Hydrogen Enhancement of Near-UV Photosensitivity of Germanosilicate Glass

D.S.Starodubov, E.M.Dianov, S.A.Vasiliev, A.A.Frolov, O.I.Medvedkov

Fiber Optics Research Center at the General Physics Institute,
Russian Academy of Sciences, 38 Vavilov st., Moscow 117942, Russia

A.O.Rybaltovskii

Science-Research Institute of Nuclear Physics, Moscow State University, Moscow 119899, Russia

V.A.Titova

Research Institute of Diagnostic and Surgery, 86 Profsouznaya st., Moscow 117837, Russia

ABSTRACT

The effect of hydrogen loading on near-UV photosensitivity of germanosilicate glass is studied. The enhanced bleaching of 390 nm luminescence band and 240 nm absorption band, as well as enhanced growth of 650 nm luminescence band in hydrogen loaded samples is observed. The increase of paramagnetic GeE' defects concentration and creation of hydrogen related paramagnetic H(II) centers is obtained. Long period index gratings with low insertion loss and index change as large as $4x10^{-4}$ are fabricated by near-UV argon laser radiation in hydrogen loaded fibers. The effect of γ irradiation on the properties of the fabricated gratings is reported.

1. INTRODUCTION

The problem of photosensitivity of germanosilicate glasses and optical fibers have attracted much attention after the fabrication of index gratings in the fiber core[1]. It has been found that the induced index change can be increased by treatment of the fibers in hydrogen atmosphere, however the role of hydrogen influence as well as the mechanism of the index change in the fiber core is not totally explained yet[2]. It is now accepted, that the photosensitivity appears in germanosilicate glass, which is synthesized in reduced conditions and connected with germanium oxygen deficient centers (GODC)[3,4]. These defects are responsible for strong absorption at 240 nm and weak absorption at 330 nm. The corresponding bands are ascribed to singlet - singlet and singlet - triplet transitions of the defects[4].

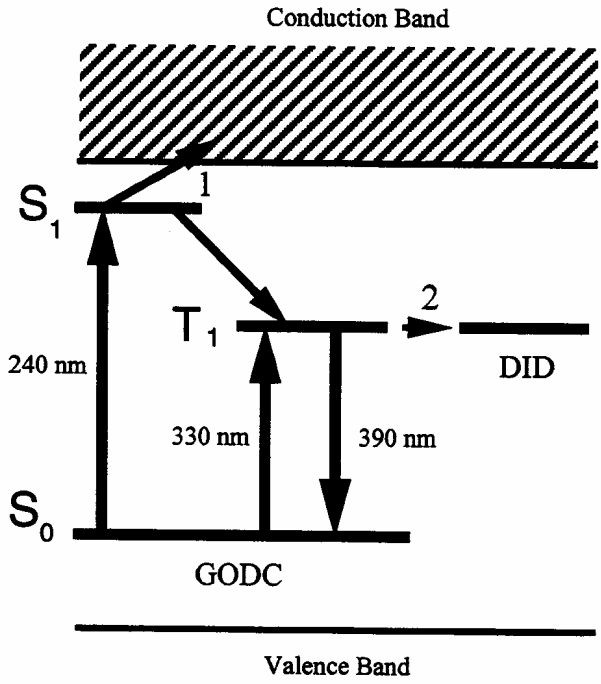

Fig.1. *Band diagram for the processes in Ge doped silica glass. GODC is germanium oxygen deficient defect. It has singlet - singlet S_0 - S_1 absorption at 240 nm and singlet - triplet S_0 - T_1 absorption at 330 nm. Triplet - singlet S_0 - T_1 transition is responsible for blue luminescence with maximum at 390 nm. There are two ways of GODC photodestruction: 1) The release of electron from excited singlet or higher-energy excited states, 2) The structural transformation from triplet state. One of the products of this reaction is drawing-induced defect (DID), which is responsible for red luminescence with maximum at 650 nm.*

There are several different physical reasons which can explain the change of index in germanosilicate glass. From one point of view the huge change of absorption in deep UV region can explain the index changes up to $3x10^{-4}$. This color center mechanism involves the photoionization of oxygen-deficient centers and the contribution of induced defects absorption due to Kramers-Kronig relation[5,6]. The other explanation involves the structure change of germanosilicate glass under UV irradiation. It has been experimentally demonstrated that the induced index change in germanosilicate glass has correlation with densification of the glass[7] and increase of tension[8]. These changes are in favor of structural modification of the glass under UV excitation. The nature of these changes is not quite clear, since the obtained changes can not be explained by only the relaxation of initial stress[8]. Moreover there is a lot of contradictions in reports about the correlation of luminescence changes and index change in the fibers during UV exposure[9-11]. The available features of photosensitivity of germanosilicate glass can not be explained with the simple model of one way of GODC photodestruction[12,13].

