In situ monitoring of the formation of nanoscale polyelectrolyte coatings on optical fibers using Surface Plasmon Resonances

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Abstract: Deposition of a conformal nanoscale polymer coating was characterized using a fiber SPR sensor. The sensor platform consisted of an unmodified gold-coated single mode fiber where SPR was excited through the coupling of the core mode into the cladding modes using a Tilted Fiber Bragg Grating. The results from this study show how the sensor can monitor in real time the formation of polyelectrolyte coatings during a process consisting of several stages of immersion. The experimental data was further calibrated by simulations and Atomic Force Microscope imaging allowing us to determine the thickness and refractive index of the adsorbed polyelectrolyte.

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References and links
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1. Introduction

In 2007, we proposed and demonstrated the first Surface Plasmon Resonance (SPR) fiber sensor implemented using a conventional unmodified single mode fiber with a tilted Bragg grating inscribed in its core [1]. Overall, SPR sensors can be used to measure refractive indices, thickness changes and the occurrence of chemical reactions or biomolecular recognition events over nanometer-scale thicknesses. SPR sensors implemented in optical fibers are small, can be used remotely, and are relatively easy to fabricate. The operating range of the tilted fiber Bragg grating-SPR (TFBG-SPR) sensor, in terms of the refractive index of the material in which it is embedded, is determined by the tilt angle of the grating. It is therefore possible to tailor the design of the sensor for applications in various media. As shown by our group earlier [2,3] a tilt angle of 10 degrees optimizes the response of the sensor for measurements made in water and other aqueous environments. In addition to its broad operating range, the sensor has an inherently small cross-sensitivity to temperature that is further simplified by the fact that one of the optical transmission features (the core mode back reflection upon itself) can be used to measure the temperature at the device in real time without interference from changes in the outer medium [3,4]. It was also demonstrated recently [5] that polarization control of the light launched into the fiber core leads to a significant improvement of the sensor response by clearly separating SPR-active and non-active cladding modes. The concept of a Bragg grating assisted SPR sensor in a conventional fiber has also been studied theoretically in great detail and showed to be able to compete with bulkier and costlier SPR devices [6].

In this paper, we demonstrate how a TFBG-SPR sensor can be used for in situ and real time detection of individual nanometer-thick polyelectrolyte layers formed during a Layer-by-Layer self-assembly process [7]. Polyelectrolytes belong to a broad class of polymer molecules that carry electrical charges that can interact with other charged molecules. Given their ability to assemble on charged surfaces and to form multilayer structures on substrates of almost completely arbitrary shapes, polyelectrolytes have found important uses in many
fields, including chemical sensing and biosensing [8,9]. In such applications, polyelectrolyte films can be used as a coating material and substrate for hosting chemical reactions [10,11], or they can be used as the sensing material itself [12]. In the work presented here, the formation of a polyelectrolyte multilayer structure was studied using alternating immersion of a gold coated TFBG-SPR optical fiber into two well known polyelectrolytes: negatively charged poly (sodium-4-styrenesulfonate) (PSS) and positively charged poly (diallyldimethylammonium chloride) (PDADMAC). Readings from the TFBG-SPR sensor make it possible to see the dynamics of the polyelectrolyte multilayer formation (build-up) through the immersion stages in various solutions. The monitoring and detection of the formation of multilayered polyelectrolyte films in situ and in real time by the TFBG-SPR sensor has several important consequences: 1) the sensing device can be used as a process monitor for the deposition on other substrates in mass production environments; 2) it is possible to fabricate fiber-optic biochemical sensors based on the polyelectrolyte-coated, gold-coated fiber grating devices with very precise layer compositions and thicknesses; and 3) the sensor can be used for the characterization of other properties of the deposited films besides thickness, such as refractive index or density (with help from complementary measurements, as shown below). These features of our TFBG-SPR sensor present a great advantage since it is generally difficult to characterize the adsorption of nanoscale coatings on non-planar surfaces using the most common thin film characterization methods such as UV-visible absorption spectroscopy [13], ellipsometry, Atomic Force Microscope (AFM) [14], Scanning Electron Microscopy (SEM) [15], or X-ray photoelectron spectroscopy [16]. This is even more difficult when the chemical reactions occur inside process chambers filled with liquids (such as those required for the LbL process).

