# Increased solubility of molecular hydrogen in UV-exposed germanosilicate fibers

**S. A. Vasiliev, O. I. Medvedkov, V. G. Plotnichenko, and E. M. Dianov**

*Fiber Optics Research Center at the A. M. Prokhorov General Physics Institute RAS, 119991, 38 Vavilov Street, Moscow, Russia*

**A. O. Rybaltovsky**

*Nuclear Physics Institute of the Moscow State University, 119992, Leninskie Gory, Moscow, Russia*

Spectral properties of photoinduced fiber Bragg gratings written in germanosilicate fibers and subjected to hydrogen loading at a pressure of $150-170$ MPa have been studied. It was observed, for the first time to our knowledge, that hydrogen dissolution in the glass network at such high pressures leads not only to a Bragg wavelength shift but also to a considerable alteration of the grating reflectivity. The relative magnitude of the latter effect is independent of the dissolved hydrogen concentration and is defined mainly by the core glass properties and the UV-irradiation conditions. The alteration of the grating reflectivity observed experimentally is explained by increased solubility of molecular hydrogen in UV-exposed germanosilicate glass. © 2006 Optical Society of America

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Serious interest to study the spectral characteristics of molecular hydrogen ($H_2$) and its interaction with the network of high-purity silica and germanosilicate glasses is due to the following reasons. First, penetration of $H_2$ molecules into optical fibers results in optical loss growth in the telecommunication wavelength range.[1,2] Second, the presence of dissolved hydrogen strongly enhances the photosensitivity of germanosilicate fibers. For this reason, $H_2$ dissolution in the fiber glass is widely used for photoinduced grating fabrication.[3] The magnitude of these effects depends on the hydrogen concentration. Therefore it is important to clarify both the limiting value of hydrogen solubility in glasses and the concentration dependences of thermochemical and photochemical reactions of $H_2$ molecules with the glass network at loading pressures $P_{H2}$ exceeding 100 MPa.

In Refs. 4 and 5 we studied spectral characteristics of $H_2$-related bands in germanosilicate fibers at a loading pressure of $150-170$ MPa with the help of absorption and Raman spectroscopy. In particular, it was shown that at such loading pressures the $H_2$ diffusivity in silica glass is noticeably increased. This phenomenon was explained by the hydrogen intermolecular interaction and was well described by an additional term in the diffusion equation. In the cited papers we also observed that $H_2$ loading of the photoinduced fiber Bragg grating (FBG) affects both the resonance wavelength (a phenomenon observed universally[6]) and the reflection coefficient. In this work we present a more detailed description and discussion of our results obtained for FBGs loaded at a pressure of $150-170$ MPa.

We used two single-mode fibers produced by modified chemical-vapor deposition (MCVD) technology. Fiber **A** was doped with 13 mol. % $GeO_2$ and had a cutoff wavelength of 1.01 $\mu$m, whereas for fiber **B** these values were 24 mol. % $GeO_2$ and 1.17 $\mu$m, respectively. The cladding diameter of both fibers was 125 $\mu$m. High-pressure hydrogen loading was performed in a chamber at a pressure of 150 MPa (for fiber **A**) and of 170 MPa (for fiber **B**) for 24 h at a temperature of 100°C.

Two spectrally separated uniform FBGs with resonance wavelengths $\lambda_{Br}$ located in the range of $1330\pm5$ nm were written in each fiber before $H_2$ loading. Gratings were produced using cw radiation of a frequency-doubled Ar-ion laser (244 nm) in the Lloyd interferometer scheme at a UV power density of approximately 50 W/cm$^2$. The fibers were not $H_2$ loaded before the grating fabrication. Fiber sections containing FBGs were recoated before $H_2$ loading. The time interval between opening the hydrogen chamber and the beginning of the measurements varied from 1.5 to 5 h. Spectral measurements of the FBG properties and the $H_2$-related absorption band at 1.24 $\mu$m were carried out at room temperature.

