle called surface plasmon polariton (SPP). Although talking about quantum particles, the full theoretical and analytic background of the topic can be covered by solving Maxwell's equation at the interface between a metal and a dielectric, taking into account the proper boundary conditions. Considering the continuity of the fields at the boundary, as well as the conservation of energy and momentum, there are two conditions that must be full-filled for the dielectric constants of the materials, expressed as:

$$\varepsilon_m(\omega) \cdot \varepsilon_d(\omega) < 0 \tag{1}$$

$$\varepsilon_m(\omega) + \varepsilon_d(\omega) < 0 \tag{2}$$

where ε_m is the dielectric constant of the metal and ε_d the dielectric constant of the dielectric material. Another important fact to be remarked is that the SPP wave propagates parallel to the interface, and decays exponentially both in metal and dielectric in the transverse direction, making the SPP always a p-polarized wave. In order to satisfy the continuity at the boundaries, the light wave that excites such a wave should be p-polarized as well. Furthermore, the wave vector (propagation constant) of the SPP wave is always higher than the wave vector (propagation constant) of the light for a certain wavelength as expressed in eq. 3. The situation is explained graphically in Fig. 1. It can be seen that the wave vector of the SPP wave in the metal-water interface (red line) has always a higher value compared to wave vector of light propagating through water (green line).

$$k_{SP}(\omega) = \frac{\omega}{c}\sqrt{\frac{\varepsilon_m \cdot \varepsilon_d}{\varepsilon_m + \varepsilon_d}} \; > \; k_{light}(\omega) = \frac{\omega}{c}\sqrt{\varepsilon_d} \tag{3}$$

Hence, a direct light cannot excite a surface plasmon resonance wave in a metal dielectric interface due to the impossibility of matching the wave vectors (conservation of momentum). This implies that the light needs beforehand some extra energy (and momentum) in order to be able to excite a SPP wave. This is achieved by means of prism coupling, gratings or even optical fiber in our case. The dispersion relation of the light wave propagating in a glass prism is drawn in blue. It can be seen that light propagating in glass, matches the wave vector of the SPP wave at a frequency $3.06 \times 10^{15}\ rad/s$ which corresponds to a wavelength of $615.6\,\mathrm{nm}$. For the sake of clarity, the graph of Fig. 1 is reproduced in Fig. 2 in terms of wavelength, demonstrating that coupling between light and plasmon wave can generally occur at wavelength around $600nm$ only.

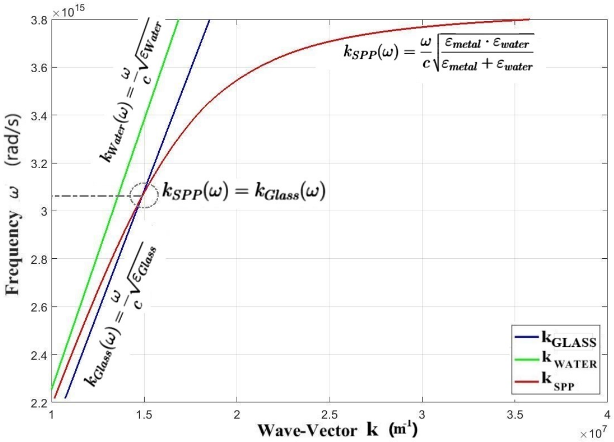

Fig. 1. Dispersion of the propagation constants (wave-vectors) of the light wave in water (green line), light wave in glass prism (blue line), and SPP wave at the metal-water interface (red line)

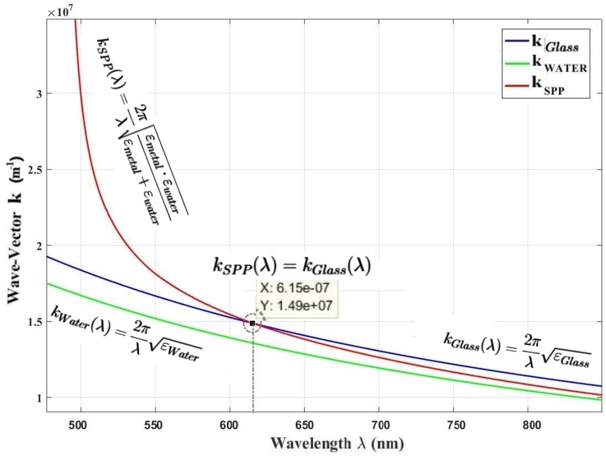

Fig. 2. Dispersion curves as a function of wavelength.