Our results are presented as follows: the TFBG-SPR platform is briefly described and its optical properties discussed in the context of the detection of conformal thin films on the outer surface of the fiber; then the fabrication of the device and measurement techniques are presented followed by the description of the LbL process and of the polyelectrolyte solutions. Experimental results for two tests are presented and discussed, with help from simulations of the coated TFBG-SPR structures. We show that it is possible to calibrate the optical response of the device to a particular process and choice of polyelectrolytes by a combination of modelling and post-fabrication final thickness measurement using AFM. It is important to note that once this calibration is made, there is no further need for AFM measurements to extract the thickness data from subsequent optical measurements with the SPR-TFBG sensor.

2. Description and implementation of the TFBG-SPR Platform

Our sensor platform utilizes the SPR effect. One of the key requirements of any optical SPR configuration is the presence of an interface between metal and dielectric materials that have optical properties suitable for the excitation of Surface Plasmon Waves (SPW) [17]. For light to excite a SPW at that interface, the SPR phase matching condition must be satisfied: the longitudinal component of the propagation constant $\beta_{inc}$ of the light wave used to excite the SPW must be equal to the propagation constant $\beta_p$ of the SPW that can be supported by these materials. $\beta_p$ is calculated as follows:

$$\beta_p = \frac{\omega}{c} \sqrt{\frac{\varepsilon_{ext}\varepsilon_m}{\varepsilon_{ext} + \varepsilon_m}},$$

where $c$ is the speed of light in vacuum, $\omega$ is the angular frequency of the light, while $\varepsilon_m$ and $\varepsilon_{ext}$ are the relative permittivity of the metal and of the material that is adjacent to the metal interface where the SPW is located (the outside surface of the metal coating in our case).

In order for the SPW to be confined to the surface without radiating into the surrounding medium, the magnitude of $\beta_p$ must be larger than the magnitude of the propagation constant of the light waves in that medium ($\beta_{ext}$). As a result it is impossible to excite a SPW with a light
wave incident from above or below the metal film unless some phase matching or other techniques are used. The usual solution for uniform structures is to use tunneling of the light from a high index medium (i.e. large $\beta_{inc}$), across the metal to its outer surface where the following condition can be met for the SPW to be excited:

$$\beta_p = \beta_{inc} > \beta_{cut},$$

(2)

The most widespread implementation of this configuration, the Kretschmann-Raether configuration, makes use of a high index glass prism with a metal-coated base [17]. For media with refractive indices lower than that of the prism, light beams incident on the base of the prism can be totally reflected (for a range of angles that depends on wavelength and the refractive indices of the media) and the associated evanescent field can be used to tunnel across the metal and couple to a SPW, provided the metal layer is not too thick.

Achieving similar conditions in glass optical fibers is possible because when the external medium has a refractive index lower than that of the glass (near 1.45 in the near infrared for silica fibers), light again is confined in the glass by total internal reflection. The challenge for fiber-based SPR sensors is to find a mechanism which would allow coupling of light propagating in the core or cladding to the SPW, and more importantly, which would provide precise control over this coupling. As noted in the Introduction, we have found a way to do this in conventional single mode fibers [1], [5], and [4] without having to use multimode fibers [18], custom-designed fibers [19], or fiber structure modifications [20,21].

