Journal of Non-Crystalline Solids 355 (2009) 1075–1079

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Photoinduced changes in UV absorption spectra of nitrogen-doped silica caused by exposure to ArF excimer laser

Alexey V. Lanin *, Artem V. Kholodkov, Oleg V. Butov, Konstantin M. Golant

Kotel'nikov Institute of Radio-engineering and Electronics, Russian Academy of Sciences, Mokhovaya 11-7, Moscow 125009, Russia

ARTICLE INFO

Article history:
Available online 21 May 2009

PACS:
270.050
310.010
310.070
430.400

Keywords:
Optical fibers
Hydrogen in glass
Oxynitride glasses
Defects
Absorption
Photoinduced effects
Silica
Nitrogen-containing glass

ABSTRACT

Absorption spectra of high-purity silica, in which 1.2% or 3.0% oxygen atoms are replaced by nitrogen, are measured in the spectral interval of 3.0–6.5 eV. Photoinduced changes of these spectra when exposed to 193 nm wavelength excimer laser radiation, pulse intensity being ~50 mJ/cm^2, are examined. Absorption spectra relaxation under subsequent annealing as well as changes brought about by saturation of glass with molecular hydrogen are studied. Parts of graded-index fiber ~1 mm in length and 200 μm thick transverse slices of a fiber preform served as samples. It is found that exposure of fiber samples to laser irradiation brings about a significant decrease of initially more intense absorption band of Si-ODC in the region of 5.0 eV and an increase of initially less intense band centered at 5.8 eV at a time. In bulk samples correlation of these bands is opposite, photoinduced changes are less expressed against structureless absorption tail increase in the spectral interval of 3.0–6.5 eV. It is shown that subsequent 20 min 700 °C annealing leads to the relaxation of photoinduced changes in absorption spectra in bulk and fiber samples. By placing irradiated samples into molecular hydrogen atmosphere at room temperature absorption bands are suppressed and transparency at shorter wavelengths of UV region is increased. Data obtained is discussed in the context of photosensitivity of nitrogen-doped silica-core fibers, which serve a technological platform for thermoresistant in-fiber Bragg gratings fabrication.

1. Introduction

Nitrogen doping of silica in the course of plasma-chemical deposition is used to create refractive index profile in fibers [1]. Such fibers are known to be photosensitive [2]. In-fiber Bragg gratings can be written into them by standard method, provided 193 nm wavelength laser irradiation is applied.

The advantage of gratings in nitrogen-doped fibers is that gratings' parameters show more stability at elevated temperatures [3] and their resistance to ionizing irradiation is relatively high [4]. That explains why Bragg gratings written in nitrogen-doped fibers can be applied as sensing elements in fiber sensors [5].

As it was established earlier, even insignificant (in the scale of several at.%) replacement of oxygen by nitrogen in amorphous silicon dioxide network results in the appearance of absorption bands in the UV region [6]. It is shown that in particular in nitrogen-doped silica rather intense absorption bands in the region of 5.0 and 5.8 eV are observed. Five electron volt (248 nm wavelength) band corresponds to a singlet-to-singlet transition of silicon oxygen deficient center (Si-ODC). High Si-ODC content in nitrogen-doped silica is explained by oxygen deficit, which is intrinsic condition of plasma-chemical process in the course of nitrogen-doped silica synthesis [1].

Band in the region of 5.8 eV is associated with transitions between the levels of some other diamagnetic center, possibly Si-ODC, modified by the presence of one atom of nitrogen in the vicinity. To this points linear character of dependence of 5.8 eV absorption band intensity on nitrogen concentration and lack of ESR signal in non-irradiated samples [6].

Important distinctive feature of photosensitivity of nitrogen-doped silica fibers is negative impact of dissolved hydrogen molecules in the glass on the rate of Bragg grating formation. Unlike germanium-doped silica fibers, in which the presence of hydrogen molecules leads to a significant increase of Bragg grating formation rate [7], presence of hydrogen molecules in glass of nitrogen-doped silica fibers significantly slows down this process [8,9]. It is of interest that hydrogen molecules diffusion in the core region with already written grating causes irreversible changes in the transmission spectrum of the grating [10].