This explains that most of SPR sensors, like those hereby described, exploit visible light to probe the quantity under measure and encode the measurement as a selective light absorption.

II. PROOF OF CONCEPT

This work presents results from SPR sensors based on MM optical fibers. The core of the fiber plays the coupling role and the metal layer is deposited immediately on its surface. The surface plasmon resonance occurs in the interface of the metal with the outer dielectric, which must have a refractive index lower than the one of the core glass, in this case 1.33-1.37 RI. SPR sensors have been known traditionally for analyzing aqueous media and gold (Au) nano layer has often been chosen as the preferred metal to exploit this phenomenon due to its fine performance against oxidation. Functionalization of the metal layer to enhance the performance or to detect specific chemicals are well known techniques, but the traditional ”Kretschmann” configuration (glass-Au-measurand) applied to optical fibers remains the preferred SPR configuration, due to its simplicity. The fabricated sensors are based on multi-mode (MM) $400\,\mu\mathrm{m}$ core fibers. A section of 2-3 cm of the fiber is uncladded and recovered with a $40\,\mathrm{nm}$ nano-layer of Au. A nano-layer of titanium (Ti) has been previously deposited, to be located between the fiber and the gold layer, in order to enhance the adhesion of Au. An important fact of the process is the non uniform distribution of the metal layer above the core of the fiber. The actual deposition is performed in two steps, one side at a time, and not uniformly by means of a rotary stage. The double step has its main advantage in terms of costs and ease of the sensor preparation process, whereas the effect on the sensors performance is comprehensively investigated in [20].

Since the sensing system is intended to be used as a refractometer for aqueous media, the fabricated SPR optical fiber sensors have mainly been characterized in the range of 1.33-1.374 in mixed solutions of water and isopropyl alcohol. Initially, the sensors have been tested using a wavelength interrogation technique in transmission by means of a broadband (470-850 nm) visible LED source (MBB1F1-Thorlabs) and an Avantes spectrometer (AvaSpec-3648) in the receiving side, as it is illustrated in Fig. 3. The sensitive part is immersed in the liquid solution performing tests of repeatability, stability and long time performance. The system has shown an overall sensitivity of 2000 nm/RIU in the full range and an enhanced sensitivity of around 2500 nm/RIU close to the water refractive index, due to the slight non-linear slope of the calibration function. The $0.3\,\mathrm{nm}$ spectrometer resolution restricts the refractive index detection limit of the system to about 10^{-4}. Nevertheless, a limit of detection in the order of 10^{-4} RIU is enough to see the temperature as a parasitic effect. Continuous tests under temperatures in the range 20 to 60 °C are performed by positioning the liquid container, filled with de-ionized water, on top of a temperature controllable hot plate. The SPR peak exhibits a blue-shift of around $12\,\mathrm{nm}$ when the temperature changes from 20 °C to 60 °C, saving one spectrum for each step of 5 °C. The temperature of the liquid is continuously monitored with a calibrated thermo-couple and Fig. 4 shows the liquid container in which the sensor gets immersed. The thermo-optic effect mentioned above and confirmed by the experiments, can bring miss-leading information. Returning to the chlorine concentration in the swimming pool example, a fixed concentration of chlorine in water of different temperatures would be read differently, giving miss-leading results. A temperature compensation method is therefore explained in details in the following section.

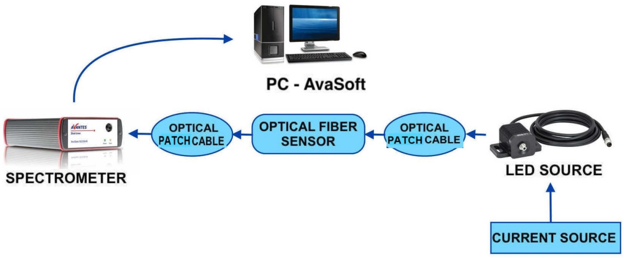

Fig. 3. Setup configuration of the device, wavelength interrogation technique in transmission. Broad-band LED light as a source and spectrometer as a receiver.

