H₂ impact on Bragg gratings written in N-doped silica-core fiber

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Abstract: The evolution of transmission spectra of Bragg gratings written in an N-doped silica-core fiber in the course of H₂ loading at a pressure of 6 MPa is investigated. It is shown, that penetration of hydrogen molecules in the region of fiber core with written gratings causes irreversible spectrum changes, which do not disappear after subsequent H₂ outcome from the fiber. Bragg gratings' spectra monitoring in the process of H₂ loading is viewed from the angle of photosensitivity mechanisms responsible for formation in N-doped silica-core fibers photoinduced Bragg gratings, capable to operate at very high temperatures.

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References and links

1. Introduction

In-fiber Bragg gratings (FBGs) imprinted in N-doped silica core fibers by means of inexpensive, commercially available excimer lasers feature enhanced vitality when heated and are used as reliable sensors for various physical quantities [1]. To write gratings in such fibers an ArF excimer laser radiation at a wavelength of 193 nm is applied. Unlike most of other fiber types (e.g. Ge-, P-doped silica-core fibers), H2 loading of N-doped fibers does not speed up the grating formation rate, but significantly slows it down [2]. It means that the presence of the dissolved molecular hydrogen in N-doped silica-core fibers enhances the relaxation rather than strengthen photoinduced changes in glass net structure. A similar enhancement of relaxation processes is observed in pure silica-core optical fibers, the H2 soaking of which significantly reduces the degradation of their spectral characteristics brought about by intense laser UV radiation transmission [3].

As was found earlier [4], putting the N-doped optical fiber with already imprinted FBGs into H2 ambience gives rise to a specific reaction of FBGs’ transmission spectra on hydrogen penetration in the core region. In particular, an anomalous behavior of FBGs’ resonance wavelengths and reflection coefficients after 20 hours of hydrogen loading at room temperature is observed. In addition to a typical behavior of FBGs’ spectra caused by the effective refractive index change due to H2 dissolution in the glass network [4,5], irreversible change in spectral characteristics even after the total hydrogen outcome from the fiber in air is observed. Such irreversible change can be reasonably attributed to hydrogen chemical incorporation in the core glass network resulted from the interaction of H2 molecules entering from the outside with chemically active defects (glass network irregularities) created by UV irradiation during grating inscription [4]. Time delay of about 20 hours corresponds to a typical time necessary for diffusion of a hydrogen molecule through cladding glass at a distance of about 60 microns at room temperature. It is known that thermochemical coupling of H2 in non-irradiated N-doped silica network accompanied by the formation of first Si-NH and then Si-OH groups starts to occur at temperatures greater than 400 °C and at room temperature runs very slowly [6]. The above testifies that it is photoinduced defects, with which H2 comes to interact.

However, the most interesting feature revealed in the preceding experiments [4] is the influence, caused by penetrated in the core region hydrogen molecules on type I and type IIa FBGs’ spectra. This influence is of similar value, but of opposite sign. If for type I gratings H2 penetration in the core region leads to irreversible decrease of the resonant reflection by ~20%, the reflectivity of type IIa grating irreversibly increases approximately by the same value. In both cases the change of reflection is accompanied by irreversible shift of Bragg wavelengths (\(\lambda_B\)) towards shorter wavelength region by ~0.1 nm. An important point is that FBGs for these measurements have been written in the same fiber under similar UV flux densities and are differed by UV irradiation time only.

Present work is aimed at further experimental investigation of the discovered peculiarities in the behavior of FBGs’ spectra characteristics caused by hydrogen molecules penetration in the core region of the N-doped silica fiber with Bragg structure written in it. In particular, we will try to clear it up to what extent these peculiarities are related to the contribution of opposite phase components of type I and type IIa grating. If, as supposed, the effect is brought about by hydrogen molecules interaction with chemically active photoinduced defects of the core glass, preliminary annealing of these defects in more thermally stable type IIa gratings must lead to the effect elimination.

2. Experiment

Transmission spectra variations are characterized by shifts of \(\lambda_B\) (Bragg wavelength) and NICC (Normalized Integrated Coupling Constant) defined as [7]:

\[
\text{NICC} = \frac{\text{Integrated Coupling Constant}}{\text{Integration Width}}
\]
\[ \lambda_B = 2 \cdot n_{\text{eff}} \cdot \Lambda, \]  

(1)

\[ \text{NICC} = \frac{\tanh^{-1}(\sqrt{R)}}{\tanh^{-1}(\sqrt{R_0})}, \]  

(2)

where \( n_{\text{eff}} \) is an effective refractive index for propagating mode, \( \Lambda \) - a spatial grating’s period, \( R_0, R \) – initial and current grating’s reflection coefficients at \( \lambda = \lambda_B \). Expressing reflection coefficients at resonance wavelengths in terms of fiber core refractive index modulation \( (\delta n_{\text{eff}}) \) in the region of the grating, one can show that \( \text{NICC} = \delta n_{\text{eff}} / \delta n_0 \) reflects a relative change in \( \delta n \) or, in other words, a change in grating’s contrast [8].

