Journal of Non-Crystalline Solids 357 (2011) 1985–1988

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

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

Effects induced by 4.7 eV UV laser irradiation on pure silica core multimode optical fibers investigated by in situ optical absorption measurements

Fabrizio Messina *, Francesco Comandè, Marco Cannas

Dipartimento di Scienze Fisiche ed Astronomiche, Università di Palermo, Via Archirafi 36, I-90123 Palermo, Italy

ARTICLE INFO

Article history:
Received 16 June 2010
Received in revised form 19 January 2011
Accepted 24 January 2011
Available online 9 March 2011

Keywords:
E' centers;
Laser irradiation;
Hydrogen diffusion

ABSTRACT

We investigated by in situ optical absorption measurements the effects induced by 4.7 eV UV laser irradiation on pure silica core optical fibers. Laser irradiation with 100 MW cm^{-2} laser intensity generates in the fiber E' centers which partially decay after irradiation due to their reaction with diffusing H_2. An absorption band peaked at 5.3 eV is observed to grow in the post-irradiation stage with a kinetics anti-correlated to the decay of the 5.8 eV band of the E' centers. The defect absorbing at 5.3 eV is proposed to be formed by trapping on pre-existing precursors of hydrogen atoms made available by breaking of H_2 on E'. We also show by repeated irradiation experiments that the 5.3 eV-absorbing center is photochemically destroyed by 4.7 eV laser light, and we estimate the cross section of this process. Possible structural models for this defect are discussed.

1. Introduction

Although several works have addressed laser-induced generation of defects in bulk SiO_2 [1–7], only a few of them have directly dealt with optical fibers, one of the most important technological applications of SiO_2. Indeed, it has generally been assumed that the understanding obtained from the study of bulk SiO_2 or of fiber preforms could be applied as well to optical fibers. Thus, only a few data concerning the effects induced by laser light on the optical absorption (OA) properties of optical fibers have been reported in literature so far [8–10], especially in the ultraviolet (UV) range where the absorption bands of the main SiO_2 point defects are located [11–13]. This is an important issue especially for fibers specifically designed to be used for the transmission of UV signals, that is multimode fibers with large core diameters fabricated from OH-rich SiO_2 [12,14]. One of the main deterioration mechanisms of amorphous SiO_2 upon exposure to high intensity laser radiation is the generation of optically absorbing point defects. The color center which usually dominates the optical absorption (OA) spectrum of irradiated SiO_2 in the UV range is the well known E'_γ center, often indicated simply as E' absorbing at 5.8 eV [11–13]. The main structural feature of this defect is a Si atom bonded to three oxygen atoms and hosting an unpaired electron ($\equiv Si^{\bullet}$). Aside from the most common E'_γ, other variants of the E' center (E'_α, E'_β, and E'_δ) have been identified based on their different electron spin resonance (ESR) signals [11,15–17]. Their absorption properties are still a matter of debate.

Studies on γ and X-irradiation of optical fibers have shown that a high concentration of OH groups generally brings about an increased resistance to irradiation [18,19]. Studies on the response of high-OH fibers to UV light have identified E' centers as the main generated defects, and have suggested them to arise from photochemical rupture of Si – H precursors [9,10]. Also, the concentration of induced E' centers was found to be significantly reduced if the fiber is loaded with high concentrations of H_2 [9]; this is likely due to passivation of induced E' centers due to their reaction with diffusing hydrogen, as observed in bulk SiO_2 [6,7,20–25]. Comparison of these studies with literature on bulk SiO_2 actually suggests quite a similar phenomenology triggered by laser irradiation in the two physical systems. Still, it cannot be taken for granted that bulk SiO_2 is equivalent to fiber-SiO_2 as concerns resistance to laser irradiation. In fact, it has been often suggested that the fiber drawing process potentially creates in the fiber defective sites which may be precursors for the generation of defects upon irradiation or introduces unresolved stresses which make the material more prone to be damaged by laser light [11,12]. A useful experimental approach to investigate these issues is the measurement in situ of radiation-induced OA, previously applied to investigate laser-induced kinetics of point defect generation and annealing in bulk SiO_2 [6,7,25]. Kinetic data are often able to yield information on defect generation that are unavailable by measuring radiation-induced effects in stationary conditions only. In the present paper we apply this approach to study the generation of point defects in UV-transmitting multimode optical fibers under high intensity UV laser irradiation.