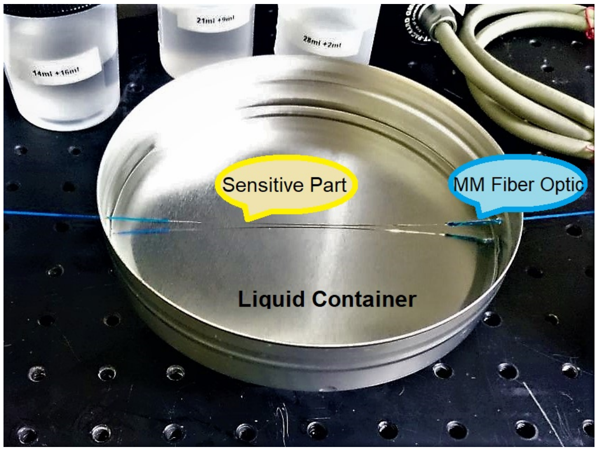

Fig. 4. Illustration of the optical fiber based SPR sensor, placed in the empty liquid container.

A. Temperature Compensation Proposal

This section proposes a temperature compensation technique for SPR fiber optic sensors. A simplified detection scheme derived from that of Fig. 3 is achieved by using a single wavelength laser source as an input, placed on the shoulder of the SPR curve and monitoring the intensity of the light transmitted to the other side by means of a photodiode. Fig. 5 illustrates the working principle of such a system. The change on the refractive index of the medium will now be read as a change in the light intensity, instead of reading the SPR wavelength peak shift. Based on this technique, the system can be expanded by adding another fiber based SPR sensor in parallel by means of a multi-mode fiber optic bundle (BFY400LS02-Thorlabs), using the same laser source, and two separate photo-diodes. Fig. 6 shows the full setup configuration of the system. Sensor 1 (in the Fig. 6) has its sensitive section covered by a solid resin with a known RI (refractive index) and is intended to be used as the temperature compensator. A continuous SP oscillation with a

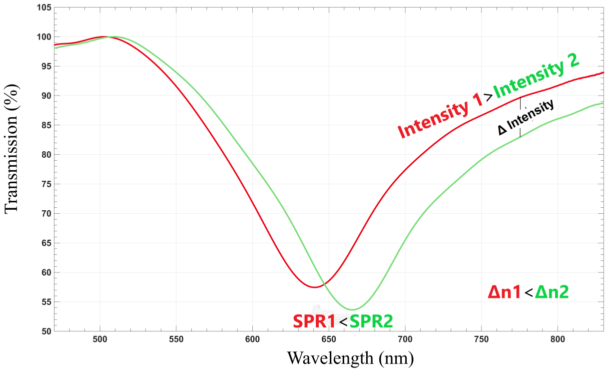

Fig. 5. Illustration of the principle of single wavelength (laser) technique, based on experimentally obtained spectra by the traditional wavelength interrogation technique. Analysis of the intensity in a single wavelength on the shoulder of the curve.

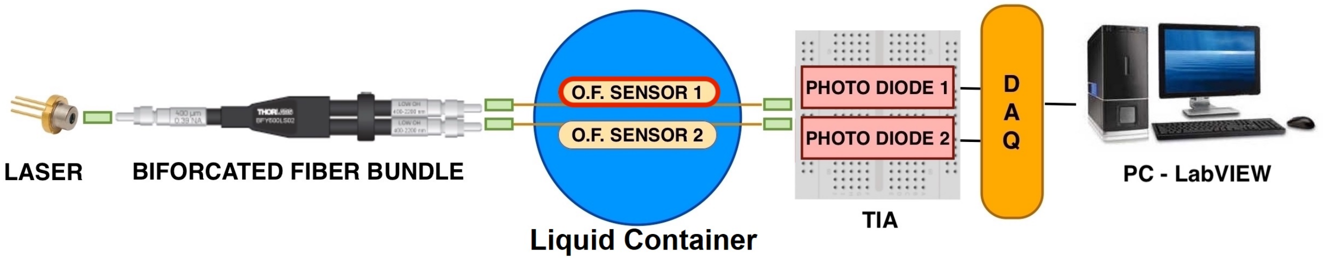

Fig. 6. Illustration of the full configuration setup based on intensity interrogation. Sensor 1 coated with resin (red) to be used for temperature compensation