Figure 1 shows dose dependences of the modulation amplitude of the induced refractive index $\Delta n_{\mathrm{mod}}^{\mathrm{init}}$ measured in fibers **A** and **B** in the first diffraction order of FBGs. It should be noted that our writing interference pattern had a high contrast, which is con-
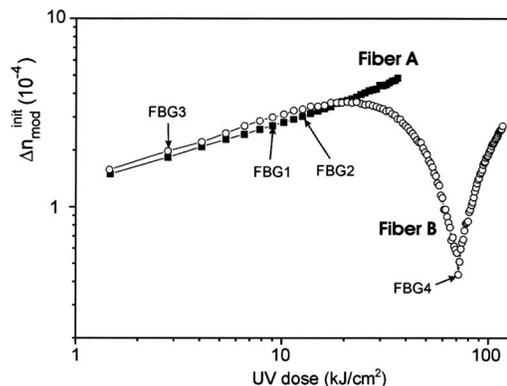


Fig. 1. Dose dependences of the modulation amplitude of the induced refractive index.

firmed by a good coincidence between $\Delta n_{\text{mod}}^{\text{init}}$ and the mean refractive index change $\Delta n_{\text{avr}}^{\text{init}}$ calculated from the FBG properties at the beginning of irradiation. As shown in Fig. 1, fiber **A** (FBG1 and FBG2) exhibits only type I photosensitivity at doses used in the experiment, whereas fiber **B** (FBG3 and FBG4) demonstrates both photosensitivity types: type I at $D < 70 \text{ kJ/cm}^2$ and type IIa (Ref. 7) at $D > 70 \text{ kJ/cm}^2$. Note that FBG3 was a type I grating, whereas FBG4 corresponds to the minimum of the index modulation lying between type I and type IIa photosensitivity regions.

Assuming that the $H_2$ concentration in the fiber core is proportional to the 1.24 $\mu$m band intensity and using the results of Ref. 1 obtained for the loading pressure of approximately 0.1 MPa, we estimated the approximate concentration of the $H_2$ molecules in our samples to be 12–13 mol. % ($\sim 3 \times 10^{21} \text{ cm}^{-3}$). It is remarkable that even at such high pressures, the intensity of the 1.24 $\mu$m absorption band remains practically proportional to the hydrogen pressure in the loading chamber.

In Fig. 2 the transmission spectra of FBG3 and FBG4 are shown before and after $H_2$ loading at two different $H_2$ concentrations in the fiber core. Note that owing to low initial index modulation of FBG4 $\Delta n_{\text{mod}}^{\text{init}} \approx 4 \times 10^{-5}$ (see Fig. 1), its peak did not show up in the initial spectrum (Fig. 2). A line points to the expected position of the peak. Strong changes of the Bragg wavelength $\lambda_{\text{Br}}$ and the reflection coefficient $R$ of both gratings caused by dissolved hydrogen are clearly seen. Full recovery of the initial spectra within the experimental error was observed after complete hydrogen outdiffusion from the fibers, which points to the reversible nature of the $H_2$-induced changes of the FBG properties.

In Table 1 the resonance wavelengths and reflection coefficients measured 1.5–2 h after the end of $H_2$ loading are presented together with the initial parameters of the gratings. The calculated changes of the index modulation amplitude and of the mean index in the gratings caused by the presence of hydrogen in the fiber core are also given in Table 1. To calculate the index modulation amplitude before ($\Delta n_{\text{mod}}^{\text{init}}$)
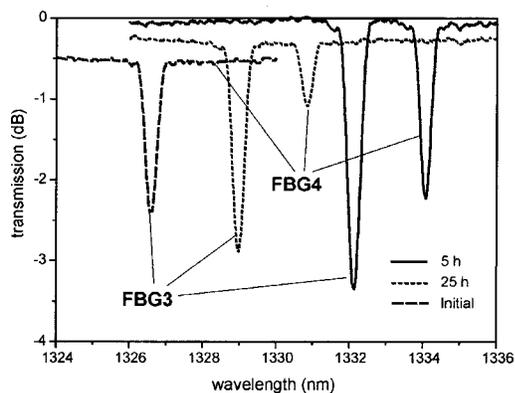


Fig. 2. Transmission spectra of FBGs written in fiber **B** measured before $H_2$ loading and 5 and 25 h after the end of $H_2$ loading. For ease of comparison two spectra are displaced along the Y axis.