Regardless experimental data accumulated on photosensitivity microscopic mechanism, its particular features, which result in more stable Bragg gratings formation in nitrogen-doped silica fibers remain unclear. Supposedly a greater thermoresistance is most likely associated not with electron rearrangement (defects recharge), but rather with the formation of a photoinduced periodic

* Corresponding author. Tel.: +7 9161707136; fax: +7 4955269152.
E-mail addresses: lanin@fo.gpi.ru, alexey_lanin@mail.ru (A.V. Lanin).

0022-3093/$ - see front matter © 2009 Published by Elsevier B.V.
doi:10.1016/j.jnoncrysol.2009.01.044

structure in a spatial nitrogen impurity distribution along fiber core, which build up the grating [5]. Formation of the above structure in its turn is brought about by local reconstruction of the glass network, appeared due to photo-stimulated excitation with a subsequent chemical bond rupture and nitrogen escape into the neighboring quasi-stable site. What remains clear is that one can expect changes in the UV absorption spectra of 'ordinary' as well as 'modified' Si-ODCs, insofar photoinduced reconstruction of nitrogen impurity centers in silicon dioxide network occurs.

In this report we present experimental results on changes observed in absorption spectrum of nitrogen-doped silica glasses and fibers in the UV region when exposed to ArF excimer laser irradiation at 193 nm wavelength. Besides in this report we offer for discussion the results obtained in the process of observation of absorption spectra restoration in the course of irradiated glass annealing and reaction of the spectra to glass saturation with molecular hydrogen. The experiments are carried out to obtain additional information relating possible mechanisms of nitrogen-doped silica-core fibers photosensitivity.

2. Experimental procedures

For samples served short fiber pieces and thin transverse slices of the preform. Parts of graded-index nitrogen-doped silica fiber ~1 mm in length, core of about 50 μm in diameter, maximum N content being ~1.2 at.% are formed and built into a fiber line by means of cutting and splicing. Input and output of probe irradiation to sample is carried out by means of a graded-index fluorine-doped-silica-core/fluorine-doped-silica-cladding fiber. UV signal is effectively delivered via pigtails from the lamp to spectrometer when recording, as loss in the pigtails on 200 nm wavelength does not exceed 3 dB.

To suppress cladding modes relatively long (of about 1 m) pigtails with loops, 1 cm in diameter each, are used. Nitrogen-doped silica core fiber and pure silica core fiber are especially fabricated for these measurements from the preforms, synthesized by SPCVD method and have in the outer diameter 125 μm. Detailed description of the technology one can find in Ref. [1].

Method of absorption spectrum recording of a short part of fiber is similar to the one described in Ref. [11]. In this reference connecting of pigtails with the part of fiber under study is carried out by V-grooves. Splicing added much to the experimental method as there appeared no need to find appropriate and transparent in the UV region immersion liquid.

Transmission spectra are recorded in 200–400 nm wavelengths band with the help of Ocean Optics S2000 spectrometer. Deuterium lamp is used as a source of light, emission of which is focused by a silica lens on the input end of the pigtail. Average emission power of the lamp in the range of 186–360 nm reaches 1.8 mW. Emission spectrum transmitted through the pigtails is used as a reference to get absorption spectrum of the parts of fiber under study.

UV irradiation of samples spliced into the measuring fiber line is carried out by side irradiation of CL5000 ArF excimer laser beam (193 nm wavelength), energy density per pulse being ~50 mJ/cm^2. Pulse duration and repetition rate are ~8 ns and 100 Hz, respectively.

Several identical samples are prepared. One sample after irradiation is saturated with hydrogen during 240 h at room temperature, pressure being 40 bar. Estimated hydrogen molecules content in the sample reaches no less than 10^{19} cm^{-3}. Another non-irradiated sample is also saturated to see absorption spectrum reaction of such 'hydrogen-loaded' glass to subsequent irradiation.