2. Materials and methods

We performed experiments on standard commercial pure SiO_2 core/F-doped SiO_2 cladding step-index multimode optical fibers

* Corresponding author. Tel.: +39 0916234218; fax: +39 0916162461.
E-mail address: fmessina@fisica.unipa.it (F. Messina).

0022-3093/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnoncrysol.2011.01.040

provided by Avantes, with 200 μm core and 20 μm cladding diameters. These are fibers specifically designed for UV transmission, whose synthetic silica core material nominally features ~1000 ppm in weight of Si–OH impurities, metallic impurities below 10 ppb, and an unstructured tail-shaped absorption spectrum in the UV range with absorption coefficients of the order of ~1 dB/m [26]. After removing the polyamide coating, fiber samples were irradiated at room temperature by 4.7 eV photons emitted by a pulsed (pulsewidth $\tau = 5$ ns) Q-switched Nd:YAG laser system. The laser was weakly focused so as to irradiate only a 3 mm-long portion of the fiber. Laser beam hit the sample perpendicularly to the fiber axis. Data reported herewith were obtained by exposing the fiber to laser intensities between 10 MW cm^{-2} and 100 MW cm^{-2} and by using a pulse repetition rate of 5 Hz. Intensity values have been calculated without taking into account refractive effects taking place at the entrance of the beam within the fiber. During and after the end of each irradiation session, we measured in situ the induced OA variations (in the 200–400 nm range) of the fibers by an AVANTES AVS-S2000 spectrophotometer, equipped by a D_2 lamp source and a Charge Coupled Device (CCD) detector, and allowing a time resolution of 1 s. To this purpose, the fiber being irradiated was inserted in the all-in-fiber transmission line used to bring light from the lamp to the CCD, thus allowing to measure in real time the kinetics of induced OA from the variations of the signal revealed by the detector. This approach also guarantees that the measured signals are associated only to features induced in the fiber core. It turns out that also light from the D_2 lamp is able to induce OA variations in the fiber; nevertheless, we verified that these effects are always several orders of magnitude smaller than those induced by laser irradiation within our experimental conditions.

3. Results

We report in Fig. 1 a typical kinetics of the absorption spectrum as measured in situ in an optical fiber sample during and after the end of an irradiation session consisting in ~10^4 UV laser pulses of 100 MW cm^{-2} laser intensity. Absorption coefficients have been calculated based on the 3 mm length of the irradiated portion of the fiber. The main absorption signal generated by irradiation is the band peaked at 5.8 eV characteristic of E' centers [11–13], the peak absorption coefficient $\alpha(5.8\text{ eV})$ at the end of irradiation being $(1.60 \pm 0.02)\,\text{cm}^{-1}$, while minor contributions to the absorption spectrum for $E < 5$ eV cannot be ruled out. The concentration of E' centers, as deduced from $\alpha(5.8\text{ eV})$, is plotted against time in the inset of Fig. 1, revealing that laser-induced growth of the defects has saturated to a value of $(2.6 \pm 0.1) \times 10^{16}\text{cm}^{-3}$ at the end of irradiation. After the laser is switched off, the induced 5.8 eV band undergoes spontaneous decay on a time scale of a few 10^3 s, as evidenced by data acquired at several delays after the end of irradiation (Fig. 1-(b)). On the other hand, a progressive increase of α in the post-irradiation stage is clearly observed in the spectral region between 4.5 eV and 5.3 eV. Least-square fitting of a representative difference absorption spectrum by a linear combination of two Gaussian bands (inset of Fig. 1-(b)) reveals that the observed modifications of the absorption spectrum can be described as the growth of a band peaked at (5.3 ± 0.1) eV with (0.68 ± 0.08) eV full width at half maximum (FWHM) concurrent to the decrease of the main peak at (5.86 ± 0.02) eV with (0.71 ± 0.02) eV FWHM. Satisfactory fits with these parameters can be obtained on the difference spectra calculated at all delay times. It is worth noting that the apparent redshift in time of the peak of the main band is actually an effect of the overlap with the growing contribution at 5.30 eV.