and after ($\Delta n_{\text{mod}}^{\text{H}_2}$) $H_2$ treatment, we used a conventional equation $\Delta n_{\text{mod}} = \lambda_{\text{Br}} \operatorname{arctanh} \sqrt{R}/(\pi \eta L)$, where $L$ is the grating length and $\eta$ is the portion of the fundamental mode power in the fiber core. At $\lambda_{\text{Br}}$ the values of $\eta$ were estimated to be 0.69 and 0.78 for fibers **A** and **B**, respectively. To obtain the value of the $H_2$-induced mean index change, the following relation was utilized: $\Delta n_{\text{avr}}^{\text{H}_2} \approx (\Delta \lambda_{\text{Br}}/\lambda_{\text{Br}}) n_{\text{avr}}$, where $\Delta \lambda_{\text{Br}}$ is the $H_2$-induced Bragg wavelength shift and $n_{\text{avr}}$ is the mean index of the FBG structure.

Time dependences of the Bragg wavelength shift measured at room temperature in the course of hydrogen outdiffusion are shown in Fig. 3. These curves have no pronounced initial region, which is usually observed at $t \leqslant 20 \text{ h}$ at loading pressures of 10–20 MPa and in which $\lambda_{\text{Br}}$ is known to remain unchanged while $H_2$ escapes from the cladding glass only. However, in our case we are dealing with the effect of accelerated outdiffusion that takes place at loading pressures of higher than 50 MPa.[4,5] In addition, it turned out that the initial shift of $\lambda_{\text{Br}}$ for fibers **A** and **B** is different and this difference is greater than the difference in loading pressure. In particular, for FBG1 and FBG2 the Bragg wavelength shift was $\sim$30 pm/MPa, while for FBG3 and FBG4 it was approximately 36 pm/MPa. In our opinion this phenomenon can be explained by higher ($\sim$20% in our case) solubility of the molecular hydrogen in a "sparser" glass with a higher germanium concentration (fiber **B**). It is interesting that if one normalizes the two dependences in Fig. 3 to their maxima at $t \approx 0$, the resultant curves will coincide.

Let us now consider the $H_2$-induced variations of the reflective coefficient observed in all the gratings. We found that the absolute value of these variations strongly depends on the germanium concentration in the fiber core as well as on the irradiation dose (see Table 1). For example, in fiber **A** the change in the modulation amplitude induced by $H_2$ loading at 150 MPa was $1.5 \times 10^{-5}$ for FBG1 written with a UV dose of 9 $\text{kJ/cm}^2$ and approximately $5 \times 10^{-5}$ for FBG2 written with 12.5 $\text{kJ/cm}^2$. The strongest modification of $24.5 \times 10^{-5}$ was observed for FBG4 (fiber **B**) written with the highest UV dose of 70 $\text{kJ/cm}^2$.

The observed phenomenon with a relative value as high as several percent (see the last column in Table 1) is unlikely to be due to UV-induced change in the strength of interaction of $H_2$ molecules with the glass network. If such a change had occurred, the UV-induced index would have amounted to several percent, too. However, the UV-induced index in our gratings is of the order of $10^{-4}$.

At the same time, the structural modification of germanosilicate glass under the action of UV light is known to be significant.[8] Therefore, in our opinion, the main reason that can explain the experimental facts is that irradiated and unirradiated germanosilicate glass features different solubility of molecular hydrogen. Because $H_2$ loading increases reflectivity of type I gratings, one may conclude that irradiated