fixed resonance wavelength, which corresponds to the RI of the resin and its thermo-optic effect, will be generated on the gold surface of sensor 1. Thus the photo-diode will receive an intensity of light modulated according to the temperature. A full calibration in the temperatures of interest, makes the SPR sensor 1 work as a thermometer. On the other hand, sensor 2 will deal with its traditional job of liquid analysis. The signals received in transmission regime by two separate photo-diodes,are converted to voltages using trans-impedance amplifiers and are stored via a data acquisition card (NI-DAQ) in a personal computer.

III. RESULTS AND DISCUSSION

The fabricated sensors have been tested in terms of sensitivity, resolution, repeatibility, long term stability and under different temperature regimes. In the wavelength interrogation mode, using the spectrometer, the system has shown a sensitivity of 2000-2500 nm/RIU, with a remarkable linear slope in small ranges of RI and slightly non-linear in wide range (1.33-1.37). The limit of detection (smallest detectable difference) is restricted by the resolution of the spectrometer ($0.3\,\mathrm{nm}$), corresponding to 1×10^{-4} RI. This barrier can be over-passed by averaging and curve fitting. An important result is the high long term stability of the system, that exhibits negligible drift during a 24 hour test, as illustrated in Fig. 7. The ac quired spectra are processed with matlab, by polynomial fitting SPR absorption peak analysis.

Fig. 8 depicts the 24 SPR peaks obtained during the 1-day long test, saving one spectrum every hour and linearly fitted. It can be observed that data points vary in the range of $620.9\,\mathrm{nm}$ - $621.8\,\mathrm{nm}$ with a standard deviation of $0.31\,\mathrm{nm}$. The fitting process with a polynomial of first degree is also plotted in order to detect any trend of the resonance peak with respect to time. The fitted curve has a positive slope of $0.0163\,\mathrm{nm/h}$ meaning that there is a very slight red-shifting of the curve over time. A closer look at the data points reveals that more than the trend, there is random noise source that might come due to the external conditions (i.e temperature variation in the room, mechanical vibrations of the system etc.). In this case longer tests in time domain, would be a way to take out the doubts whether there exists an increasing trend or not.

Very similar tests are performed using the intensity interrogation method, exploiting a single laser wavelength from the

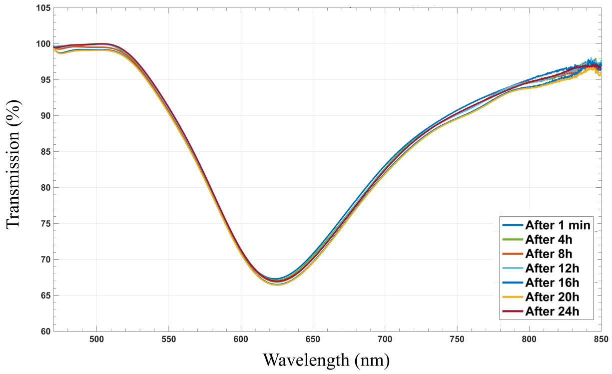

Fig. 7. Transmission spectra experimentally obtained during a 24 hours test. The SPR peak drift is in the order of $0.3\,\mathrm{nm}$. Seven curves plotted, respectively after 1 min, 4 hours, 8 hours, 12 hours, 16 hours, 20 hours and 24 hours after the sensor is immersed in de-ionized water.