One of the possible ways to solve the present contradictions of the photosensitivity features is to consider two ways of GODC photodestruction[14], namely due to photoionization from excited singlet state and due to triplet state related photochemical reaction[15,13,16]. The presence of triplet state related mechanism has been experimentally demonstrated using the direct excitation of triplet state by near-UV light[13,17,18].

The presence of two ways of GODC photodestruction raises up a question about the contribution of each way to the change of refractive index. Mention should be made, that the experiments with singlet state excitation by 5 eV light should involve both mechanisms of photodestruction because of fast and efficient singlet to triplet relaxation. More than 90% of defects, which are excited to singlet state come to triplet state at room temperature[19], therefore the experiments with singlet state excitation can not give the answer about the contribution of singlet state related photoionization mechanism to the index change. On the other hand we have experimentally demonstrated the fabrication of index gratings in germanosilicate fibers with index change as large as $\sim 2 \times 10^{-4}$ by direct triplet state excitation[20]. Moreover we have found that triplet state related mechanism is responsible for efficient fabrication of drawing-induced defects (DID) with luminescence band at 650 nm[13,18], which was found to correlate with index change during 5 eV singlet-singlet excitation[21].

To obtain the further confirmation of the important role of triplet state related mechanism of GODC photodestruction in this paper we have investigated the effect of hydrogen loading on near-UV photosensitivity of germanosilicate glasses and fibers.

2. EXPERIMENT

We have studied 8 mol.% GeO_2 - doped 300 μm thick fiber preform samples in our experiments on luminescence changes during near UV exposure. During the measurements of luminescence dynamics the UV radiation was focused into ~ 60 μm spot by a fused silica lens. Two channels of side luminescence registration were used to measure the dynamics of blue and red luminescence at the same time. In experiments with the measurements of 240 nm singlet-singlet absorption we have used 10 mol.% GeO_2 doped 30 μm thick films on silica glass substrates. The films were prepared by MCVD process. The films were covered with aluminum foil with 2 mm aperture in order to use the same region of the film in luminescence and absorption measurements. Room temperature hydrogen loading with 2 weeks duration was performed at hydrogen pressure 24 atm. for all the samples. The Coherent Innova 200 argon laser in near-UV multiline mode with external line selection by a prism was used in our experiments. UV light was modulated by a chopper for luminescence measurements. The induced paramagnetic centers were studied using 9.4 GHz ESR spectrometer.

3. LUMINESCENCE AND ABSORPTION STUDIES

During the experiments with hydrogen loaded samples we have observed the increase of photosensitivity to near-UV light. The strong increase of red luminescence signal and increase of degree of blue luminescence bleaching were observed. The obtained time dependencies of 390 nm blue luminescence bleaching and increase of 650 nm red luminescence band for hydrogen - free and hydrogen - loaded samples during near UV exposure are shown in Fig.2.

