Label-free sensitivity of long-period gratings enhanced by atomic layer deposited TiO$_2$ nano-overlays

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Abstract: In this paper, we discuss an impact of thin titanium dioxide (TiO$_2$) coatings on refractive index (RI) sensitivity and biofunctionalization of long-period gratings (LPGs). The TiO$_2$ overlays on the LPG surfaces have been obtained using atomic layer deposition (ALD) method. This method allows for a deposition of conformal, thickness-controlled, with well-defined optical properties, and high-RI thin films which are highly desired for optical fiber sensors. It has been found that for LPGs working at a dispersion turning point of higher order cladding modes only tens of nanometers of TiO$_2$ overlay thickness allow to obtain cladding mode transition effect, and thus significant improvement of RI sensitivity. When the TiO$_2$ overlay thickness reaches 70 nm, it is possible to obtain RI sensitivity exceeding 6200 nm/RIU in RI range where label-free sensors operate. Moreover, LPGs with TiO$_2$-enhanced RI sensitivity have shown improved sensitivity to bacteria endotoxin (E. coli B lipopolysaccharide) detection, when TiO$_2$ surface is functionalized with endotoxin binding protein (adhesin) of T4 bacteriophage.

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References and links


38. P. J. Lemaire, R. M. Atkins, V. Mizrahi, and W. A. Reed, “High pressure H₂ loading as a technique for achieving cladding mode, respectively.


1. Introduction

Numerous of chemical and biological substances can be detected by measurement of refractive index (RI) of their liquid solutions, e.g [1]. That is why RI sensors have a wide range of applications in chemistry, food industry, and biochemistry. Such sensors are expected to provide high sensitivity to RI of external medium and immediate response. Sensors based on long-period gratings (LPGs) can easily meet these requirements. The LPG is a structure typically made by periodic (period Λ) modulation of refractive index within core of a single-mode optical fiber [2]. The modulation induces coupling between core mode and mth cladding modes resulting in appearance of a series of resonance attenuation peaks in LPG's transmission spectrum [3]. These resonance wavelengths λ_m are defined by (1), where n_{eff}^c and n_{eff}^clm are effective refractive indices of core and mth order cladding mode, respectively.

\[ \lambda_m = \left( n_{eff}^c - n_{eff}^{clm} \right) \Lambda \]  

(1)

The value of n_{eff}^{clm} depends on the external RI (n_{ext}), and thus the latter has a direct influence on spectral response of the LPG. Namely, the increase of n_{ext} increases n_{eff}^{clm} and...
finally induces the resonant wavelength shift toward shorter wavelengths, e.g. [3]. The effect gets stronger when \( n_{\text{cl}} \) is closer to that of cladding, which is typically made of fused silica \( (n_0 = 1.458 \text{ RIU}) \). However, it has been shown that coating LPG with high-refractive index (high-\( n \)) overlay leads to shift of the highest RI sensitivity range towards its lower values [4]. Such modification depends on overlay thickness and its optical properties, mainly refractive index. The most popular methods for tuning the RI response through the use of nano-coatings are based on immersing the LPGs in a liquid precursor. Some of the liquid-precursor-based deposition techniques are Langmuir-Blodgett [4], sol-gel [5], and electrostatic self-assembly (ESA) [6]. However, these methods do not provide efficient control of properties of the overlays or are very time consuming. To overcome some of the mentioned disadvantages the Atomic Layer Deposition (ALD) can be used as an alternative. It belongs to a group of chemical vapor deposition (CVD) methods, and allows for the deposition of thin films on various substrates with atomic scale precision [7]. Thus, the ALD gives precise control of the overlay properties on whole length of the grating. The method is based on the gas-solid reactions occurring at the surface of substrate and belongs to a group of layer-by-layer techniques. The majority of ALD reactions use two chemicals, usually called precursors. The growth of films with ALD typically includes four steps: exposure of the surface to the first precursor, purge of the reaction chamber to remove the non-reacted precursors and the gaseous reaction by-products, exposure to the second precursor, and again purge or evacuation of the reactor chamber. The surface reactions can be accomplished using thermal chemistry or with the assistance of plasma [8]. The process temperature depends on the precursor and is typically in the range of 30 to 150 °C [9]. The major limitation of ALD is its low growth rate. However, the growth rate can be compensated by the increased size of the reactor and the deposition of multiple samples.