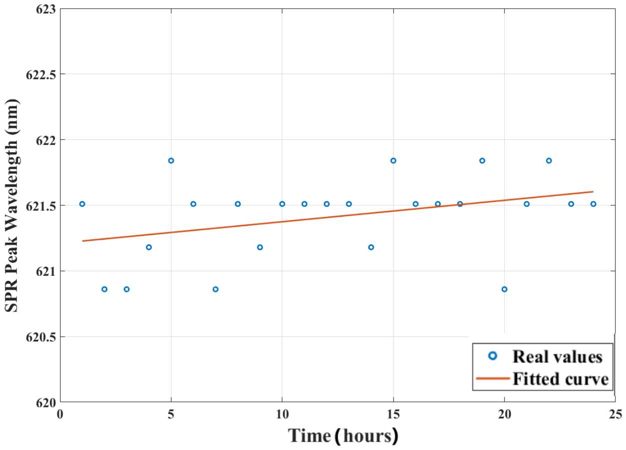

Fig. 8. 24 SPR peak wavelengths obtained during a 1 day long test saving one spectrum every 1 hour (blue dots). Fitting curve of 1^{st} degree polynomial with respect to time (red line).

source and a photo-diode as the receiver. The sensitivity is in the order of 5 V/RIU and the limit of detection determined by the resolution ($2.5\,\mathrm{mV}$) of the DAQ (NI-USB 6009) is in the order 5×10^{-4} using the simplest trans-impedance amplifier (composed of a single op-amp and resistor between the inverting input and the output). The drawback of this scheme is the analog circuitry which can behave as noise source. On the other hand, analog conditioning can be designed for low noise through a differential amplification scheme in order to get a smaller limit of detection [21].

In order to prove the parasitic effect introduced by temperature, several tests under different temperatures regimes are performed, giving results that resemble those of the literature. Fig. 9 shows the curves obtained for temperatures varying from 20 °C up to 60 °C with a step of 10 °C. In the whole range of 40 °C variation, a $12\,\mathrm{nm}$ SPR peak blu-shift is measured. Considering that this shift is totally due to the thermo-optic effect of water (Δn of water), it would correspond to a $\Delta n = 4.8 \times 10^{-3}$, thus a change of $1.2 \times 10^{-4} RIU/^{\circ}C$. In fact it is important to mention that the shift of the SPR peak is not only due to the thermo-optic effect of the liquid. Indeed, thermo-optic effects of all the materials that take part in the experiment must be considered, hence besides the thermo-optic effect of the de-ionized water ($\Delta n_{H_2O}/^{\circ}C$), the effect of gold ($\Delta n_{Au}/^{\circ}C$) and of silica in the fiber core ($\Delta n_{SO_2}/^{\circ}C$) should be considered [22]. The combination of these three contributions together brings the result obtained experimentally and presented in Fig. 9.

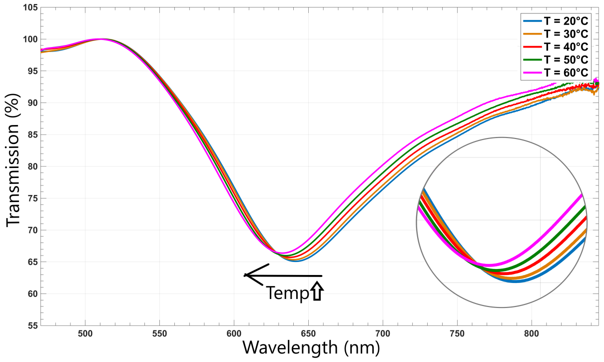

Fig. 9. Curves obtained experimentally in different de-ionized water temperature. Increasing the temperature from 20°C to 60°C with a step of 10°C are plotted. There is a total of $12\,\mathrm{nm}$ blue-shift of the SPR peak with increasing the temperature.

IV. CONCLUSION

A sensing system for refracrtive index measurement of aqueous media based on SPR optical fiber sensors has been experimentally investigated. The highlight of this work is the importance of the effect of the temperature in the fiber optic based SPR sensors. Depending on the application, temperature would introduce an uncertainty range in the order of 1×10^{-4} RIU up to 1×10^{-3} RIU. This prevents the performance of such sensors. In section II-A a novel SPR system is proposed with a possible temperature compensation technique. Low cost, portability, stability and ability to make real time, label free and in-vitro measurements are the key advantages of this system. There is further work to be carried out in analyzing the quantity of chlorine in swimming pool water, which is a real application of measuring a small fraction of refractive index change, with an important impact of the temperature.

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