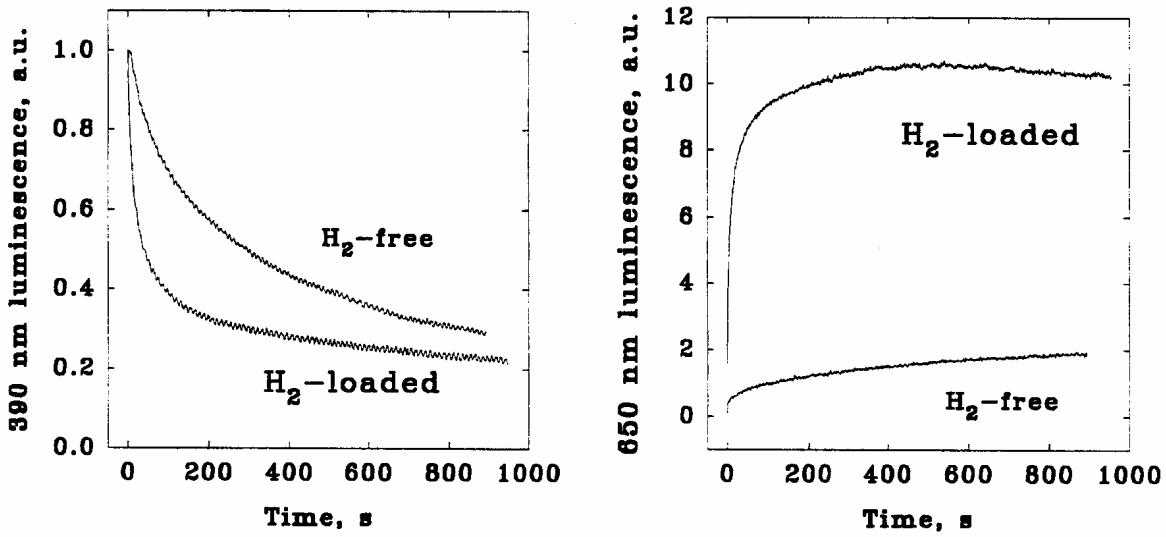

Fig.2. *Dynamics of 390 nm blue luminescence bleaching and 650 nm red luminescence growth in the samples with and without hydrogen loading.*

To understand the difference in defect transformation mechanism we have compared the luminescence spectra for hydrogen free and hydrogen loaded samples with near-UV excitation. Our measurements have shown, that the spectra of blue and near-UV induced red luminescence are almost the same in the samples with and without hydrogen, we have seen only one luminescence band with maximum at 650 nm with our near UV excitation of luminescence. The presence of this red luminescence band with maximum at 650 nm in the samples without hydrogen further demonstrates, that this luminescence is not connected with hydrogen - associated defect[22].

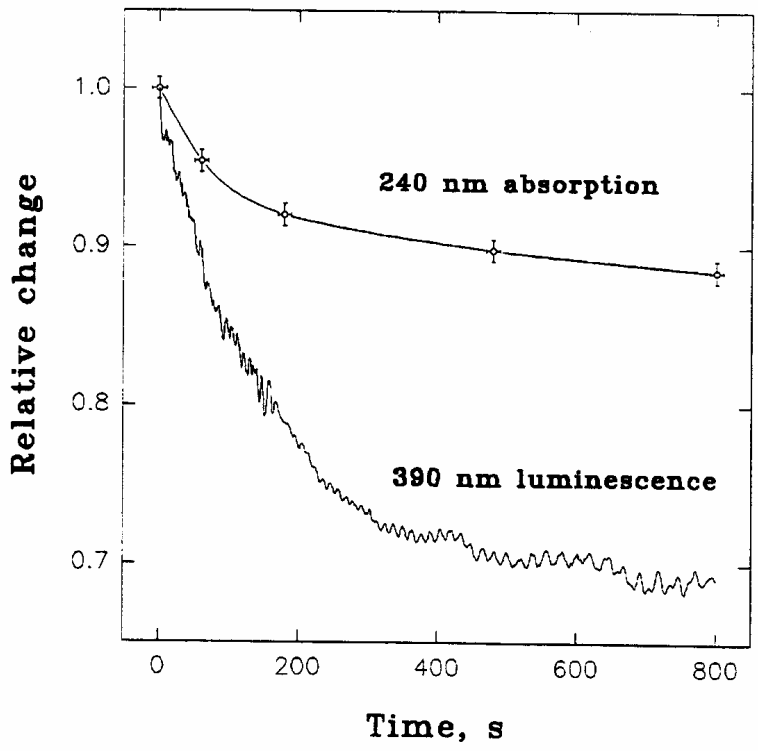

Fig.3. *Time dependencies of 390 nm blue luminescence and 240 nm absorption in hydrogen loaded 10 mol.% GeO_2 doped film exposed to 150 mW of 351 nm linearly polarized light.*

To get the final proof that we observe the photodestruction of GODC by near UV light we have studied the behavior of 5 eV absorption band in near UV processed samples. In the first experiment we have exposed hydrogen-free and hydrogen loaded films by 1.4 W of multiline near-UV radiation through 2 mm diaphragm (the intensity ~50 W/cm^2) for 4 hours. The relative decrease of absorption at 242 nm was 10% in hydrogen-free sample and 55% hydrogen loaded sample. Then we have studied the dynamics of the singlet-singlet absorption band bleaching under triplet state excitation in hydrogen loaded samples. Figure 3 illustrates the dynamics of 242 nm absorption band bleaching and decrease of blue 390 nm luminescence during exposure of germanosilicate films by 150 mW of 351 nm linearly polarized light. The bleaching dynamics are similar, however one can see the difference in degree of bleaching for 390 nm luminescence and 242 nm absorption. This difference is connected with orientational behavior of the luminescence bleaching by near-UV linearly polarized radiation, which we have demonstrated recently[23]. The analogous behavior of the bleaching has been reported for 266 nm excitation[15].