In our previous works we reported results on modification of the RI response of the LPG-based sensors with hard and high-\( n \) overlays deposited from gas precursors with a radio-frequency plasma-enhanced chemical-vapor-deposition (RF PECVD) method [10–12]. The properties of the films can be easily changed over a wide range of refractive index values by varying the gas composition and other deposition parameters [13]. However, the control of the film thickness in nanometer range and symmetrical deposition around the fiber with this method are still challenging. Moreover, we also investigated modification of RI response of the LPG with deposition of \( \text{Al}_2\text{O}_3 \) overlay with ALD method [14]. Since \( \text{Al}_2\text{O}_3 \) belongs to a group of relatively low-refractive-index materials \( (n \text{ at } \lambda = 1550 \text{ nm reaches } 1.62 \text{ RIU}) \), the thickness of the deposited overlay must be high (over 200 nm for optimal thickness at \( n_{\text{cl}} = 1.3330 \text{ RIU} \)) in order to effectively tune RI sensitivity of the devices [15]. For such thick overlays long ALD processes are required, which may be both time consuming and expensive.

In this paper we present detail investigation of high-\( n \) titanium dioxide (\( \text{TiO}_2 \)) thin overlays applied as both improvement of the RI sensitivity and interfacing with bio-overlay. \( \text{TiO}_2 \) shows high temperature and high electrical resistance as well as high hardness, low optical absorption, and biocompatibility [16,17]. It has been used as an antireflection coating on infrared detectors [18], optical resonance filters [19] or as planar waveguiding structures [20]. It has been shown that when \( \text{TiO}_2 \) overlay is deposited on LPG with sol-gel method it adsorbs water molecules and can be applied for humidity sensing [21,22]. Also nanoporous ESA deposited \( \text{TiO}_2/\text{polyion overlay on LPGs has been used for low-molecular-weight chemicals detection [23]. Refractive index of these sol-gel and ESA deposited material is typically below 2 [15,23,24]. When uniform and non-porous \( \text{TiO}_2 \) overlay is deposited, e.g., using evaporation by electron beam, the LPG can be applied for RI sensing [25]. In this work high-\( n \) \( \text{TiO}_2 \) is deposited on LPGs surface with the use of ALD technique [26]. The \( \text{TiO}_2 \) films are applied for fine tuning of spectral properties of the LPGs, and in consequence their RI sensitivity. In this experiment we deposited the overlays on LPGs working at dispersion
turning point (DTP), where the highest sensitivity can be obtained [27,28]. Presented study of a few different TiO$_2$ coatings gives dipper experimental insight into resonance behavior at the vicinity of DTP. Moreover, combining effect of DTP and higher order cladding mode transition induced by deposition on the overlay allows for maximizing sensitivity of the LPG, especially in RI range employed by label-free biosensors [29,30]. It has been shown that surface of TiO$_2$ can be functionalized with a number of molecules, which bind to it by electrostatic [31] or chemical [32] interaction. In this paper we report evidences of successful TiO$_2$ surface biofunctionalization with green fluorescent protein and for a first time bacteriophage adhesins, i.e., proteins capable for specific binding of bacteria or its endotoxins, i.e., lipopolysaccharide (LPS) [33]. It has been shown that proteins can physically adsorb to TiO$_2$ surface [34]. Furthermore, in this work chemical TiO$_2$ surface functionalization with nickel ions and histidine-tagged proteins have been applied. Polyhistidine-tags are one of the most popular systems used for affinity purification of polyhistidine-tagged recombinant proteins expressed in *Escherichia coli* and other prokaryotic expression systems [35]. The system is also used in BIACORE analysis of proteins using a chelating NTA sensor chip [36]. Selective binding of His-tagged protein to Nickel ions allows relatively easy and quick acquisition of the desired protein preparation or its immobilization to a surface. Moreover the system allows for the sensor’s regeneration [37].

2. Experimental details

2.1 LPG manufacturing

In this experiment we used commercially available germanium-doped Corning SMF-28 single-mode optical fiber. High pressure hydrogen loading has been used to increase photosensitivity of the fiber [38]. A set of LPGs was fabricated by UV irradiation of 4 cm long fiber section with KrF excimer laser and chromium amplitude mask with $\lambda = 226.8$ µm. After the UV-writing, the LPGs were annealed in 150 °C for 3 hours in order to release the hydrogen, and thus stabilize the properties of the gratings [39]. After the fabrication, the LPGs were immersed in hydrofluoric acid (HF) in order to reduce the fiber cladding diameter. During that process resonant wavelength was shifted up to DTP. It is a common procedure applied for maximizing the LPG sensitivity [40]. In this experiment, highly concentrated HF (40%) and subsequently HF buffer (6 to 1 volume ratio of 40% NH$_4$F in water and 49% HF in water) were used. After this step the transmission spectrum of the LPG was investigated in order to determine shift of the resonance wavelength induced by etching. This process cycle was repeated several times to achieve DTP at $\lambda \approx 1600$ nm. Just before achieving DTP etching solution was changed to HF buffer in order to increase precision of the process control in determination of resonant wavelength of the LPG.

