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Tuning properties of long-period gratings by plasma post-processing of their diamond-like carbon nano-overlays

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Abstract

This work presents an application of reactive ion etching (RIE) for effective tuning of spectral response and the refractive index (RI) sensitivity of diamond-like carbon (DLC) nano-coated long-period gratings (LPGs). When oxygen plasma is applied the technique allows for an efficient and well controlled etching of hard and chemically resistant DLC films deposited on optical fibers. We show that optical properties of DLC, especially its refractive index, strongly depend on thickness of the film when it is thinner than 150 nm. The effect of DLC nano-coating deposition and etching on spectral properties of the LPGs is discussed. We have correlated the DLC properties with the shift of the LPG resonance wavelength and have found that both deposition and etching processes took place less effectively than on the electrode when the LPG sample was held above the electrode in the plasma reactor. An advantage of plasma-based etching is a capability for post-processing of the nano-coated structures with a good precision, as well as cleaning the samples and their re-coating according to requested needs. Moreover, the application of RIE allows for post-fabrication tuning of RI sensitivity of the DLC nano-coated LPGs.

Keywords: optical fiber sensors, long-period gratings, refractive index sensing, chemical vapor deposition, plasma, thin films, diamond-like carbon, optical properties, reactive ion etching

(Some figures may appear in colour only in the online journal)

1. Introduction

Long-period gratings (LPGs) have been known for over a decade. LPGs are a periodic modulation of the refractive index along the length of an optical fiber. Under special phase-matching conditions, the grating couples the fundamental core mode (LP_{01}) to discrete cladding modes (LP_{0m}) that are attenuated due to absorption and scattering. The coupling is wavelength-dependent, so one can obtain a spectrally selective loss. A number of sensors based on the LPGs have been proposed for temperature, strain, hydrostatic pressure, bending and refractive index (RI) sensing (e.g. [1, 2]).

It has been shown that the deposition of some overlays can significantly increase or even initiate the sensitivity of LPG structures to certain external influences. Deposition of the high-refractive-index nano-coatings significantly modifies the sensitivity of the LPG structures to variations in external refractive index (n_{ext}) [3]. Such coatings make it possible to optimize the interactions of the light guided in the fiber and in the coating, thus tuning the intrinsic sensitivity of optical fiber devices to a certain range of the measurand. A required sensitivity in the specified range of n_{ext} can be achieved with good precision by adjusting the thickness and the optical properties of the coatings. Successful tuning of the RI response

through the use of nano-coatings has been reported by a number of authors (e.g. [3]). However, control of the deposited film thickness in the nanometer range is challenging and, in some cases, the deposition process must be repeated in order to achieve expected spectral tuning and in consequence RI sensitivity. In our previous works we reported the results on modification of the RI response of the LPG-based sensors with high-refractive-index diamond-like carbon (DLC) nano-overlays deposited with radio-frequency plasma-enhanced chemical-vapor-deposition (RF PECVD) method [4, 5]. The DLC films are known for their high mechanical and chemical resistance, that is why their wet chemical processing is difficult [6].

An interesting solution for tuning sensing properties of nano-coated devices is a modification of properties of the already deposited coatings. Such an approach has been applied to thin gold films, when surface plasmon resonance (SPR) effect has been considered [7]. It has been proven there that thin gold film can be optimized in thickness using electrochemical methods in order to meet the requirements for SPR-based sensing. For hard and chemically resistant DLC films, it has been shown that it is possible to etch the film using a reactive ion etching (RIE) process where plasma is applied [8]. The etching effect, as well as surface properties, namely wetting and roughness of the post-processed DLC films, highly depends on gas composition in the plasma chamber and etching process parameters [8]. Due to high refractive index of the DLC films, precision in determination of their properties must be higher than when other lower-refractive-index materials are applied as overlays for optical devices [3].

In this work we investigate the capability for modification of the DLC nano-overlays deposited on the LPGs using the RIE method. The influence of process time and sample elevation in the plasma reactor on properties of the films is discussed. DLC etching selectivity referred to fused silica substrate is also investigated. Finally, we discuss influence of the etching process and its parameters on spectral response of the DLC-coated LPGs and on their RI sensitivity. The experimental results are correlated with the results of numerical simulations.