Key characteristics of fiber and gratings used in our experiments are listed in Table 1. Fibers are drawn from preforms synthesized by the SPCVD method [9]. Gratings 3 mm in length are imprinted at the same for corresponding grating type exposure dose with the help of CL5000 ArF excimer laser radiation at a wavelength of 193 nm, fluence per pulse being 150 mJ/cm². Pulses duration and repetition rate are ~8 ns and 100 Hz correspondingly. All in-fiber gratings are written with the help of the same phase mask produced by Ibsen Photonics with a period \( \Lambda_{\text{pm}} = 1066 \) nm. Bragg gratings transmission spectra are recorded by an Agilent 86140B spectrum analyzer connected to a PC. The spectra are typical for “standard” Bragg gratings with FWHM ~0.4 nm. Some dispersion of \( \lambda_B \) values for corresponding grating types can be associated with instabilities of the laser beam.

<table>
<thead>
<tr>
<th>Grating #</th>
<th>Fiber core glass composition</th>
<th>Fiber core diameter (microns)</th>
<th>Cut-off wavelength (nm)</th>
<th>UV exposure dose (kJ/cm²)</th>
<th>( \lambda_B ) at room temperature (nm)</th>
<th>Grating reflection at ( \lambda = \lambda_B ) (dB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>I</td>
<td>0.60</td>
<td>1549.87</td>
<td>1550.10</td>
<td>4.4 (0.9 annealed)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>IIa</td>
<td>4.50</td>
<td>1549.10</td>
<td>1548.68 (annealed)</td>
<td>11.3</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>SiO₂+N (4 at. %)</td>
<td>0.041</td>
<td>1200</td>
<td>1549.19</td>
<td>11.3 (12.6 annealed)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>IIa</td>
<td>2.10</td>
<td>1548.61 (annealed)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Experiments are carried out with the use of a special chamber designed for \( \text{in situ} \) monitoring of the reaction of fibers transmission spectra to annealing in hydrogen atmosphere at a permanent pressure of up to 15 MPa. Chamber design and the description of measurement technique one can find in more detail in references [4] and [6].

FBGs #3 and #4 are preliminary annealed in air at 700 °C during 20 minutes. As a result, \( \text{NICC} \) of type I FBG (Grating #3) decreased by more than 70% (resonance reflection coefficient decayed down to 0.9 dB), whereas \( \text{NICC} \) of type IIa FBG (Grating #4) increased approximately by 10% (resonance reflection coefficient raised up to 12.6 dB).

Fiber samples with annealed gratings (#3 and #4) and their reference counterparts (#1 and #2) are put in the vessel in molecular hydrogen ambience at a pressure of 6 MPa and kept for 330 hours at room temperature. After that hydrogen was exhausted from chamber. During both hydrogen in- and out-diffusion stages gratings transmission spectra are automatically registered over equal periods of time and filed by the PC.

3. Results

Figures 1, 2 illustrate variations of gratings’ spectra characteristics during hydrogen molecules entrance and extraction at room temperature. It is seen that after \( \tau \sim 20 \) hours from putting in \( \text{H}_2 \)
ambience, abnormal behavior of FBGs’ spectra parameters takes place for samples #1 and #2. Time interval of ~20 hours corresponds to the diffusion length \( L = \sqrt{D \cdot \tau} \), which in silica at room temperature amounts ~60 microns. Therefore, it is quite reasonable to associate the observed abnormalities with the beginning of hydrogen molecules entrance in the core region of the fiber.

![Graph 1](image1.png)

**Fig. 1.** Bragg wavelengths change during hydrogen entrance and extraction at room temperature.

![Graph 2](image2.png)

**Fig. 2.** NICC change during hydrogen entrance and extraction at room temperature.

As is seen from Fig. 1, the character of \( \lambda_B \) dependence and, according to Eq. (1), \( n_{\text{eff}} \) on time at \( \tau > 50 \) hours correlates in general with the H\(_2\) concentration variation in the core region: \( n_{\text{eff}} \) initially grows due to the increase of H\(_2\) concentration, but at \( \tau > 330 \) falls down at a rate limited by the out diffusion process through the cladding.

Phenomena depicted in Fig. 1, 2 are well reproducible as was experimentally established on various gratings. Uncertainties in the data do not exceed symbol sizes in plots.
It is evident from figures that samples pre-annealing in air significantly affects the behavior of FBGs’ parameters during H2 saturation. Irreversible abnormalities disappeared. $\lambda_B$ and NICC of gratings #3 and #4 returned to their initial values after full out-diffusion of H2 to an accuracy of the measurements.