Figure 1 presents a schematic diagram that highlights the analogy between the most common bulk optic SPR platform (the Kretschmann-Raether configuration that uses angle or wavelength scanning to tune $\beta_{inc}$ [17]), and the wavelength selective excitation of individual cladding modes by a TFBG. In this configuration, we can individually and separately excite over one hundred cladding modes just by changing the wavelength of the core guided light, making it very easy to find modes that are phase matched to a wide range of SPR conditions. Once a SPR has been identified in the fiber transmission spectrum, the differential response of the cladding mode resonances that are phase matched to the SPW can be used to monitor very precisely any changes of the SPR conditions. In particular, we can measure changes induced by thickness or refractive index modifications in the material that is immediately adjacent to the metal coating, within the evanescent tail of the plasmon wave field. Since the structural integrity of the fiber is not compromised in this configuration, the sensor structure is reliable and very easy to mass-produce at low cost.

Fig. 1. Analogy between the TFBG and prism-based excitation of plasmon waves by resonant tunneling across a metal layer from a material with a refractive index higher than the surrounding medium.

The main characteristic of the TFBG is that planes of raised refractive index are tilted away from the perpendicular to the fiber’s longitudinal axis. Gratings with relatively small tilt angles ($2^\circ - 10^\circ$) allow the excitation of several tens of cladding modes [3,22] as shown in Fig. 2. Each of the excited modes is guided by the cladding with effective indices ranging from less than 1.300 to approximately 1.445 (for the resonances shown). When this fiber is coated with a thin metal layer, this range of effective indices corresponds to the possible plasmon effective indices that the grating can couple to.
Fig. 2. Transmission spectrum of a bare TFBG with 10° of tilt measured in air.

The propagation constant of each cladding mode in the spectrum of Fig. 2 can be found from the phase matching condition between the core mode, each cladding mode, and the grating period of the TFBG:

\[
\beta_{\text{core}}(\lambda_i) + \beta_{\text{clad}}'(\lambda_i) = \frac{2\pi \cos(\theta)}{\Lambda},
\]

(3)

where \( \theta \) is the tilt angle of the grating, \( \Lambda \) is the period of the grating, and each propagation constant \( \beta = 2 \pi n_{\text{eff}} / \lambda \) must be evaluated at the wavelength at which the coupling occurs for the given cladding mode [22]. In particular, the dispersion of the fiber refractive indices with wavelength must be taken into account in order to reproduce the spectrum of Fig. 2.

The combination of Eqs. (1) to 3 makes it possible to determine which cladding mode can be used to excite SPR for a given set of grating parameters and refractive indices of the materials used. Therefore, as shown in [5], by monitoring the SPR wavelength shift (through the shifts in the amplitudes and wavelengths of the cladding modes which are coupled to the SPR) we can extract very precise information related to the change of the bulk refractive index of the dielectric in proximity to the surface of the metal. We show here that nm-scale thin films can also be measured accurately.

4. Experimental Methods

4.1 Fabrication of the Sensor

The fiber used to fabricate the sensors was a standard single-mode telecommunication fiber (Corning SMF-28) that was saturated with hydrogen prior to writing the grating; the fiber was kept for 14 days at room temperature in a pressure vessel maintained at a pressure of 140 atm to increase its photosensitivity to the ultraviolet light used in the process of grating writing.

The 1 cm-long tilted gratings were written in the fiber core using the phase mask technique with excimer laser irradiation at 248 nm. To obtain a “tilted” grating, we rotated the fiber and phase mask together around a vertical axis that was perpendicular to the fiber. The tilt angle of the grating determined the wavelength separation between the core mode (Bragg) resonance and the peak of the envelope of the cladding mode resonances in transmission [3]. The tested gratings had a 10° tilt with a Bragg resonance at 1601 nm. As shown in Fig. 1, this choice of grating parameters resulted in a relatively wide cladding mode spectrum (over 100 nm), centered near 1550 nm, which allowed the sensor to work in various aqueous
solutions with refractive indices around 1.31-1.34 (we need cladding modes with effective indices slightly higher than the outside medium index to couple to SPR). All gratings were subjected to a thermal stabilization process that involved a quick anneal (approximately 1 minute at 400°C) to remove the unstable portion of the ultraviolet induced refractive index change and a 12 hour annealing at 120°C to outgas all remaining hydrogen.