4. ELECTRONIC PARAMAGNETIC RESONANCE STUDIES

To further understand the role of hydrogen in triplet - related photodestruction mechanism we have performed ESR studies of irradiated samples. For near-UV exposure of hydrogen - free samples we have observed the formation of only E' centers (see Fig.4) in contrast with 5 eV laser excitation where the signal from electron trap Ge(1) centers is also observed. The estimation of concentration of induced E' centers after 4 hours of 1.4 W exposure in the first experiment was ~$2x10^{18}$ cm^{-3}. This result is in agreement with our notion, that there is no releasing of electron (no photoionization) during triplet excitation of GODC with its trapping on Ge(1) center. Another possible explanation of this observation is that near - UV radiation can effectively bleach Ge(1) centers.

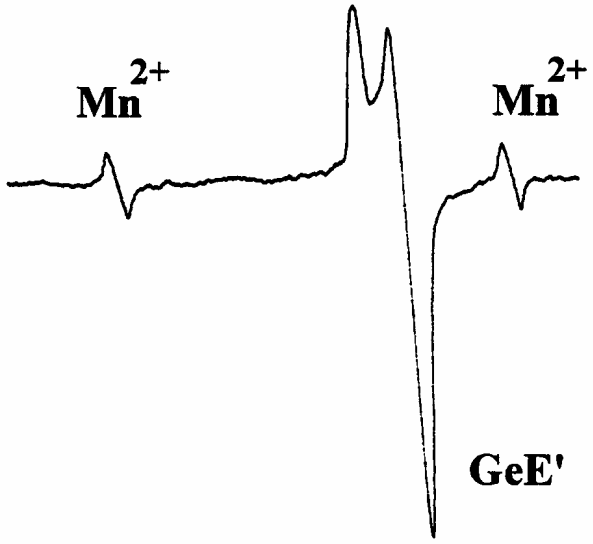

Fig.4. *ESR spectrum of hydrogen-free germanosilicate film after near-UV Ar laser exposure. Mn^{2+} marker is used to show the field scale.*

In hydrogen - loaded samples we have obtained efficient formation of GeE' centers and H(II) hydrogen - associated defects, which are responsible for 11.9 mT doublet in electronic spin resonance. The presence of the hydrogen - associated centers is a direct confirmation of hydrogen related reaction in germanosilicate glass. The estimated concentrations of the hydrogen - associated centers and E' centers are ~$4x10^{18}$ cm^{-3} and $2x10^{19}$ cm^{-3} correspondingly. Mention should be made, that the concentration of the induced hydrogen - associated centers can be even higher, then concentration of E' centers after near-UV exposure.

