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Interaction of Molecular Hydrogen with the Doped Silica Core of an Optical Fiber at Elevated Temperatures

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Abstract—Optical fibers with cores made of germanosilicate, phosphosilicate, and nitrosilicate glasses are loaded by molecular hydrogen at a pressure of 10 MPa and room temperature. Then, preloaded fibers are kept in a hydrogen atmosphere at the same pressure and various fixed temperatures up to 700°C and the transmission spectra of the fibers are measured *in situ* at a constant temperature with equal time intervals. The kinetics of the chemical interaction between hydrogen and the silica is determined by analyzing an increase in the optical absorption at the overtones of OH and NH groups. © 2004 MAIK "Nauka/Interperiodica".

INTRODUCTION

The interaction of hydrogen with optical fibers is of interest mainly due to the experimental data on the effect of hydrogen on the practically important properties of optical fibers, such as the optical loss increase spectrum, radiation-induced losses, and photosensitivity.

It is well known that glasses are permeable to gases, especially to hydrogen and helium [1]. Hydrogen dissolved in a glass "heals" radiation-induced color centers—point defects induced in the glass by ionizing radiation—and, thus, decreases additional optical losses [2].

Saturation of the optical fibers with molecular hydrogen is used in the technology of in-fiber Bragg gratings [3]. An increase in the photosensitivity of a fiber upon saturation with molecular hydrogen is a key factor, for example, in fabricating fiber lasers and amplifiers based on the effect of stimulated Raman scattering in phosphosilicate optical fibers [4, 5]. Hydrogen saturation increases the photosensitivity of phosphosilicate fibers to a level sufficient for writing the Bragg gratings using 193-nm radiation of an ArF excimer laser [6].

At the same time, the hydrogen molecules present in silica cause additional resonance light absorption with a complex spectrum [7]. At elevated temperatures, hydrogen interacts with the oxygen atoms of the glass network and is incorporated into this structure in the form of hydroxyl groups. The overtone of the optical resonance absorption of OH groups at a wavelength of 1.38 μm falls within a spectral range that is important for telecommunication applications; therefore, an increase in the concentration of these groups deteriorates the properties of communication lines.

Previously [8, 9], it was demonstrated that, at temperatures below 500°C, molecular hydrogen diffuses into fused silica via interstices without significant chemical interaction with the glass network. However, the problem of determining the effect of temperature on the chemical interaction of hydrogen with fiber cores doped to different levels with various impurities is still a challenge. Solving this problem would allow one to determine the optimum temperatures for the saturation of optical fibers with molecular hydrogen to a level not involving noticeable chemical interaction. Such data would make it possible to optimize the process of saturation, since an increase in the temperature substantially decreases the time required for the complete saturation of materials with a gas. For example, at temperatures below 100°C, it takes about 20 h to reach the maximum hydrogen concentration (in equilibrium with the ambient gas atmosphere) in a standard optical fiber. An increase in the temperature to 300°C shortens this time to a few hours, and, at 500°C, this process takes only a few minutes.

EXPERIMENTAL

To date, most experiments devoted to the saturation of optical fibers with molecular hydrogen were performed without controlling the dynamics of gas penetration into a glass network. As a rule, fiber samples were placed in a hermetically sealed vessel filled with gas at a certain pressure and kept there at a preset temperature for a certain time. Then, the samples were extracted from the vessel for optical measurements. This technique cannot provide monitoring of the optical properties of a sample and, hence, the hydrogenation dynamics *in situ* during hydrogen saturation.

A key point in our experiments is the design and use of a special chamber for the saturation of optical fibers with molecular hydrogen. With this chamber, we can monitor the dynamics of hydrogen penetration and interaction with glass atoms at room and elevated temperatures using optical spectroscopy. Monitoring of the intensities of absorption peaks characteristic of the molecules dissolved in the glass and the atomic groups formed as a result of reactions at elevated temperatures makes it possible to analyze the dynamics of changes in the concentrations of these species.

The setup created for the saturation of optical fibers with molecular hydrogen consists of a high-pressure vessel in the form of a reactor tube connected with two stainless steel buffer tanks (Fig. 1). Loops of the optical fiber to be studied are placed in the reactor, and its ends are led out through seals in the flanges. The ends can be connected to outside spectrometric equipment. The total length of the optical fiber accommodated in the vessel is 10 m. The reactor is equipped with an external heater, which allows the dynamics of changes in the optical spectra to be traced at a reactor temperature of up to 700°C. The setup design provides local heating of the fiber virtually without increasing pressure in the vessel over the whole working temperature range.