The spectral response of the LPGs was investigated in wavelength range of 1100 to 1650 nm using Yokogawa AQ6370B spectrum analyzer and Yokogawa AQ4305 white light source, and in the range of 1200 to 2250 nm using Yokogawa AQ6375 spectrum analyzer and NKT Photonics SuperK COMPACT supercontinuum white light laser source.

2.2 TiO$_2$ nano-films deposition and characterization

The TiO$_2$ thin films were deposited on the LPGs and reference silicon wafers using the TSF200 system (BENEQ, Vantaa, Finland). The reference silicon wafers went through the Radio Corporation of America cleaning procedure. The LPG samples were cleaned in isopropanol. For the TiO$_2$ deposition processes, water and titanium (IV) chloride (TiCl$_4$) were used as an oxygen and titanium precursors, respectively. Between gas pulses the chamber was purged with nitrogen. Thickness of the nano-films was controlled by number of cycles of the ALD process. Temperature during the process cannot be too high due to the polymer coating
of fiber cladding and it was set to 85 °C. Moreover, it is known that low deposition temperature promotes amorphous structure of TiO\textsubscript{2} and improves its optical properties [20].

The properties of the TiO\textsubscript{2} films deposited on the reference silicon wafers, such as their thickness ($d$), refractive index ($n$) and extinction coefficient ($k$) were determined by a Horiba Jobin-Yvon UVISEL spectroscopic ellipsometer. The ellipsometric model for TiO\textsubscript{2} analysis is described by the New Amorphous dispersion formula.

2.3 LPG measurements

The RI sensitivity was measured by immersing LPGs in mixture of water and glycerine with $n_D$ ranging from 1.333 to 1.472 RIU units (RIU). Refractive index of the liquids was measured using Rudolph J57 automatic refractometer working with resolution of $2 	imes 10^{-5}$ RIU. Between the immersions, the LPG was rinsed with deionized water and then dried in air. Sensitivity of the LPGs was calculated as resonance wavelength shift induced by variation of RI in a specific range. Temperature and strain were kept constant during the RI measurements.

2.4 TiO\textsubscript{2} surface biofunctionalization

The procedure of chemical preparation of the TiO\textsubscript{2} surface and then protein binding comprised of the following steps. First, the fiber was immersed in the 0.01% acetic acid and 2% (3-Glycidyloxypropyl) trimethoxysilane solution in T = 90 °C for about 3 h, then it was left for about 16 h at T = 20 °C in the 0.01M NaHCO\textsubscript{3} buffer (pH = 10) with 20 mM N-(5-amino-1-carboxypentyl) iminodiacetic acid solution. Next, the sample was immersed in 10 mM NiCl\textsubscript{2} and 5 mM Glycine solution for about 2 h in room temperature. Finally, after washing in 0.01 M NaHCO\textsubscript{3} buffer the LPG was immersed in the adhesin solution with concentration of 50 µg/ml for about 1 h. The steps we followed here with TiO\textsubscript{2}-coated LPG are similar to those described in [33,37], i.e., we use \textit{E. coli} B bacteriophage g37 adhesin and corresponding \textit{E. coli} B lipopolysaccharide (LPS) as a positive test for adhesin-LPS binding. However, in comparison to experiments shown in [33,37] we used slightly different functionalization procedure, i.e., lower 16 h-long process temperature (from T = 60 °C to T = 20 °C) and lower concentration of N-(5-amino-1-carboxypentyl) iminodiacetic acid. The change in long incubation process temperature and use of smaller amounts of the acid should prevent any possible damage to the thin overlay, prevent from surface etching and decrease costs of the process.

In turn, used as reference TiO\textsubscript{2}-coated and oxidized SiO\textsubscript{2} wafers was immersed in green fluorescent protein (GFP) tagged with 6xHis on its N-terminus (EMD Millipore Corporation) (the procedure is specific for his-tag binding capability) for about 30 minutes, and then washed with deionized water.