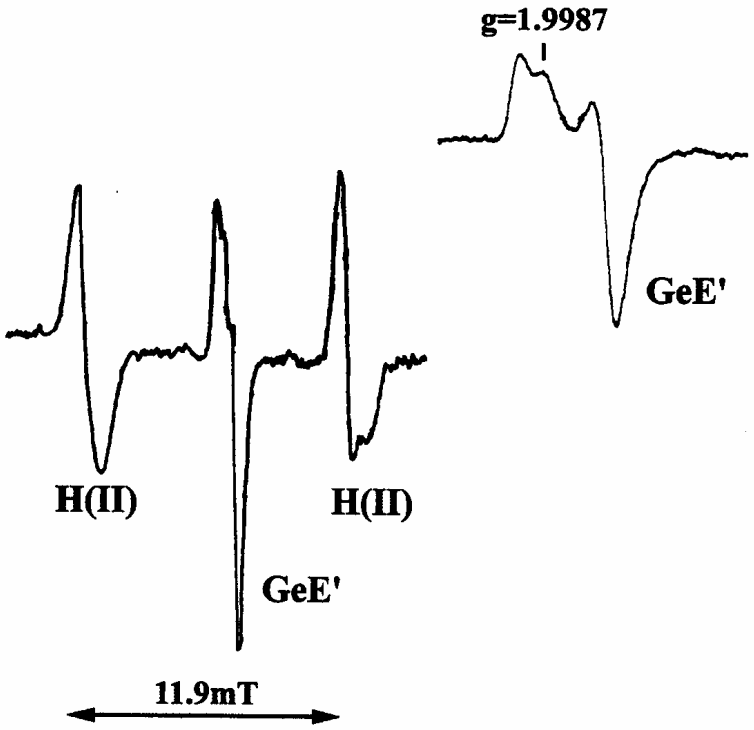

Fig.5. *ESR spectrum of hydrogen loaded germanosilicate film after near UV Ar laser exposure. The spot diameter is 2 mm, UV power is 1.4 W, irradiation time is 3 min. The blowup demonstrates the new band with g=1.9987±0.0005.*

In our experiments with hydrogen-loaded samples we have observed the new ESR signal with g = 1.9987±0.0005 (see Fig.5) [25]. The absence of this center in hydrogen - free samples gives the evidence, that the formation of this new signal is controlled by hydrogen.

In all ESR measurements we couldn't see the signal from paramagnetic nonbridging oxygen hole centers (NBOHC) even in cooled samples[26,27]. This result demonstrates, that the fabricated by near UV light DID is not NBOHC[21], but probably diamagnetic germanium-related defect. Our annealing experiments have shown that DID is stable at least to 350°C. This result is in agreement with results of recent experiments with proton implanted germanosilicate glasses[28], and also demonstrates the difference of NBOHC and DID.

5. NEAR UV INDUCED FIBER GRATINGS IN HYDROGEN LOADED FIBERS

The hydrogen enhancement of the near-UV photosensitivity is of particular interest for the fiber index gratings formation in context of our experiments with partial erasure of long-period grating by UV argon laser radiation and fabrication of long-period gratings by near-UV light. We have used our point by point technique to compare the grating fabrication efficiency in hydrogen-free and hydrogen loaded fibers. The obtained result for 10 mol.% GeO_2 doped fiber with cutoff wavelength at ~1 μm is shown in Fig. 6. We have found that the essential feature of the near-UV fabrication technique is very low insertion loss in the fiber after the grating preparation. The estimation of the loss gives the value less than 5 dB/m for CW near UV light. At the same time the value of the near UV induced index change in the samples with hydrogen increased up to $\sim 4 \times 10^{-4}$. These features demonstrate the most important benefit of near UV fabrication method compared to the usual method of gratings fabrication with 240 nm light.

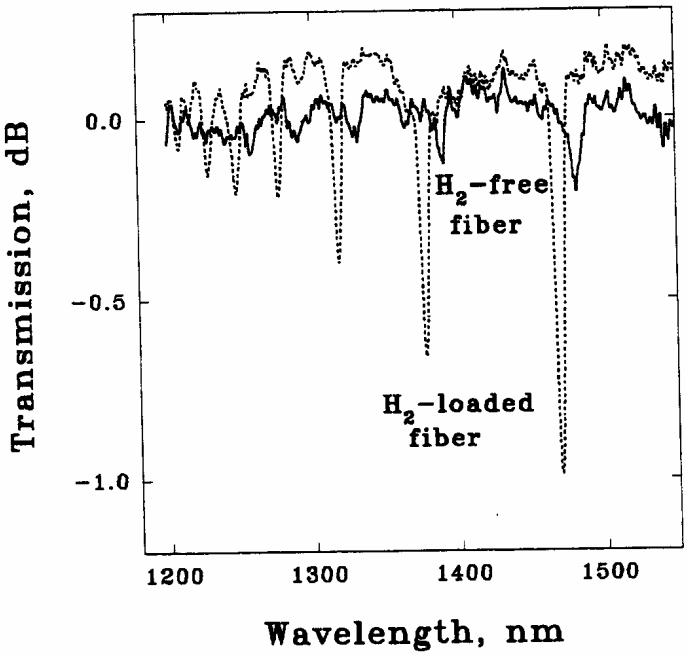

Fig.6. *Transmission spectra of long-period gratings, which were fabricated in 10 mol.% GeO_2 doped fiber with and without hydrogen loading. The writing power is 15 mW, the wavelength is 334 nm.*

We have made attempts to write the gratings using pulsed near-UV light, namely third harmonic of Nd:YAG laser. Our experiments have shown, that for pulsed radiation the losses are much higher in hydrogen loaded fibers. We think that these losses appear due to multiphoton processes, which can lead to release of electrons and new defect creation.