The final step in the preparation of the sensor involved the deposition of a gold layer on the surface of the fiber where the grating was located. The gold coating was deposited using a table-top vacuum sputtering system with the fiber axis parallel to the target. To render the coating relatively uniform around the circumference, two depositions were carried out with a fiber rotation of 180 degrees between depositions. For the two tests reported here, we used nominal gold film thicknesses of 20 and 50 nm respectively, as determined by the thickness measured on a flat control sample in the same sputtering system.

4.2 Measurement setup

The optical transmission of the sensors was carried out using two different kinds of instruments. For the first set of measurements, an Optical Sensing Analyzer (model Si720 from Micron Optics) was used in combination with a Polarization Controller from JDS Uniphase and the measurement resolution was set to 0.0025 nm. The polarization controller was used to optimize the linear polarization of the light incident on the grating [5]. This system allowed the interrogation of the sensor at a rate of 1.2 seconds per full spectrum measurement. In the second case, an un-polarized broadband amplified spontaneous emission source (JDS Uniphase) and an optical spectrum analyzer (ANDO AD6317B) with the resolution set at 0.015 nm were used to interrogate the sensor over long periods (several hours) at a low recording rate of around 1.5 minutes per full spectrum measurement. The use of unpolarized light decreased the sharpness of the SPR response (since only half the light was in the correct polarization to excite the plasmon wave on the metal), but still allowed accurate measurements to be made. However, the measurements obtained with the fast sweeping source are slightly noisier.

During the experiments, the sensors were fixed by a UV-sensitive adhesive in a 7.5 by 2 cm plastic cell provided with a carved out indentation (45 mm by 5 mm) which was filled with the various solutions during the tests. A glass slide was placed on top of the fluid-filled cell during each measurement step to ensure that evaporation did not occur: without this precaution the sensor would pick up the refractive index changes caused by evaporation in the small volume of the cell. All experiments were conducted at a constant temperature of 23°C. In principle this does not matter since the TFBG itself is inherently temperature-insensitive [3], and the intrinsic temperature sensitivity of the TFBG-SPR effect has been found earlier [4] to be negligible relative to the shifts that were observed here.

4.3 Layer-by-Layer deposition method

The two oppositely charged electrolyte solutions used in this study were prepared from a poly(diallyldimethylammonium chloride) solution (PDADMAC; 35 wt % in water, MW <100,000), and poly (sodium-4-styrenesulfonate) (PSS; MW~70,000), both from Aldrich Inc. A stock solution of 10^{-3} M NaCl was prepared using 18.2 MΩ cm de-ionized water as a solvent. This solution was used for making 1mg/ml of PSS and PDADMAC solutions.

Before the experiment, the gold-coated sensors were cleaned with ethanol and 18.2 MΩ cm de-ionized water. To deposit the polymers on the surface of the sensors, the sensors were first fixed in the cell. Second, the cell was filled with 800 µL of PDADMAC solution for 10 minutes; this was followed by a wash with de-ionized water (the washing step lasting approximately 4 minutes) and then the fiber was left to dry in air. The same process was repeated with the PSS solution. These four steps constitute the formation of one PDADMAC-PSS bilayer consisting of pair of PDADMAC and PSS monolayers. The four-step procedure
was repeated four times during the first test in order to deposit 4 bilayers and 15 times during second test in order to deposit 15 bilayers.

SPR measurements were recorded during the sensor immersions in the polyelectrolyte solutions, and also during the immersions in de-ionized water that took place in between the polymer depositions.

5. Experimental Results

5.1 Optical transmission measurement

A typical transmission spectrum of the sensor immersed in the polymer solution is presented in Fig. 3. The circled region on the spectrum shows which cladding modes tunnel across the gold film [5], thereby incurring loss and decreasing the amplitude of the corresponding resonances (see Fig. 1 for a comparison with a transmission spectrum with no SPR).