2. Experimental details

A set of LPGs was written with a computer-assisted precision arc-discharge apparatus [9]. A 10 cm long piece of Fibrecore PS1250/1500 photosensitive fiber has been spliced between two input and output Corning SMF28 fibers. The LPGs were induced in PS fiber only. The gratings were written with period of Λ = 190–193 μm and the typical number of periods required for appearance of a grating effect was 200–270. For such samples a dispersion turning point (DTP) of $LP_{0,11}$ can be achieved at $\lambda \sim 1550$ nm. It is worth mentioning that DTP [1] is equally often called a turnaround point [10]. The optical transmission of the fiber in the range of λ = 1100–1700 nm was monitored during the LPG fabrication processes in order to obtain the desired spectral attenuation notches. We used a NKT Photonics SuperK COMPACT supercontinuum white light laser source and Yokogawa AQ6370C optical spectrum analyzer for the LPG transmission measurements.

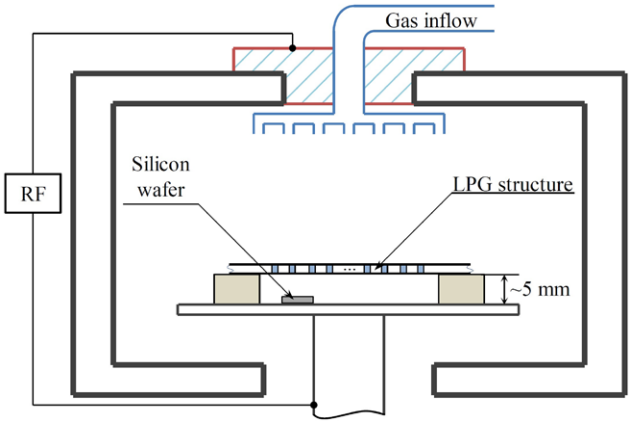

Figure 1. Schematic representation of the LPG and silicon wafer placement in the process chamber. The elements are not to scale.

The DLC thin films were deposited on the LPGs and on the reference silicon wafers using the Oxford PlasmaPro NGP80 system. The LPG samples were cleaned with isopropanol before placing them in the plasma reactor. Then the LPG samples and the reference Si wafers were placed on a U-type holder 5 mm above the electrode and next to them on the electrode, respectively. The RF PECVD was preceded by 1 min long plasma cleaning in Ar. The DLC deposition was from 2–20 min in length and took place with a CH_4 flow of 50 sccm, pressure 30 mTorr, power 150 W and temperature 20 °C. Additionally, in order to estimate influence of distance between the sample and the electrode on deposition rate, a half of 2in Si wafer has been placed vertically in the reactor and this deposition process was 20 min in length.

The RIE process has been performed using the same Oxford PlasmaPro NGP80 system. We used O_2 plasma with O_2 flow 100 sccm, pressure 100 mTorr and power 100 W. Temperature during the processes was set to 20 °C and the etching time was from 0.5–2 min. During the etching processes the LPG samples and reference Si wafers were also held 5 mm above and on the electrode, respectively (figure 1). The influence of distance between the sample and the electrode also for etching has been estimated using a half of 2 in Si wafer placed vertically in the plasma reactor. Before the etching, the wafer placed on the electrode has been coated with DLC in a 20 min long process. Subsequent etching was 1 min in length.

The properties of the DLC films including their thickness (d), refractive index (n) and extinction coefficient (k) were measured on reference silicon wafers using a Horiba Jobin-Yvon UVISEL spectroscopic ellipsometer according to procedure described in [11] and [12]. The measurements were performed after DLC deposition, as well as after the RIE process in order to determine the deposition and etching effect, respectively.

The RI sensitivity of the LPGs has been measured for samples immersed in glycerin/water mixtures with n_D from 1.3330–1.3628. RIs (n_D) of the mixtures were determined using a VEE GEE PDX-95 refractometer working with an accuracy of $\pm 10^{-4}$ RI unit (RIU). The LPGs were kept under the same tension and temperature during all the experiments.