Each fiber sample was studied in two stages. In the first stage, a sample was hydrogen-saturated at room temperature. The saturation degree was estimated from the time dynamics of the absorption peak at 1.24 μm, which corresponds to the first vibrational overtone of a hydrogen molecule [7].

In the second stage, optical fibers saturated with dissolved molecular hydrogen were held at various temperatures above room temperature. During heating, the fibers were in a hydrogen atmosphere at a nearly constant pressure. In this stage, we paid particular attention to the absorption band near 1.4 μm, which is associated with a combination of the bands of Si–OH (at 1.385 μm) [7, 10, 11], Ge–OH (1.41 μm) [10, 11], and H_2O (1.42 μm) [11], and to the band of Si–NH (1.505 μm), which is manifested in optical fibers with a core made of nitrogen-doped silica [12].

The optical absorption spectra were recorded on an automated computer-assisted setup (Fig. 2). The light of a halogen lamp is filtered, diaphragmed, and focused by a silica lens through a chopper on the entrance slit of a monochromator. The image of the exit slit is focused by a lens on the edge face of a fiber that is placed in the vessel to be saturated by molecular hydrogen (Fig. 1). The intensity of the light passed through the system is measured in the lock-in mode with a GaAs-based photodiode; the output signal from this photodiode is fed to the input of a lock-in amplifier. A computer adjusts the monochromator to the required wavelength and periodically reads information from the lock-in amplifier and accumulates it in a data file. The dynamic range of the apparatus is ≈20 dB. The available spectral range is
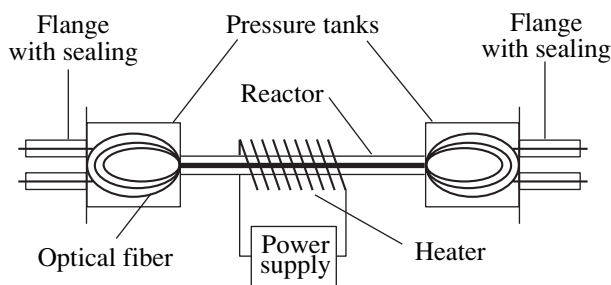
Fig. 1. Schematic diagram of the experimental setup for saturating optical fibers with molecular hydrogen and monitoring the optical transmission spectra.
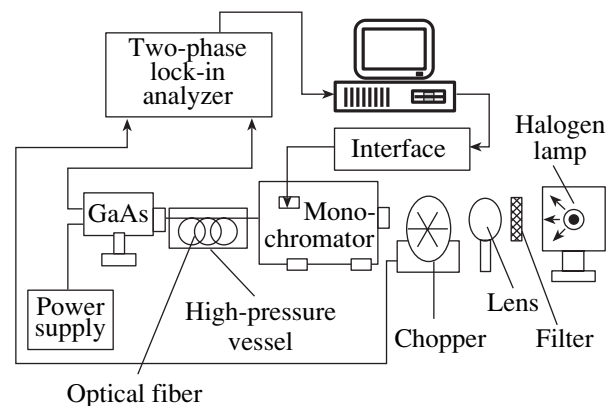

Fig. 2. Schematic diagram of the automated experimental setup for recording the optical absorption spectra of hydrogenated fibers.

190–1700 nm. In this study, we recorded the absorption spectra of optical fibers in the range 1000–1600 nm.

The main parameters of the fibers under study are given in Table 1. Sample 1 is a standard SMF-28 optical fiber (Corning) with the core of germanosilicate glass. Sample 2 is an MCVD-produced germanosilicate optical fiber containing about 26 mol % GeO_2 in the core. Sample 3 is an MCVD-produced optical fiber with a core made of phosphorus-doped silica. Sample 4 is an optical fiber with a core made of nitrogen-doped silica, which was fabricated by reduced-pressure plasma-chemical vapor deposition [12].