3. Results and discussion

3.1 Properties of the TiO\textsubscript{2} nano-overlays

Thickness and optical properties of the LPG’s overlay have significant influence on a spectral response of the LPG to $n_{ext}$. During our experiments we determined that the deposition rate reaches 0.1 nm per cycle. The result proves that the thickness of the TiO\textsubscript{2} films can be controlled with sub-nm precision. The dispersion curves and variation of optical properties of the TiO\textsubscript{2} films deposited on reference silicon wafers versus their thickness is shown in Fig. 1. Since $k$ is negligible in the infrared (IR) spectral range, we focus our discussion solely on dispersion of $n$. The most significant changes in $n$ of the deposited TiO\textsubscript{2} are seen in spectral range between 260 and 660 nm. In the investigated range of LPG response (i.e., IR), the variations of $n$ are only slightly dependent on wavelength, Fig. 1(a). Furthermore, the thickness has also slight, but noticeable influence on $n$ of the TiO\textsubscript{2} films, Fig. 1(b). The highest changes of TiO\textsubscript{2} $n$ can be observed for its thickness below 50 nm (about 0.004 RIU/nm). With the increase of the overlay thickness above ~50 nm its optical properties.
stabilize and can be assumed constant. The effect of evolution in film’s $n$ with its thickness has also been observed for sol-gel deposited TiO$_2$ [15] as well as other thin films and vapor-based deposition methods [41]. In contradiction to Al$_2$O$_3$ films, also deposited with ALD, where $n$ decreases with thickness [14], at initial stage of the film growth the $n$ of TiO$_2$ increases reaching about 2.27 RIU at $\lambda = 1550$ nm, Fig. 1(b). The increase in $n$ of TiO$_2$ with thickness of the film may be induced by material densification [41], as well as stress induced in the film by the substrate [42]. The obtained $n$ is significantly higher than for films obtained with other deposition methods [15,23,24].

*Fig. 1. Influence of TiO$_2$ film thickness on its optical properties, where (a) shows dispersion curves of $n$ and $k$, and (b) relation between $n$ at $\lambda = 1550$ nm and the thickness.*

### 3.2 RI sensitivity measurements

Measurements of the RI sensitivity for three samples were compared before and after the deposition of TiO$_2$, Figs. 2 and 3. In Fig. 2, it can be seen that there is a significant difference between responses of sample with and without TiO$_2$ overlay. For LPG sample without the overlay when it is immersed in water ($n_D = 1.33302$ RIU), the resonance at $\lambda \sim 1600$ nm is experiencing DTP. For the same sample with the thinnest overlay ($d = 47.3$ nm), the DTP repeats in the air ($n_D = 1$ RIU) and the resonance is shifted towards lower wavelength range as a result of immersion in water. Further, the resonance at DTP for the sample with slightly thicker overlay ($d = 50.5$ nm) is already experiencing double-resonance effect in air and then
it also shifts towards lower wavelength in water. It can be seen that thanks to high \( n \) of the \( \text{TiO}_2 \) overlay only couple of nm difference in its thickness strongly modifies LPG response. Interesting development of double-resonance effect is shown in Fig. 2(b), where sample with 70.0 nm thick overlay is examined. This sample, like in case of 50.5 nm thick one, already shows a double-resonance split in the air, but after immersion in water the two resonances reappear joined just before split at DTP. When the \( n_{\text{ext}} \) increases the resonances further separate in wavelength. The results prove that for high-\( n \) overlays only tens of nanometers in thickness are essential for full mode transition [43].

![Fig. 2. Transmission spectrum of the LPG sample with and without TiO\(_2\) overlays of different thickness (a) 47.3 nm, 50.5 nm, and (b) 70.0 nm when surrounded by air (\( n_0 = 1 \) RIU), water (\( n_0 = 1.333 \) RIU) and a high-RI liquid (\( n_0 = 1.374 \) RIU). The arrows indicate wavelength shift induced by immersing the LPG in water (dashed) and between water and high-RI liquid (double-lined). Different spectral range shown in (b) comes from application of different optical analyzers for the sample before and after deposition.](image_url)