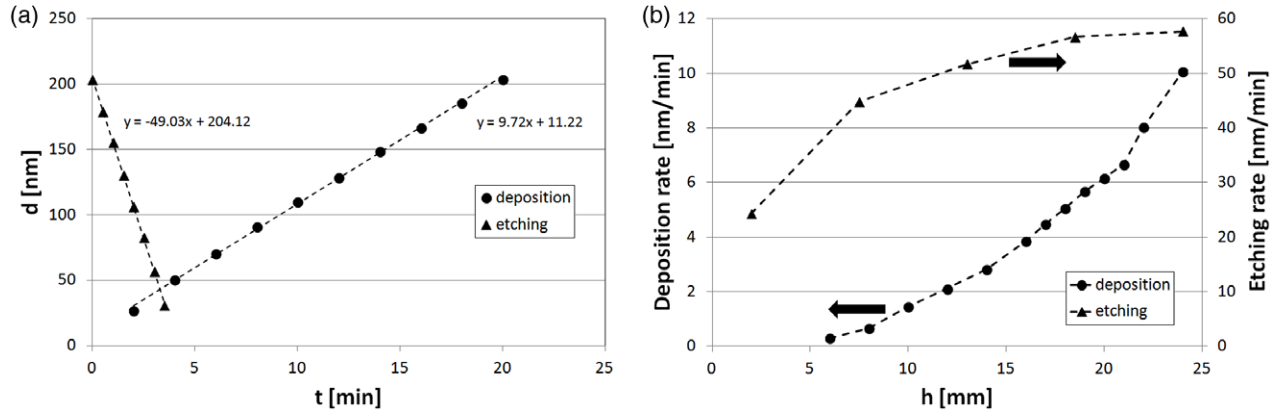

Figure 2. Evolution of the DLC film thickness measured on reference silicon wafers with (*a*) process time and (*b*) height above the electrode. The influence of the height has been investigated on Si wafers placed vertically in the reactor during the processes.

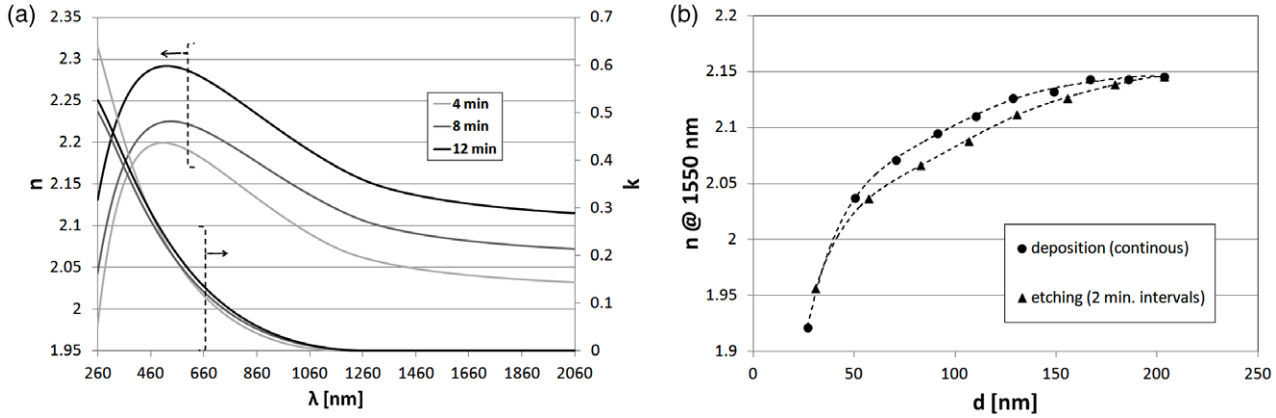

Figure 3. Influence of deposition and etching time on optical properties of the DLC where (*a*) shows dispersion of *n* and *k* for deposition time of 4, 8 and 12 min and (*b*) shows dependence between *n* (at $\lambda = 1550$ nm) and *d* for etching and deposition processes. The deposition processes took from 2–20 min. The series of 2 min long etching processes was performed on the sample obtained as a result of 20 min long deposition.