RESULTS AND DISCUSSION

As a result of saturation of the optical fibers with molecular hydrogen, the optical absorption in the near infrared (NIR) region increases (Fig. 3). The total optical losses also increase, and well-resolved absorption bands corresponding to various H_2 vibrational states appear. According to [13], the absorption of 3.4 dB/km at a wavelength of 1.24 μm corresponds to a molecular hydrogen concentration of 10^{18} cm^{-3} in the glass network. Thus, the molecular hydrogen concentrations in samples 1–4 saturated at room temperature can be esti-
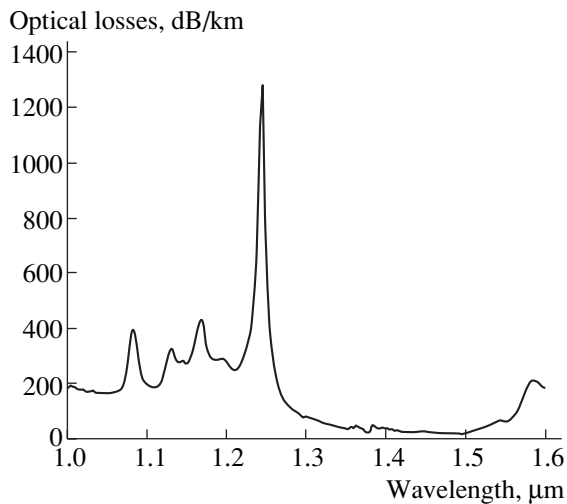
Table 1. Parameters of optical fibers

Sample no.	Core material/diameter	Cladding material/diameter	Type	Difference between core and cladding indices of refraction
1	Ge : SiO$_2$/8.5 μm	SiO$_2$/125 μm	Single-mode	0.0055
2	Ge : SiO$_2$/19.2 μm	SiO$_2$/125 μm	Multimode	0.035
3	P : SiO$_2$/19.5 μm	SiO$_2$/125 μm	Multimode	0.01
4	N : SiO$_2$/10 μm	SiO$_2$/125 μm	Multimode	0.042

mated as 3.78×10^{20}, 4.29×10^{20}, 2.64×10^{20}, and 1.7×10^{20} cm^{-3}, respectively.

Note that, in this stage, the samples do not exhibit an increase in the optical absorption by hydroxy groups, since molecular hydrogen does not interact with the glass network at room temperature. However, the absorption related to molecular hydrogen dissolved in the glass increases. This means that the diffusion rate of H$_2$ at about 20°C significantly exceeds the rate of formation of hydroxy groups due to chemical interaction. Thus, before annealing, the H$_2$–SiO$_2$ system is in thermodynamic equilibrium; that is, the fibers are saturated with molecular hydrogen. The measurements show that, upon subsequent heating, the molecular hydrogen concentration in the glass network remains the same to an accuracy of 2%.

Active hydrogen incorporation into the glass with the formation of hydroxyl and NH groups becomes significant when the samples are heated to various temperatures above room temperature. The temperatures of the onset of the chemical interaction are found to be 300°C for sample 1, 200°C for sample 2, and 400°C for samples 3 and 4.
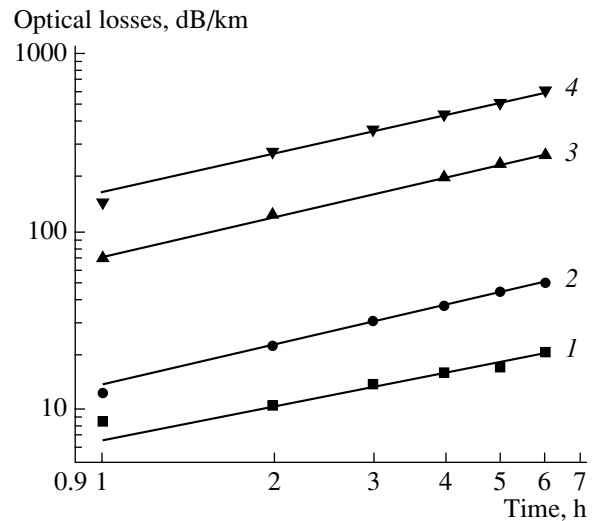
The induced absorption spectra were resolved into bands corresponding to various hydroxyl and HN groups by means of the ORIGIN software package. Thus, we determined the contribution of each band to the induced absorption and followed the band dynamics.