One more irradiated sample is annealed during 20 min in air in the oven, temperature being 700 °C. Non-irradiated sample is also annealed to reveal the contribution of the annealing as such to changes of absorption spectra in non-irradiated glass.

Similar experiments are carried out with double side polished transverse slices of the preform with nitrogen-doped silica core. Diameter of doped core is ~4 mm, slices thickness is ~200 μm. Preform with a step index profile is especially synthesized for these experiments using the SPCVD technology. Nitrogen content in glass core, estimated as to refractive index profile comprises ~3 at.%. This exceeds three times average nitrogen content in graded-index fiber core. Preform slices are irradiated perpendicular to the surface step-by-step increasing the dose. Absorption spectrum of the sample is measured after each portion of irradiation in the wavelengths range of 186–486 nm with the help of Perkin Elmer Lambda 900 spectrometer. Wide dynamic band of spectrometer and small thickness of slices allowed us to operate with samples irradiated to the dose of ~5 kJ/cm^2, which exceeds by an order of magnitude value of maximum irradiation dose, to

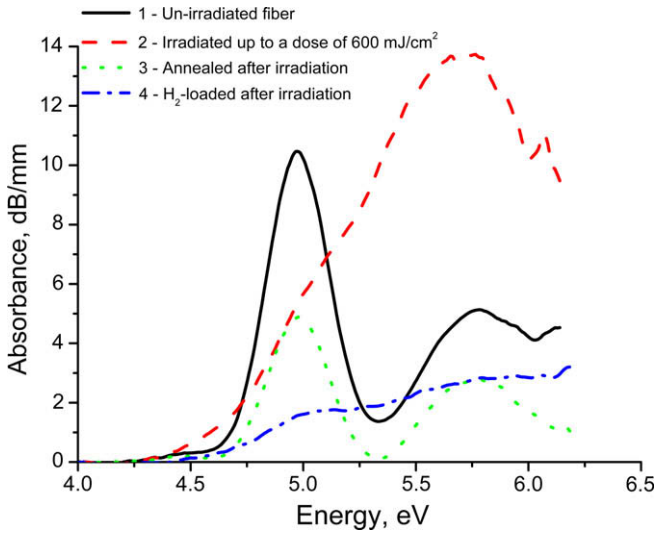

Fig. 1. UV absorption spectrum before (curve 1) and after (curve 2) side exposure of nitrogen-doped silica-core fiber to ArF laser beam up to a dose of 0.6 kJ/cm^2. Absorption spectra recorded after annealing of irradiated samples in air (curve 3) and hydrogen loading (curve 4) are also depicted.

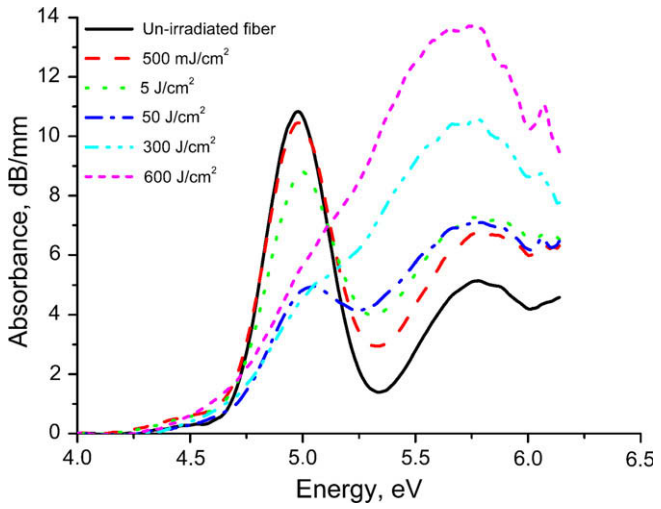

Fig. 2. UV absorption spectra of a nitrogen-doped silica-core fiber subjected to different doses of ArF laser exposure.