Response of the sample with and without TiO\(_2\) overlay to \( n_{\text{ext}} \) up to \( n_0 = 1.47201 \) RIU has been investigated next. For the etched LPG with no overlay the resonance at \( \lambda \sim 1600 \) nm is close to DTP up to \( n_{\text{ext}} \sim 1.36 \) RIU. Above this value the spectral separation of the resonance takes place and the one at lower wavelength experiences shift towards shorter wavelengths,
Fig. 3(a). It can be seen that when RI gets closer to the one of cladding material, i.e., fused silica ($n_D = 1.458$ RIU), cladding modes interact more with external medium and that is why the sensitivity of the device is increased [44]. For the LPGs with the TiO$_2$ overlay, shown in Figs. 3(b) and 3(c), there is a significant shift with $n_{ext}$ of the resonance formed initially at $\lambda \sim 1600$ nm and slight shift of two other resonances at about $\lambda \sim 1175$ nm and $\lambda \sim 1150$ nm. The shift highly depends on the overlay properties. If the overlay’s $n$ and thickness, as well as the $n_{ext}$ are properly selected, the lowest order cladding mode starts to be guided in the overlay inducing shift of the higher order cladding modes to the nearest lower order ones [12,27,43]. When the mode transition takes place, the grating reaches the highest RI sensitivity. Comparing sensitivities of the LPGs before and after TiO$_2$ deposition, there can be observed a significant increase of RI sensitivity below $n_{ext} = 1.44$ RIU induced by the TiO$_2$ overlay, Fig. 4. The sensitivity to external RI for the resonance shifting in a wide spectral range can be assumed as linear for each sample in three $n_{ext}$ ranges. In the lower RI range it is highly influenced by DTP, while for higher $n_{ext}$ it increases as a result of mode transition effect. For $d = 47.3$ nm the sensitivity in $n_{ext}$ between 1.36 and 1.41 RIU is over 4300 nm/RIU, which is over 2.2 times higher than sensitivity of a bare LPG for the resonance at the same $n_{ext}$ range. In this range the increase in sensitivity is influenced by the operation close to the DTP. Increase in TiO$_2$ overlay thickness shifts the high sensitivity towards lower $n_{ext}$ range and makes the influence of both DTP and mode transition effect more visible. For the overlay thickness of 70.0 nm, the high sensitivity range is shifted close to RI of water ($n_D = 1.3330$ RIU), and reaches there over 6200 nm/RIU. Similar sensitivity has been observed for LPG with no overlay where only effect induced by DTP is employed, but it reached there over 6000 nm/RIU in range only up to $n_{ext} = 1.334$ RIU [33]. When the LPG is coated with TiO$_2$, the high sensitivity range is up to $n_{ext} = 1.34$ RIU and covers the range used for label-free detection [33]. When $n_{ext}$ is above 1.34 and 1.39 RIU, the sensitivity reaches 3000 and 5500 nm/RIU, respectively. In this case the sensitivity above 1.39 RIU is highly influenced by mode transition effect. For $n_{ext}$ above 1.41 RIU, the resonance takes place of the one initially appearing at 1150 nm and the sensitivity drops down significantly. The resonance in the vicinity of 1175 nm has already experienced mode transition for samples immersed in water and takes place of the nearest lower order cladding mode. It must be noted here that thanks to combined effects of DTP and transition of higher order cladding modes, the obtained RI sensitivity is almost 19 fold higher than reported for TiO$_2$-coated LPGs working away from DTP [25]. The RI sensitivity shown here is according to our best knowledge both the highest and measured in the broadest RI range (close to that of water) ever reported. Higher sensitivity reported by Pilla et al. [29] has been measured for higher external RI, which is too high for label-free sensing.
4. TiO$_2$ surface biofunctionalization

LPG and reference Si wafer coated with 70 nm thick TiO$_2$ were bio-functionalized with bacteriophage adhesin and GFP, respectively. The outcome of the experiment performed with GFP is depicted in Fig. 5, where we show photos of the functionalized sample surface with areas incubated and non-incubated in GFP. The GFP absorbs light in the spectral range of 395-425 nm and emits in green spectral region. This outcome indicates correct course of the procedure showing the binding of GFP to the TiO$_2$ covered surface, Fig. 5(a). Similar effect can be observed for sample coated with SiO$_2$, which can be treated as a good reference to other typically functionalized fiber cladding materials, Fig. 5(b).

The positive results acquired for the bulk sample preceded the fiber sensor experiments which aimed to test adhesin-binding to TiO$_2$ surface. The results of the procedure are shown in Fig. 6, which depicts consecutive stages of the experiment after surface functionalization. In Fig. 6(b) and 6(c) the first stage, i.e., washing in NaHCO$_3$ buffer ($n_D = 1.3335$) has been omitted due to indistinguishable separation between two minima, Fig. 6(a). The sensor has been designed to have the two minima merged at DTP exactly at this stage of the experiment in order to achieve the highest possible sensitivity. The next step, which is incubation in bacteriophage adhesin solution, is uncovered thanks to high sensitivity. During 30 minute
incubation the process of binding adhesin to the fiber’s surface is observed as continuous wavelength shift, i.e., separation of the minima, Figs. 6(b) and 6(c). The difference between signal before and after this stage is noticeable and equals to about 10 nm per side. Since bacteriophage adhesin is very small in size (the total length is just over 20 nm) [45], for its observation a high sensitivity of the sensor is desired. The effect of adhesin binding to the fiber’s surface has never been observed in our earlier works where fused silica was employed as a sensor’s surface [33,37].