The numerical simulations of the LPGs were performed for the grating using Optigrating v4.2 software by Optiwave. We assumed fiber properties reported elsewhere [9, 13]. Due to limited accuracy of a fiber drawing process, especially in terms of its diameter, which is given by the manufacturer with accuracy of $\pm 1\,\mu$m, the properties of the fiber were slightly tuned in order to obtain good match of the simulated and measured spectra.

3. Results and discussion

3.1. Influence of the DLC deposition and etching process parameters on properties of the films

From the point of view of optical sensing, the most important parameters of the nano-coating are their optical properties i.e. *n* and *k*, as well as *d* [3]. Evolution of these parameters of DLC films with time of deposition and etching processes, as well as sample placement in the plasma reactor is shown in figures 2 and 3. It can be seen that both *n* and *d* strongly depend on plasma process duration (figures 2(*a*) and 3(*a*)). Slight increase and decrease of *k* with deposition and etching time in the visible spectral range can be seen, but in infrared where the LPG devices operate, the *k* can be neglected (figure 3(*a*)). For films where *d* is below 150 nm, changes of *d* are followed by *n*. The dependence takes place for both deposition and etching, but for etching the *n* decreases more with decrease in *d* than in case of deposition (figure 3(*b*)). When *d* is thicker than 150 nm, the *n* tends to stay independent of *d* and for such films it can be assumed that both deposition and etching modify only *d* of the films. The changes in optical properties of the DLC films with deposition time have been discussed before in [14] and found to be induced by plasma modifications of the DLC films' structure and composition during the process. Moreover, for thin films there is a strong influence of the substrate on their properties and the film must be treated as an interface where stress is cumulated [11].

For the applied process parameters, deposition and etching rates measured on Si wafers placed on the electrode reach 9.7 and 49 nm min^{-1}, respectively (figure 2(*a*)). When the processes kinetics is investigated on vertically oriented Si wafers, it can be seen that both processes take place most effectively at the top of the Si wafer (figure 2(*b*)). Due to sample elevation in the reactor, the *n* and *d* of the overlays on LPG samples are expected to be lower than those obtained on reference wafers

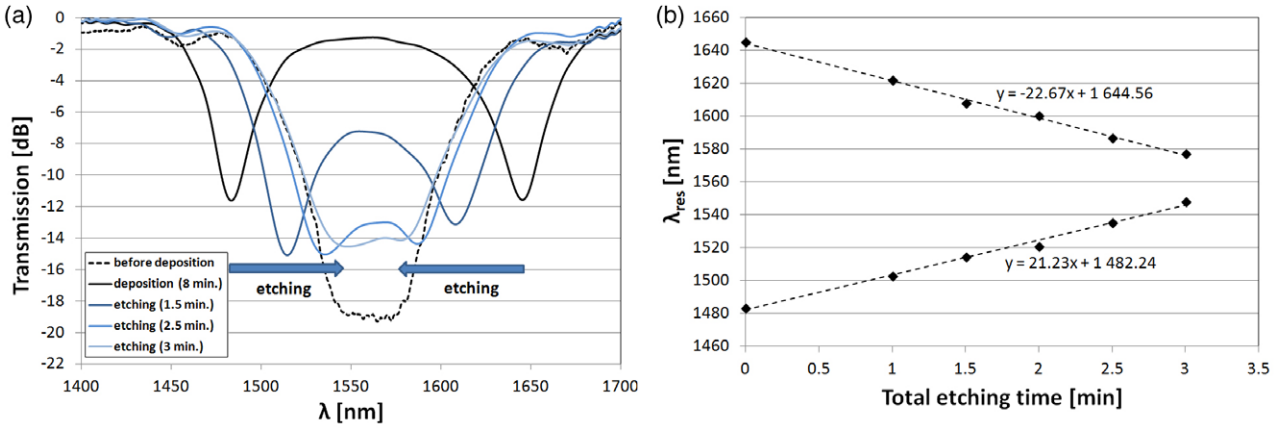

Figure 4. Evolution of (*a*) transmission spectra and (*b*) corresponding resonance wavelength shift for LPG with DLC film deposited in 8 min long process and etched in O_2 plasma for up to 3 min.