![Image of a transmission spectrum](image)

Fig. 3. Transmission spectrum of a TFBG-SPR sensor interrogated using polarized light and immersed in the polyelectrolyte solution. The location of the SPR-coupled set of cladding modes is shown with the circle. The arrow points at the cladding modes whose amplitudes are used to infer the SPR shift (see text for details).

Any change in the refractive index of the material within the evanescent tail of the plasmon wave will cause a change of the effective index of the surface plasmon mode (as seen from Eq. (1), and therefore a wavelength shift in the position of SPR. Position of the centre of SPR region could possibly be found as the centre of the envelope which could be used to fit top or bottom of the resonances shown with the red circle in Fig. 3. Since the wavelength shifts resulting from the deposition of monolayers of polyelectrolytes are expected to be much smaller than the spectral width of the SPR, it is expected that the traditional way to track SPR through fitting might result in a low signal to noise ratio. Therefore, as explained in more detail in [5], we measured the amplitude change of several individual cladding mode resonances located on the edge of the SPR (the most sensitive resonance is the one shown with an arrow in Fig. 3) instead of trying to fit the SPR envelope at each step. The SPR wavelength shift in nm was then calculated by dividing the amplitude change of the resonance in dB by the local slope of the SPR envelope (dB/nm).

5.2 SPR Film growth measurement and interpretation of the experimental results

Results of the two experiments, corresponding with the deposition of 4 and 15 bilayer structures are shown in Figs. 4 and 5. The main idea behind conducting two tests was to not
only show the reproducibility, but also to explore the real-time dynamics of the polyelectrolyte coating formation over short and long time scales (thin and thick final layers).

During the first test, data was acquired every 1.2 seconds, providing an insight into the formation of the polyelectrolyte coating from the first second of the first immersion. The sensor response during immersions in the polymer solutions, each lasting 10 minutes, was combined with responses measured in water (the drying steps cannot be shown because the SPR effective index for air as the outer medium lies outside the range of effective indices accessible with our device). Each immersion in water lasted around 1 minute and can be recognized in Fig. 4 by a strong downward SPR signal change due to the refractive index mismatch between polymer solutions and water. The inset displayed in Fig. 4 shows a combination of the sensor responses measured only in water (data related to soaking in polymer solutions was eliminated).

Overall, Fig. 4 shows a step-by-step positive SPR change following the deposition of each bi-layer. However, a closer look at the SPR shifts during the deposition of bi-layers reveals the surprising result that the shift is essentially inexistent during the immersions in the two polymer solutions, but jumps sharply following the rinsing and drying steps, especially after the immersion in the second polyelectrolyte. The inset of Fig. 4 further shows definite positive SPR shifts during the short rinsing stages.

The results of the second experiment where a “thicker” 15-bilayer structure was deposited are shown in Fig. 5. Several measurements were taken during each of the 10-min immersions in the polymer solutions. SPR dynamics during the rinsing steps has been removed from the figure to highlight the growth of the film during each immersion. The results of this second test confirm those of the first and indicate a monotonic increase of the SPR wavelength as a result of the deposition of the first 22 monolayers. This increase is very regular except for the first few layers, where the polymer film is beginning to form, and the last few layers where the growth is more inconsistent. As discovered in the first test, here SPR growth mostly stems from intermediate steps consisting of rinsing in water and drying in the air.

![Fig. 4. Change of the SPR wavelength observed during the immersions in the polymer solutions and during soaking in water. Each 10-min immersion in the polymer solution is followed by a 1-min immersion in deionized water. Inset shows SPR change observed in water. Shown data was smoothed using moving average filter.](image-url)
5.3 Experimental verification of the film deposition

An AFM scan of the sensor surface before and after the deposition of the 15 bi-layers was conducted to corroborate the SPR measurements. The scanning was performed in semi-contact mode and the scan of the film was completed several days after the deposition when the polymer coating had completely dried out.