**Table 1. Parameters of the Tested FBGs Before and After $H_2$ Loading**

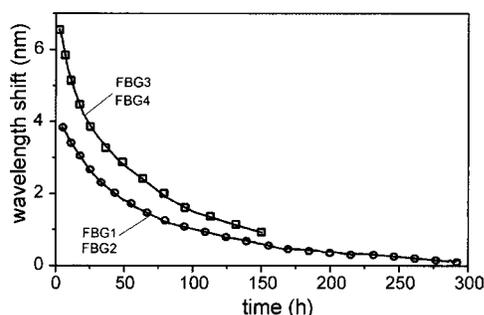| Grating | GeO$_2$ content (mol.%) | $L$ (mm) | $D$ (kJ/cm$^2$) | $p_{H_2}$ (MPa) | $R$ (dB) Initial | $R$ (dB) H$_2$ Loaded | $\Delta n_{mod}^{H_2} - \Delta n_{mod}^{init}$ (10$^{-5}$) | $\lambda_{Br}$ (nm) Initial | $\lambda_{Br}$ (nm) H$_2$ Loaded | $\Delta n_{avr}^{H_2}$ (10$^{-3}$) | $2\frac{\Delta n_{mod}^{H_2} - \Delta n_{mod}^{init}}{\Delta n_{avr}^{H_2}}$ (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| FBG1 | 13 | 1.5 | 9 | 150 | 1.8 | 2.0 | 1.5 | 1328.4 | 1332.3 | 4.3 | 0.7 |
| FBG2 | 13 | 1.2 | 12.5 | 150 | 1.4 | 1.9 | 5 | 1330.3 | 1334.2 | 4.3 | 2.3 |
| FBG3 | 24 | 1.8 | 3 | 170 | 1.7 | 3.3 | 8.5 | 1325.85 | 1332.1 | 6.8 | 2.5 |
| FBG4 | 24 | 1.6 | 70 | 170 | <0.1 | 2.1 | 24.5 | 1327.5 | 1334.1 | 7.2 | 6.8 |



Fig. 3. Bragg wavelength shift measured during $H_2$ out-diffusion from the fibers. The curves for the two gratings written in each fiber coincide with the experimental accuracy.
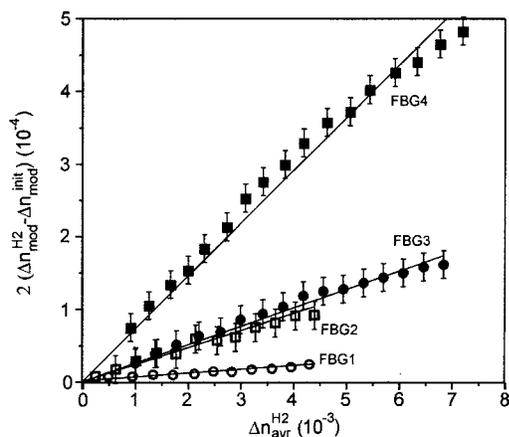


Fig. 4. $H_2$-induced variation of the FBG modulation amplitude versus the $H_2$-induced mean index change.

germanosilicate glass has greater $H_2$ solubility. This additional UV-induced solubility increases with germanium concentration in the glass network and with UV exposure of the glass. To estimate the value of relative UV-induced solubility $\beta$ we used a simple relation $\beta = 2(\Delta n_{mod}^{H_2} - \Delta n_{mod}^{init})/\Delta n_{avr}^{H_2}$, where the factor 2 is due to the fact that the total $H_2$-induced index difference between the irradiated and unirradiated glass regions is 2 times higher than the measured $H_2$-induced change of the FBG modulation amplitude. The values of $\beta$ obtained for all the gratings are given in Table 1. It is 0.7% for FBG1 and an order of magnitude greater for FBG4. Figure 4 shows the ex-

perimental dependences of value $2(\Delta n_{mod}^{H_2} - \Delta n_{mod}^{init})$ as a function of $\Delta n_{avr}^{H_2}$. One can see that all the dependences are linear with a slope equal to $\beta$. Linearity of these dependences testifies that the relative UV-induced solubility is independent of the hydrogen concentration in the fiber core.

One possible mechanism of the enhancement of $H_2$ solubility in UV-irradiated glass is as follows. It is known that under the action of UV radiation, the network of germanosilicate glass is rearranged, which is accompanied by a disruption of bonds and the formation of rings of a lower order.[8] Such rearrangement occurs, apparently, owing to stretching or breaking of weak bonds at the boundaries of clusters forming the glass network. This can lead to a reduction of the cluster size with a simultaneous increase of the size of less dense regions suitable for the penetration of $H_2$ molecules. This can be the main reason for the increased solubility of hydrogen in germanosilicate glass exposed to UV radiation.

In conclusion, we observed, for the first time to our knowledge, increased solubility of molecular hydrogen in germanosilicate glass subjected to UV irradiation. This phenomenon can strongly modify the reflectivity of photoinduced fiber gratings.

S. A. Vasiliev's e-mail address is sav@fo.gpi.ru.

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