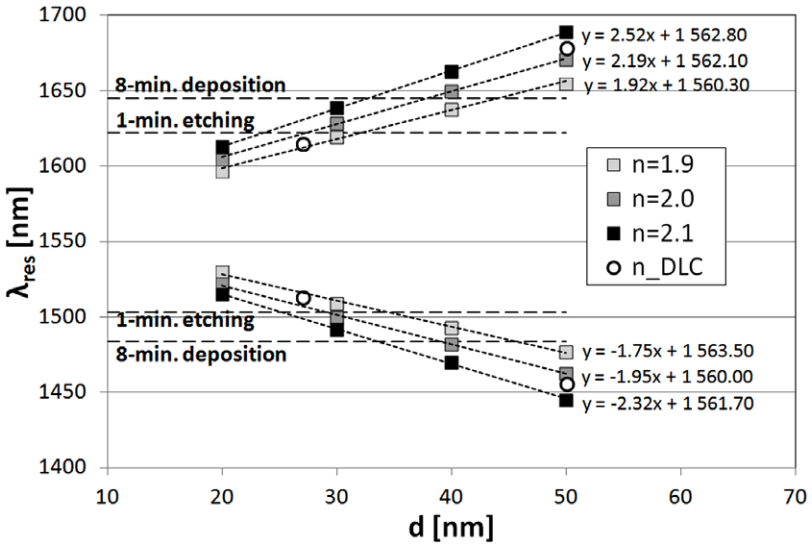

Figure 5. Simulated shift of the resonance wavelengths induced by deposition of overlay with n of 1.9, 2.0 and 2.1. Results for d and n of the DLC films according to data shown in figure 3(*b*) are shown for comparison. In simulations it has been assumed that there is no dispersion of n of the overlay. Resonance wavelength values measured after 8 min long deposition and 1 min long etching were marked as horizontal lines.

placed directly on the electrode. Deposition and etching rate on samples placed on the electrode next to vertically oriented wafers are 9.1 and 43 nm min^{-1}, respectively. The values are slightly lower than those obtained when no vertically oriented wafer was placed in the reactor. The effect can be related to the so called 'loading effect', where effectiveness of the process decreases with amount of material in the reactor during the process [15].

The etching rate strongly depends on applied process parameters, including composition of reactive gases and power of the RF generator [16]. In order to confirm high selectivity of DLC etching in O_2 plasma over fused silica fiber cladding, we tried to etch oxidized Si wafers with O_2 plasma. Even after tens of minutes of etching process with different power, we have found its negligible effect on the SiO_2 substrate. The finding is very important when application of O_2 plasma etching is considered for LPGs, since the process will not result in reduction of the fiber diameter after etching away of the DLC overlay. Such process offers a good control of the over-etching effect.

3.2. DLC deposition and etching effect on LPGs

There are many influences that can shift the resonance wavelengths λ_{res}^{m} of a LPG. According to equation (1), which describes a λ-dependent coupling from the guided core mode to the mth cladding mode where n_{eff}^{01} is the effective refractive index of the propagating core mode, n_{eff}^{0m} is the effective refractive index of the mth cladding mode and Λ is the period of the LPG, the shift can be induced by a variation of either the Λ of the grating or the n_{eff} of the modes.

$$\lambda_{res}^{m} = \left(n_{eff}^{01} - n_{eff}^{0m}\right)\Lambda \tag{1}$$

DLC deposition and O_2 plasma etching effect on the transmission spectra of the LPGs for DLC overlays with different thicknesses is shown in figure 4. The investigated grating operates near to DTP where its sensitivity to a number of parameters is the highest [1, 17]. An increase in DLC thickness increases spectral separation between the observed resonances, where in turns O_2 plasma etching induces a shift of the resonances back towards their positions before the overlay

