Optical fiber humidity sensor based on surface plasmon resonance in the infra-red region

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ABSTRACT

Here, the fabrication and characterization of a novel optical fiber humidity sensor based on surface plasmon resonance (SPR) in the infra-red region is presented. Firstly, an indium tin oxide (ITO) coating is deposited onto a 200 µm core diameter optical fiber causing the shift of the SPR wavelength to the infra-red region. Then, the LbL method is used to deposit a polymeric coating onto the ITO layer. The variations in the external humidity originated changes in the thickness and refractive index of the polymeric coating and hence in the resonance.

Keywords: Humidity sensor, Indium tin oxide, Layer by Layer, Plasmon resonance, Optical fiber

1. INTRODUCTION

It has been many years since the first discovery of surface plasmons in the early 20th century [1]. Since then until now, surface plasmon resonance (SPR) spectroscopy has evolved remarkably motivating numerous works in the chemical and biosensing area, especially in the last decades [2-3]. Nevertheless, the first described Otto-Kretschmann configuration [4-5] and the later optical fiber configuration presented by Jorgenson & Yee [6] have been traditionally limited by the utilization of noble metals such as gold and silver as the SPR supporting coatings, with the Plasmon resonance wavelength in the visible and near infra-red regions. In this work, it is first described the fabrication of Indium Tin Oxide (ITO) coated optical fibers, which present the effect of plasmon resonance with the plasmon resonance wavelength shifted to the infra-red region [7]. These devices are used as substrates to deposit an additional polymeric coating by using the traditional Layer-by-Layer electrostatic self assembly method [8-10]. The polymers used here are the well-known poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA) whose optical properties (thickness) vary with the relative humidity of the medium [11-13]. Hence, the changes in thickness and refractive index of the polymeric coating in contact with the SPR supporting layer, ITO in this case, derive in variations of the SPR wavelength allowing the indirect measurement of the relative humidity of the surrounding medium. Finally, the response of these new devices is characterized for variations of the relative humidity in the range from 20% to 80%, obtaining a variation of approximately 65 nm in the SPR wavelength. To our knowledge, this is the first time that this kind of sensors is described in literature.

2. EXPERIMENTAL

In this work, the polymers PAH and PAA were used as the sensitive materials. Indium(III) chloride, tin(IV) chloride pentahydrate and TWEEN® 80 were used to prepare the solutions for the ITO coating fabrication. All these materials were purchased from Sigma-Aldrich and their chemical structures are shown in Figure 1.

The SPR-based optical fiber humidity sensors fabrication was performed in a three-step process.
Firstly, ITO coated optical fibers were prepared via a sol-gel dip coating method as previously described by Ota et al. [14] using precleaned 200 µm core diameter PCS optical fibers (Thorlabs Inc.). The previous preparation of the optical fibers for the deposition consisted on removing the buffer, the plastic cladding and cleaning the fibers in an ultrasonic bath with detergent, ultrapure de-ionized (DI) water and acetone, consecutively. The deposition process was repeated up to 10 layers with a 30 min. annealing process at 500 ºC between each layer and a post annealing process at 300 ºC for 3 hours under nitrogen atmosphere.

![Fig. 1. Molecular structure of the chemicals used in this work.](image)

Then, a sensitive PAH-PAA coating was deposited onto the ITO coated optical fibers using the Layer-by-Layer (LbL) traditional process. The ITO-coated fibers were dipped into a KOH solution prior to the deposition in order to create a superficial charge. 10mM PAH and PAA solutions were prepared with DI water (Barnstead Diamond Inc) and adjusted to pH 4.0 using NaOH and HCl. After that, the optical fibers were sequentially dipped into the cationic (PAH) and anionic (PAA) solutions for 2 min. with a rinse step in DI water between each step in order to remove the excess of material. This process was repeated up to 50 bilayers [8-10].

Finally, the optical fibers were perpendicularly cleaved at both ends using an automatic fiber cleaver (LCD-200, Vytran Inc.) to obtain a 70 mm portion. Then, these fragments were attached to 200 µm pigtails using an automatic fusion splicer (FITEL S176, Furukawa Co. Ltd.).

The setup used to obtain the transmission spectra and the wavelength of the maximum attenuation peaks is schematically represented in Figure 2. It consisted on a halogen lamp (DH-2000, Avantes Inc.) as the light source and a NIR 512 spectrometer (Oceanoptics Inc.) connected to a PC. The sensitive region was introduced into a climatic chamber (Angelantoni Inc.) in order to monitor the changes of relative humidity (RH).
Atomic force microscopy (AFM) measurements were performed in tapping mode (Innova, Veeco®), with a silicon cantilever (RTESP, Vesco) as a useful tool to investigate the surface morphology. Besides, scanning electron microscopy (SEM) were obtained (Auriga FESEM, Carl Zeiss®), in order to estimate the thickness of the fabricated films.

3. RESULTS AND DISCUSSION

AFM and SEM analysis were performed to study the fabricated sensors. In Figure 3a an AFM image of the PAH-PAA coated fiber is shown. The film observed in this picture is homogeneous and continuous and the average RMS roughness calculated by this technique is 2.02 nm. In figure 3b a SEM image and zoom of the perpendicularly cleaved cross section of the sensor is shown. This image reveals the ITO film and PAH-PAA coating thicknesses of approximately 300 and 150 nm respectively.

Fig. 2. Experimental transmission setup.

Fig. 3. a) AFM image of the PAH-PAA film coating the ITO layer. b) SEM image of the sensor cross section.
In order to analyze the sensors response these were subjected to cyclic variations of RH in the range from 20 to 80%. The transmission spectra and absorption peaks were measured using the experimental setup explained before. In Figure 4a the absorption peaks corresponding to different RH values are shown. It can be seen that the absorption peak is moved to the right at the same time that the RH is raised. In Figure 4b it is represented the maximum absorbance wavelengths when the RH is varied from 20% to 80% and down again. The maximum wavelength variation is approximately 65 nm, so the average sensitivity of this sensor is 1.08 nm/%HR in the studied range. Moreover, it can be also observed in Figure 4b the high repeatability of these sensors where difference between the values at the end and the beginning of the cycle is inappreciable.

**Fig. 4. a) Absorption spectra when the sensor is subjected to different RH values and b) Maximum attenuation wavelength vs. RH values from 20% to 80% and down again.**

4. **CONCLUSIONS**

In this work, a novel humidity sensor based on SPR in the infra-red region has been presented. An ITO thin film has been deposited onto optical fibers in order to create a conductive transparent layer, which supports the SPR phenomenon in the infra-red region. Additionally, a PAH-PAA film has been coated onto the ITO layer using the LbL method. Besides, the fabricated devices have been proven to vary their reflection index with the external relative humidity originating variations in the SPR maximum absorption peak wavelength. Finally, these devices have shown high repeatability and good linearity in the studied RH range (from 20 to 80%) with an average sensitivity of 1.08 nm/%RH. These devices are described here for the first time as an example of the possibility of using the infra-red region of the spectra associated to the SPR based sensors.

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