Figure 4 shows the experimental time variation of the absorption band intensities for hydrogen-saturated fiber 4 heated to various temperatures. The other fibers exhibit analogous dynamics of increase in the optical losses. The solid lines show the absorption by the hydrogen bound to the silica network, according to the approximation of the chemical reaction rate [14]

$$\Delta\alpha = k(T, p)t^{x},$$

where $\Delta\alpha$ is the increase in the optical losses, dB/km; $k(T, p)$ is the proportionality constant (which is a function of the absolute temperature T and the molecular hydrogen partial pressure p); t is the annealing time, h; and x is a constant that depends on the type of the optical fiber and can be determined from the approximation in Figs. 4–7.

The values of x for optical fibers 1–4 are given in Table 2.

Optical losses, dB/km

Fig. 3. Optical absorption spectrum of sample 1 saturated by molecular hydrogen at room temperature. The absorption lines of H$_2$ dissolved in silica (1.24, 1.59, 1.54, 1.197, 1.168, 1.146, 1.132, and 1.083 μm) are characteristic of samples of all types.

Optical losses, dB/km

Fig. 4. Dynamics of an increase in the optical losses of fiber 4 related to the absorption by NH groups (at 1.505 μm) at different temperatures: (*1*) 400, (*2*) 500, (*3*) 600, and (*4*) 650°C.

The factor $k(T, p)$ can be considered as the rate constant of chemical bond formation as a result of the chemical interaction of glass with hydrogen. At a constant hydrogen pressure, the temperature dependence of $k(T, p)$ can be described by the Arrhenius equation [14]

$$k = Ae^{-\frac{E}{RT}},$$

where A is a constant depending on the glass composition, dB/km h^x; E is the reaction activation energy, kJ/mol; T is the absolute temperature, K; and $R = 8.31$ J/(mol K) is the universal gas constant.

The values of the Arrhenius parameters obtained from the experimental data for various optical fibers are listed in Table 3. When heated to 400°C, fiber 1 does not exhibit a significant increase in losses in the short-wavelength region. Additional optical losses did not exceed 30 dB/km at each temperature. There were no loss increments in the long-wavelength region as well. Nor did we not detect the Ge–OH band at 1.41 μm.

The main loss increment in fiber 2 was related to the absorption by Si–OH (at 1.385 μm) and Ge–OH (at 1.41 μm) hydroxy groups. The short-wavelength losses strongly increased (the losses increased to 320 dB/km at a wavelength of 1 μm within 6 h at 250°C), but we detected no increase in the long-wavelength region. The absorption intensity at the Ge–OH (1.41 μm) overtone was significantly higher than at the Si–OH (1.39 μm) overtone, which was related to a high germanium concentration in the fiber core (about 26 mol %).

Fiber 3 features a sharp increase in the absorption in the long-wavelength region, because of which we could not continue the experiment after 6-h heating at 400°C. However, at 300°C, we detected no increase in the optical absorption. The intensity of absorption by molecular water (at 1.42 μm) was found to be higher than the intensity of absorption by the hydroxy groups (at 1.39 μm). The character of the absorption increment upon heating of this sample is much like that observed for the ultraviolet radiation-induced increase in the losses of phosphosilicate optical fibers saturated by molecular hydrogen (when absorption at wavelengths above 1.6 μm also increases and gives an intense wing in the range 1.2–1.6 μm) [11].

It should be noted that, when nitrogen-doped hydrogen-saturated molecular optical fibers are heated, the rate of increase in the absorption by the OH groups is less intense as compared to that by the NH groups by a factor of 1.5–4, depending on the temperature. Fiber 4 exhibits an increase in the optical losses in the short-wavelength spectral region.