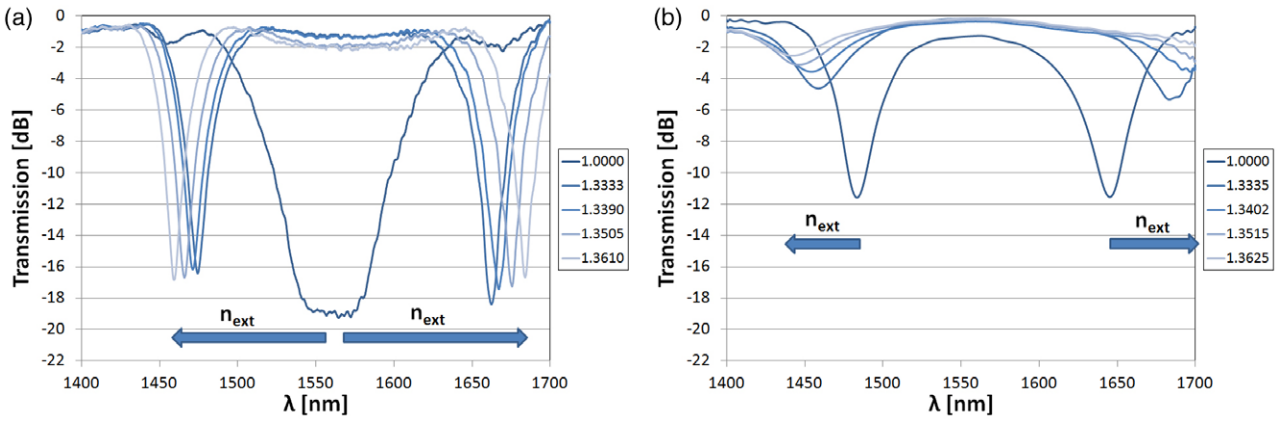

Figure 6. Evolution of transmission spectra induced by variation in n_{ext} for (*a*) LPG with no overlay and (*b*) with DLC overlay deposited in 8 min long process.

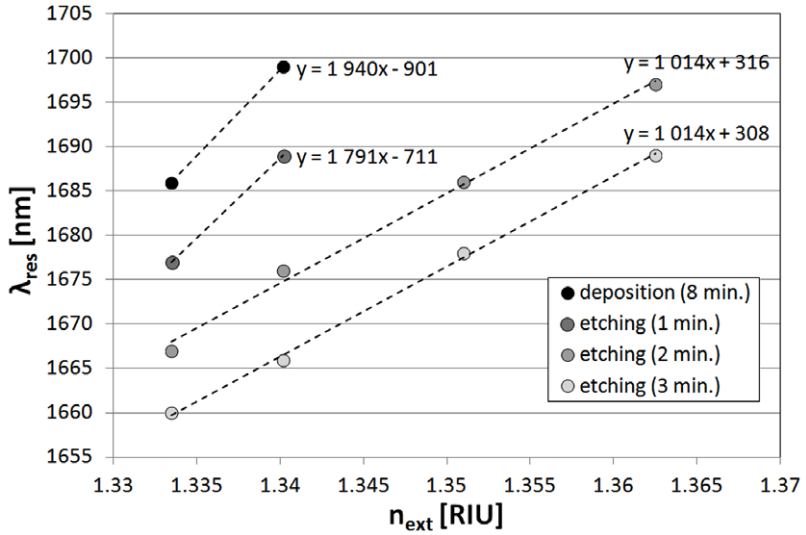

Figure 7. Resonance wavelength shift observed at for $\lambda > 1550$ nm and induced by variations of n_{ext} for LPG with DLC film deposited in 8 min long process and then etched in O_2 plasma with 1 min long intervals. Sensitivity of the grating without the overlay in the same n_{ext} range reached 770 nm/RIU.

deposition. The decrease in thickness of the overlay, and as shown above also their n, induces a shift in the n_{eff}^{011} and, in line with equation (1), causes red and blue shifts for the resonance observed at lower and higher wavelength reaching 21.23 and −22.67 nm min^{-1}, respectively. These results prove that the reduction in DLC overlay properties is induced by the etching. After 3 min total etching the DLC overlay deposited in 8 min long process has been almost entirely etched away. The effect can be observed in figure 4(*a*) as a recovery of the LPG spectrum to its shape before the deposition. When the results of processes kinetics obtained on reference Si wafers are compared to those obtained on LPG, it can be found that on LPGs the etching is not 5 times that on Si, but only less than 2.6 times faster than deposition. The difference is a consequence of different location of Si and LPG samples during the deposition and the etching experiments. Placing LPG above the electrode may significantly reduce the etching kinetics when compared to the process effectiveness directly on the electrode [18].