Images (a) and (b) in Fig. 6 show the surface of the sensor before and after the deposition of a polymer film while Fig. 7 shows the height profile of the surface of the polyelectrolyte coating across the boundary of a scratch made on the coating. The scratch was made mechanically and was introduced in order to determine the thickness of the deposited structure. The total thickness of the deposited layers (gold plus polymer) was found to vary between 22 and 60 nm with an average thickness of 36.8 nm. Removing the gold thickness from this measurement (20 nm), we obtained an average value of 16.8 nm for the polymer layer, i.e. 1.12 nm per bi-layer, consistent with values reported for this type of deposition [23]. As expected, there is a large variance in the total thickness (easily observed in Fig. 6(b)) as the deposition appears non-uniform.

Fig. 5. The SPR wavelength change during the deposition of a thicker polymer film (measurements acquired only in the polymer solutions).

Fig. 6. (a) AFM image of the gold coating before deposition of the polyelectrolyte film. (b) AFM image of the gold coating with 30 monolayers of the polyelectrolytes. The image was taken near the boundary of a scratch which was done to remove the polymer coating in order to determine its thickness.
6. Data analysis and discussion

6.1 Layer build-up dynamics

For the high temporal resolution measurement reported in Fig. 4, the most striking feature is that the bi-layer organization appears rather unexpectedly to occur mostly during rinsing and drying stages instead of during soaking in the polyelectrolytes. The negative SPR jump observed during water rinsing is caused by the lower refractive index of the water relative to the buffer solutions that were used for the polyelectrolyte deposition. But the gradual positive SPR shifts observed during the rinsing stages also indicate that the films become optically denser. These shifts do not converge to a steady value however and this may be an indication that the process had not stabilized and that different layer densities might have occurred if longer rinsing durations had been used.

The fact that the real-time data recorded during the adsorption of the polyelectrolyte molecules does not show a significant SPR shift, while soaking in water and drying steps always results in a SPR increase, may be explained by the ionic strength of the solutions used and its impact on the configuration of the polyelectrolyte molecules. More specifically, polyelectrolyte chains in an aqueous solution of ionic salt (1 mM NaCl), assume a coiled configuration due to the screening of charge along the polymer chain by counter ions in the solution. Adsorption of polyelectrolytes with such coiled configuration to the surface of the sensor results in a layer with a certain thickness and density that is strongly related to the amount of coiling [24]. However, when the sensor with the adsorbed polyelectrolyte molecules is immersed in deionized water, most of the counter ions are expelled from the polymer matrix [25]. Then the charge density in the polymer chains increases and in turn stresses the polymer backbone into a flatter configuration, making the film denser. This process repeats for each group of deposited bi-layers.

The longer term measurements reveal the same kind of build-up with distinct SPR shifts occurring mostly right after the rinsing step of each bi-layer, but also that the net shift following each bi-layer is not uniform. We believe this to be due to the fact that the layers themselves are not uniform, as shown by the subsequent AFM images of the final coatings. These observations indicate the potential of our TFBG-SPR as a real-time process monitoring tool for nanoscale deposition processes in liquids.

6.2 Extracting additional information from the SPR shift data

The shift of the SPR resonance arising from the deposition of a thin coating on the surface of the fiber depends on the thickness of the added layer but also obviously on its refractive index.
Numerical simulations were performed to confirm the experimental results obtained from the sensor and to evaluate the refractive index of the deposited polymer film. The simulations were carried out using a complex fiber mode solver from Photon Design (FIMMWAVE) to find the effective indices of the fiber cladding modes that tunnel across into the SPR. The simulated structure was made up of the SMF fiber, a gold coating of 20 nm, and a thin dielectric coating with various thicknesses and refractive indices. In all cases pure water was used as the outer medium. The parameters used in the simulation are given in Table 1 (we used material refractive index values for a wavelength of 1545.335 nm; the dispersion of the material was taken into account).