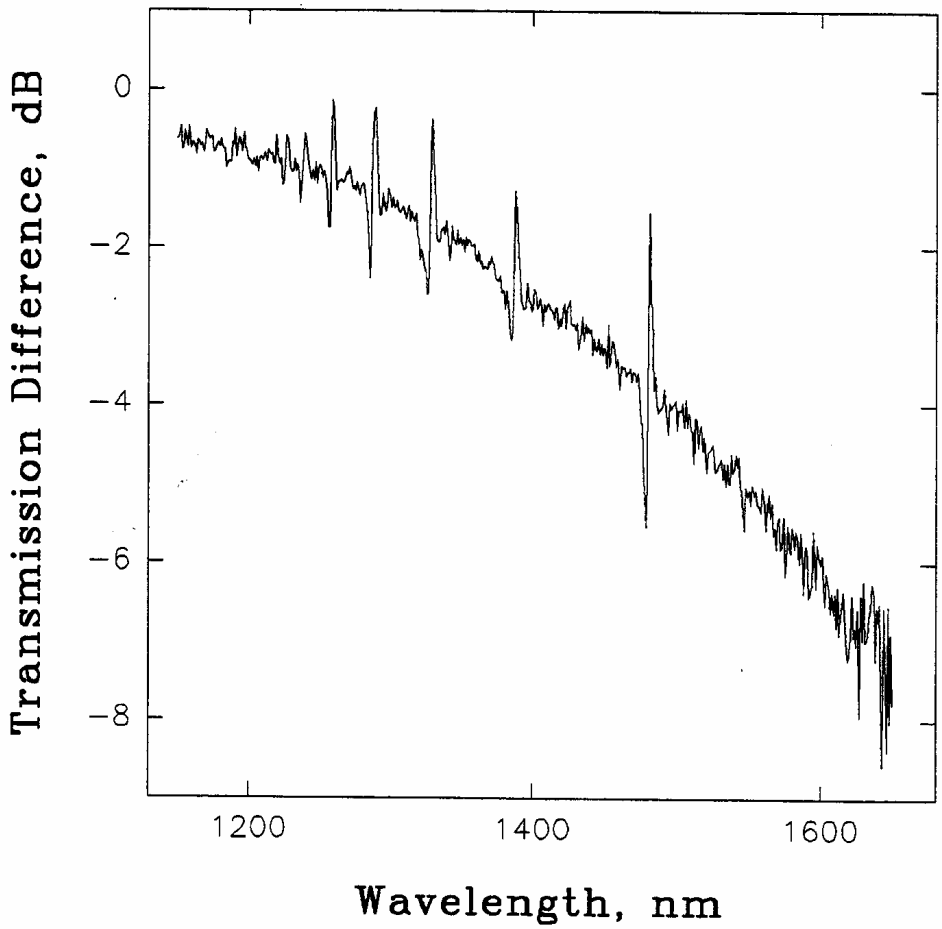

Fig.7. *The spectral dependence of the difference in transmission for the long period grating in hydrogen loaded fiber, which appeared after γ irradiation with doze 10^4 rad.*

The long-period gratings, which were written with near UV technique, were tested for resistance to γ irradiation. The irradiation doze was 10^4 rad. For the sample without hydrogen loading we have obtained only the small change in the strength of the grating resonances. At the same time the grating in hydrogen loaded sample have demonstrated higher sensitivity: we have observed also the change in the peaks positions. The difference spectrum for the long period grating in hydrogen-loaded fiber before and after the irradiation is shown in Fig.8. We hope that this property of long-period gratings can be used for sensors.

6. CONCLUSIONS

In the present paper we report for the first time to our knowledge the activation of near-UV photosensitivity of germanosilicate glass by hydrogen. The enhanced near-UV bleaching of 390 nm luminescence band and 242 nm absorption band in hydrogen - loaded samples is obtained. ESR analysis of near UV processed samples gives the evidence of photochemical reaction of germanium doped glass with hydrogen. Near-UV induced luminescence band with maximum at 650 nm is connected with germanium-related diamagnetic defect, and can be increased by hydrogen loading. The enhanced fabrication of index gratings with low insertion loss in hydrogen-loaded fibers demonstrates the advantage of index grating fabrication by near-UV light.

7. ACKNOWLEDGMENTS

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