It should be noted that in the course of hydrogen loading $\delta n_{\text{eff}}$ of grating #4 monotonously decreases with $n_{\text{eff}}$ increase. The same behavior is observed at $\tau > 50$ hours from the beginning of the experiment for unannealed (reference) grating #2 (see Fig. 2). Similar character of spectra evolution is observed in unannealed type IIa FBGs written in germanosilicate fibers (see [4] and references therein). Such behavior of spectra finds quite reasonable explanation in the assumption regarding the presence of an alteration of molecular hydrogen content along the fiber core correlated with grating’s period. In its turn it testifies that it is the appearance of a periodic core diameter variation, which brings about formation of a “negative” part of the contribution to the photoinduced propagating mode effective refractive index change in the process of type IIa grating inscription both in N-doped and Ge-doped fibers. The origin of such core diameter corrugation may be associated with the inhomogeneous photoinduced deformation of glass in the vicinity of core-cladding interface caused by the irradiation process. Such a phenomenon was first discussed in [10] and will be described in more detail in further publications.

Greater NICC change in the course of hydrogen loading of grating #3 (type I) as compared to grating #4 (type IIa), Fig. 2, is associated with the fact that NICC reflects a relative change of the refractive index modulation. Absolute changes of the resonance reflectivity for gratings #3 and #4 amount 0.2 dB and 1.2 dB respectively.

4. Discussion

The revealed abnormalities in the behavior of gratings’ spectra, which start to develop as H2 molecules appear in the core region, are caused by the interaction of hydrogen molecules with active centers formed in the core glass as the result of UV irradiation in the course of gratings writing [4]. Classification of such centers and their thermo-chemical properties in N-doped silica one can find in reference [11]. Estimation based on characteristic diffusion time extracted from Fig. 1, 2 of how many H2 molecules reached the core in 20 hours yields for an upper limit of such centers concentration a value of $\sim 10^{19}$ cm$^{-3}$.

The decrease of type I grating contrast (NICC) means that molecular hydrogen by entering fiber core causes the relaxation of photoinduced changes in glass network structure responsible for the refractive index change. These changes may have been associated with photoinduced network compaction [12] and/or larger susceptibility defects formation [13].

Obviously, if there is a relaxation mechanism associated with the presence of H2 molecules, the grating formation rate as a function of irradiation dose shall decrease. In favor of the presence of such mechanism speaks the dynamics of gratings writing observed in the N-doped silica fiber exposed to hydrogen loading at room temperature prior to gratings writing (see Fig. 3). It is seen that grating formation in this case runs much slower as compared to the same fiber free of hydrogen.

As a result of 20 minute long annealing at 700 °C in air, changes of $\lambda_B$ and NICC in the process of subsequent hydrogen loading become reversible and completely correlate with the increase of hydrogen molecules concentration in the core region via the diffusion through the cladding (see Fig. 1, 2). As for irreversible changes associated with hydrogen entrance, they are observed only in unannealed gratings both of type I and type IIa. The character of irreversible changes in gratings’ spectra as a function of H2 loading time for both gratings types testifies that the major role in the irreversible processes play defects induced as early as type I grating is formed. It also suggests that type IIa grating contains an opposite phase component of type I grating, that agrees with references [10,14,15] and is indicative of significant differences in mechanisms of these two types grating formation.
It should be noted, that at the stage of H$_2$ extraction ($\tau \approx 330$ hours) the changes in $\text{NICC}$ are similar for correspondent annealed and reference grating types (see Fig. 2). These changes correlate with the rest H$_2$ content in the core region, which decreases with time according to the diffusion law. It gives ground to state that the arrival of hydrogen molecules in the core region as well as preliminary annealing lead to the suppression of both type I grating and a rest of its component in type IIa grating.

5. Conclusion

Loading of N-doped silica-core fibers with molecular hydrogen significantly slows down the rate of photoinduced Bragg gratings writing by means of an ArF excimer laser irradiation, which essentially distinguishes this fiber type from other photosensitive silica based fibers. Penetrating in the core region with already written grating, hydrogen molecules enter into reaction with photoinduced chemically active centers (network irregularities) even at room temperature. These reactions bring about partial decay of resonance reflectivity of type I and the enhancement of type IIa gratings, and cause a shift of the resonance wavelengths to a shorter-wavelength region. It is shown that these processes are irreversible, and for their completion H$_2$ molecules concentration in the core region of $\sim 10^{19}$ cm$^{-3}$ is enough.

We demonstrated that preliminary 20 minute long annealing in air at a temperature of $\sim 700$ °C leads to the relaxation of photoinduced active centers, able to enter into reaction with hydrogen molecules at room temperature. As a result of such pre-annealing, the changes of gratings spectra in the process of H$_2$ saturation and subsequent gas extraction become totally reversible and are governed only by the concentration of H$_2$ molecules currently dissolved in the glass network of the core region.

Comparison analysis of the behavior of types I and IIa gratings spectra demonstrated, that the formation of chemically active network irregularities, interacting with the dissolved in glass molecular hydrogen already at room temperature occurs at a stage of type I grating formation. It is established that it is the contribution of such irregularities in $n_{\text{eff}}$ modulation, which is responsible for anomalous behavior of gratings spectra at hydrogen loading, and it is type I grating annealing that leads to elimination of all irreversible processes in the course of H$_2$ loading of type IIa grating.