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<th>Table 1. Refractive indices of the materials used</th>
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For each value of coating thickness and refractive index, the mode solver calculates the real and imaginary parts of the effective index of all the cladding modes using a cylindrical Finite difference algorithm. The SPR-modified modes are identified by a larger value of the imaginary part of their effective index [5]. Figure 8 shows two sets of cladding mode effective indices corresponding to the fiber without and with a dielectric coating, both immersed in water. A well-defined SPR peak consisting of a group of lossy cladding modes appears very clearly in each case. As can be seen from Fig. 8, the position of the SPR peak shifts towards longer wavelengths if a coating with a refractive index higher than the refractive index of the solution in which the sensor is immersed was deposited.

The simulations allowed us to plot the expected SPR effective index shift values with increasing coating thickness for various values of the refractive index of the coating (Fig. 9). In order to overlay the experimental results on the same graph and hence to determine which film refractive index provides the best fit to our data, we had to convert SPR wavelength shifts into effective index shifts and also assign a thickness value to each layer. Since SPR shifts were measured in water, the “dry” average final thickness measured with the AFM had to be converted into a fully hydrated thickness prior to adding the measured SPR vs thickness values on the simulation template. According to the experimental results, the total SPR wavelength shift due to the deposition of the 15 bi-layer structure was 5.99 nm. Using Eq. (3), this total shift corresponds to a change in plasmon effective index of 0.01. For the thickness, the AFM result on the final dried film gave an average thickness of 16.8 nm but it is estimated that the coating was twice as thick when fully hydrated [29], i.e. approximately 33.6 nm of overall thickness or 2.24 nm per fully hydrated bi-layer.
Fig. 8. Distribution of the effective indices of the modes (real and imaginary parts) supported by a gold-coated circular waveguide when (a) the waveguide was immersed in water and had no coating (pink curve); (b) and when the waveguide was immersed in water and had a 30 nm dielectric coating with a refractive index of 1.435, (black curve).

Fig. 9. Black dots: change of the plasmon effective index (from the position of the centre of the envelope used to fit SPR-coupled resonances) due to the deposition of thin dielectric film on the surface of the gold coating. Straight colored lines: simulated changes of the plasmon effective index as a function of the thickness of a deposited film, for various values of the film refractive index.

With these considerations taken into account, we get that for the regular portion of the film growth (roughly from 50 to 220 minutes on Fig. 5) the results of Fig. 9 show that the average slope of the effective index change calculated from the experimental data matches best the effective index shifts expected from the deposition of a polymer with refractive index of 1.515 (hydrated). As a final note on these results, the response of the TFBG-SPR sensor that we use actually represents an average of several shorter measurements since the grating is 1 cm long and the plasmon propagation distance for our configuration is of the order of 500 µm (calculated from the peak values of the imaginary part of the effective index). Therefore, while the AFM scan revealed the highly irregular structure of the deposited film (Fig. 6(b)), our sensor measurement averages these irregularities and we feel confident that the SPR response can be interpreted using the average thickness of the coating determined by the AFM.
7. Conclusion
The results presented in this paper indicate that TFBG SPR sensors implemented in metal-coated standard telecommunication optical fiber are well suited for in situ characterization of the self-assembly of polyelectrolyte layers on the surface of an optical fiber. In the example provided, individual bi-layers had thicknesses of the order of 1.12 nm (once dried) and the sensor response provided real-time monitoring of the film growth during the deposition of 15 bi-layers with good linearity. A final, post-process AFM measurement on the deposited film provided the calibration factor between the thickness change and wavelength shift of the SPR resonance and also, indirectly through modeling of the SPR behavior, the refractive index of the final film (1.515 while fully hydrated in the process container). The overall results indicate that this fiber SPR sensor is also well suited to be used as a probe for the monitoring of liquid-phase deposition processes for various dielectric coatings on other substrates (of any form) in real time and in situ.

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