Furthermore, it can be seen that incubation in LPS solution induced significant increase in spectral separation of the resonances, Fig. 6(a). The fiber sensor reacts to the difference in RI of PBS (n_D = 1.3346 RIU) and LPS-water solution only at the first stage of the experiment, where the value of resonance shift returns to that of water, Figs. 6(b) and 6(c). This means that the effect of RI difference is negligible and the separation of the resonances is mainly a result of binding of the LPS to bacteria adhesin which build up a thicker bio-overlay. At this stage we observe significantly higher response to LPS incubation than we have been able to do earlier. Namely, LPS incubation causes about 40 nm shift of each resonance, whilst the highest response at this stage for sensors with no TiO_2 overlay did not exceed 20 nm. Next, the extensive sample washing which followed the incubation in LPS resulted in removal of weakly, i.e., physically bound bio-material and allowed for comparison of signal responses at two stages of sample immersion in PBS. The measured shifts are 10.4 and 17.7 nm for left and right resonance, respectively. Higher shift of the right resonance has been observed before and results from longer wavelength range for this resonance [30].

Results presented in Fig. 6 are compared to those reported in [37], where fused silica surface had been functionalized. First as described above, it can be seen that the response to the immersion in LPS in case of TiO_2-coated LPG is much higher than for bare LPG. Since the RI of LPS solution, i.e. its concentration, is in both cases the same (250 μg/mL), the effect
is due to higher sensitivity in the same $n_{\text{ext}}$ range for the TiO$_2$-coated sample. Next, we can see that the received difference in responses when PBS levels are compared, is only $\sim$10 nm (Fig. 6(b)) versus $\sim$15 nm reported in the case of the sensor without the overlay. This result can be explained by the following factors: slightly different functionalization procedure, which might have made the sensor surface less protein adhesive, and the washing procedure used in case of the fiber with overlay, which was changed from water to alternated water and NaHCO$_3$ buffer solution flows. Moreover, in this experiment we intentionally used higher flow rates to additionally test the sensor’s robustness and capability of positive results in harsh testing conditions. Intensive sensor washing might have induced more material removal from the sensor’s surface and thus its lower response.

Finally, taking into account the significant wavelength shift of both minima and results of the experiment with GFP presented in Fig. 5, we are convinced that the applied functionalization procedure fulfilled its task. The results prove that TiO$_2$-coated LPG keeps high sensitivity despite harsh biofunctionalization procedure. According to our best knowledge this work reports for the first time successful direct chemical functionalization of high-$n$ overlay, which tunes sensitivity of the LPG. Up to date shown label-free sensing approaches with LPG working at mode transition employed physical adsorption of biomolecules [46] or application of additional interfacial layer for chemical functionalization of the overlay [47].

5. Conclusions

Besides application of TiO$_2$ as antireflection coatings, the TiO$_2$ film can be successfully applied for effective tuning of RI sensitivity of LPG. The range of high RI sensitivity is determined by initial working conditions of the LPG and proper selection of number of ALD process cycles. Since the ALD method allows to determine the thickness of the overlays at a sub-nm scale, the sensitivity can be precisely tuned. Moreover, the capability of ALD process to take place at low temperatures makes it possible to deposit high-$n$ TiO$_2$ overlays ($n$ above 2.2 RIU in IR spectral range) on UV-induced LPGs without damaging the grating. Thanks to deposition of 70.0 nm thick TiO$_2$ overlays we obtained over 2.8 fold higher RI sensitivity for selected $n_{\text{ext}}$ ranges than for a bare LPG. We have obtained sensitivity reaching 6200 nm/RIU in RI range up to $n_{\text{ext}} = 1.34$ RIU. Furthermore, taking into account significant sensitivity increase and robustness of the structure with overlay, it can be stated that the developed platform is very promising for application in label-free biosensing. We have shown successful direct chemical functionalization of the TiO$_2$ surface with protein receptors, and application of TiO$_2$-coated LPG for bacteria lipopolysaccharide detection.

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