Simulation and measurement results obtained after the DLC deposition and etching were compared next. It can be seen in figure 5 that separation between the resonances increases with both d and n. Since the properties of the DLC on the LPG are difficult to measure, the simulations were performed for three different n of the DLC, which were assumed to be constant with d and in addition assuming influence of d on n as shown in figure 3(*b*). Correlation of resonance wavelengths obtained after the deposition with results of the simulations allowed for estimation of d on the LPG, which was found to be between 33 and 45 nm when assuming $n = 2.1$ and 1.9, respectively. When $d(n)$ is considered, the estimated deposition rate is ~4.6 nm min^{-1} and etching rate is ~8 nm min^{-1}. The values reaching 47% in the case of deposition and 16% for etching rate measured on reference Si wafers placed on the electrode are caused by elevating the sample in the plasma reactor and must be considered in the design of the optical fiber devices fabricated using plasma-based methods.

3.3. RI sensitivity of DLC coated and etched LPGs

The effect of the variations of n_{ext} in the range from 1–1.36, for LPG sample with no coating and with overlay deposited

in 8 min long process, are compared in figure 6. Deposition of the DLC overlay strongly modifies response of the LPG to n_{ext}. First of all, the overlay shifts the LPG working point away from DTP, which results in decrease of RI sensitivity in the range 1–1.333 RIU [1, 19]. However, simultaneously the DLC overlay tunes the LPG towards cladding mode transition, where one of the cladding modes is guided in the overlay, causing reorganization of all the other cladding modes. The effect results in high RI sensitivity of the LPG in an n_{ext} range dependent on properties of the overlay [20]. The mode transition effect also causes reduction in depth of the resonances. Thus, the etching performed as a post-processing procedure of DLC-coated LPGs allows for tuning spectral response of the LPG towards DTP or mode transition.

The measurements clearly show the influence of the etching process on the resonance wavelength shift with variations of the n_{ext} (figure 7). The etching process induces for the presented sample a significant reduction in RI sensitivity in the range 1.3330–1.3628. Moreover, the sensitivity obtained as a result of the etching is close to that for the samples without the overlay. This effect allows for treating the etching process as a good solution for sample recovery after, e.g., biofunctionalization process by completely removing the biofunctionalized DLC layer or removing both the DLC layer with deposited biolayer on top of it, and makes possible its recoating.

4. Conclusions

The plasma etching in O_2 can be used for effective post-processing of hard and chemically resistant DLC overlays deposited on LPGs. When the LPG sample is held above the electrode in the plasma reactor, one must expect that the properties of the overlay and its etching conditions are different than those obtained for reference wafers placed directly on the electrode. By correlating results of measurements and simulations, we have found that both deposition and etching rates on LPGs elevated by 5 mm above the electrode are reduced down to about 47% and 16% of the rates on reference wafers placed on the electrode for deposition and etching processes, respectively. Moreover, it has been found that optical properties of the DLC film strongly depend on its thickness, especially when the films are thinner than 150 nm. The dependence is clearly visible for both deposition and etching and must be taken into account in the design process of the nano-coated LPG-based devices.

The DLC etching in O_2 plasma shows high selectivity, i.e. the SiO_2 etching effect is negligible, which makes the process worthwhile in application for (depending on demand) very accurate modification of the DLC overlays or removing of the entire overlay and the LPG recoating. With such a process, the RI sensitivity of the DLC nano-coated LPG-based sensors can be effectively modified by appropriate plasma post-processing.

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