Figure 5 shows the resulting spectra of the induced optical losses in the optical fibers under study after all annealing cycles in a hydrogen atmosphere. The decrease in the absorption in the range 1.08–1.24 μm upon heating of the molecular-hydrogen–saturated
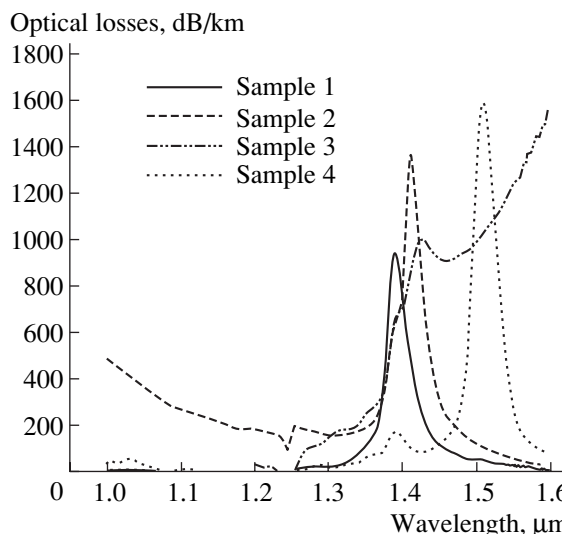

Fig. 5. Induced optical losses in various samples: Si–OH groups absorb at 1.385 μm; Ge–OH, at 1.41 μm; H$_2$O, at 1.42 μm; and Si–NH, at 1.505 μm.

optical fibers is related to a decrease in the molecular hydrogen solubility in silica with increasing temperature, along with simultaneous chemical reactions in the glass network with the formation of OH and NH

Table 2. Values of x for various samples of optical fibers

Sample no.	Si–OH groups (1.39 μm)	Ge–OH groups (1.41 μm)	Molecular water (1.42 μm)	Si–NH groups (1.505 μm)
1	0.79 ± 0.02	–	–	–
2	0.85 ± 0.04	0.93 ± 0.04	–	–
3	0.92 ± 0.05	–	0.76 ± 0.02	–
4	–	–	–	0.71 ± 0.02

Table 3. Arrhenius parameters for various samples of optical fibers

Sample no.	k, dB/km h^x		
	at 1.39 μm	at 1.41 μm	at 1.505 μm
1	$3.89 \times 10^7 e^{-\frac{72.43}{RT}}$	–	–
2	$1.61 \times 10^{10} e^{-\frac{83.82}{RT}}$	$8.8 \times 10^{12} e^{-\frac{108.19}{RT}}$	–
3	The experimental data obtained are insufficient to calculate the preexponential factor and activation energy		
4	–	–	$3.51 \times 10^7 e^{-\frac{95.04}{RT}}$

groups. Therefore, the corresponding absorption band intensities also decrease.

CONCLUSIONS

The rates of increase in the optical losses of molecular-hydrogen-saturated optical fibers upon heating depend on the fiber-core composition. The threshold temperatures of the onset of interaction between molecular hydrogen and various silicate matrices are also different. For each type of optical fiber, we propose temperature conditions for their fastest saturation by H_2 without chemical interaction between molecular hydrogen and the glass.

The threshold temperatures depend strongly on the concentration of dopants in the fiber core. For example, in standard low-doped germanosilicate sample 1, Si–OH groups begin to form only at 300°C, whereas in high-doped sample 2, this phenomenon starts at 200°C. The intensity of absorption by the Si–OH groups at 1.39 μm reaches 200 dB/km in sample 2 at 250°C before leveling off, whereas in low-doped sample 1 the absorption does not reach this value even at 350°C.

Heavily doped sample 2 features a rapid increase in absorption by Ge–OH groups, which is more intense than the absorption by Si–OH groups. In sample 1 with low germanium content, the band at 1.41 μm was not detected at all.

The nitrosilicate matrix of the fiber 4 core is less sensitive to chemical interaction with molecular hydrogen, although it has a high (more than 4 at. %) nitrogen concentration. Even after annealing at $T = 650$°C, the band at 1.39 μm is an order of magnitude smaller than that in the germanosilicate samples held at 250–350°C. Apart from the band at 1.39 μm, the spectrum of fiber 4 contains a more intense band at 1.505 μm, which is associated with absorption due to the Si–NH bond vibrations. However, this band increases at relatively high (above 400°C) temperatures.

Optical fiber 3 contains a low phosphorus concentration; the threshold of interaction with molecular hydrogen in this fiber is higher than that in germanosilicate samples and is lower than in the nitrogen-doped optical fiber.

Apart from the increase in the optical absorption by hydroxy groups, we would like to note a strong increase in losses in the long-wavelength range for fiber 3 and in the short-wavelength range for fiber 2.

Thus, the kinetics of interaction between glasses and molecular hydrogen depends substantially on their compositions.

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