In Fig. 2 the post-irradiation kinetics of $\alpha(5.8\text{ eV})(t)$ detected on the peak of the absorption band of the E' centers is reported. We also show the kinetics of $\alpha(4.9\text{ eV})(t)$ as a measure of the amplitude of the 5.3 eV band growing in the post-irradiation stage evidenced by Fig. 1-(b). The spectral position of 4.9 eV (as opposed to the peak position) was chosen in order to avoid interference from the larger 5.8 eV band. Comparison between the decay kinetics of $\alpha(5.8\text{ eV})(t)$ and the growth of $\alpha(4.9\text{ eV})(t)$ clearly suggests an anticorrelation between the behaviors of the two contributions. The correlation plot in the

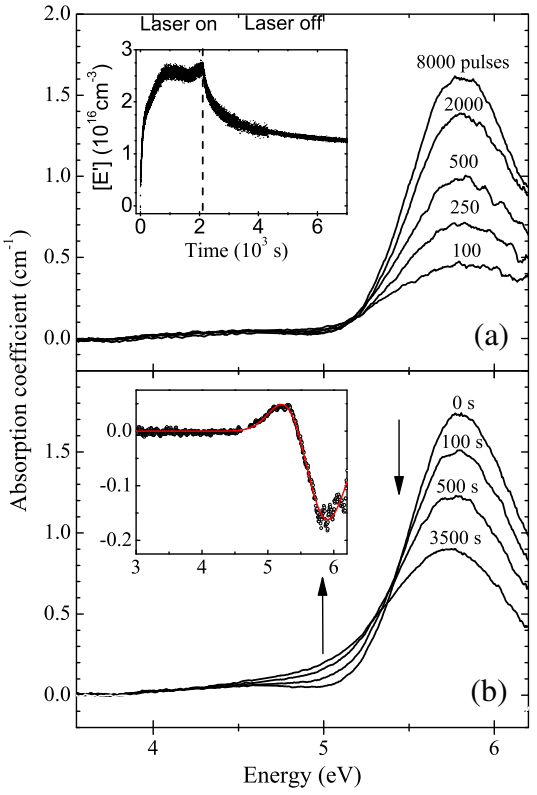

Fig. 1. Absorption spectrum measured in pure silica core optical fibers after selected numbers of pulses during (a) and at selected times after the end (b) of the Nd:YAG laser irradiation session. Labels in panel (b) represent delays from the end of the irradiation session, while the arrows highlight the modifications observed in the spectrum with growing time. Inset of panel (a): Kinetics of the E′ center concentration as deduced from the time dependence of the 5.8 eV absorption coefficient. Inset of panel (b): difference between the spectrum measured at t = 50 s after the end of irradiation and that measured at t = 0. The full red line is the result of least-square fitting of the difference spectrum with a linear combination of two Gaussian bands (see text for further details).

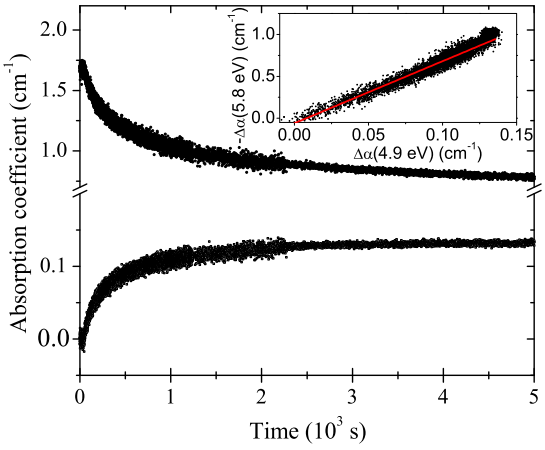

Fig. 2. Absorption coefficient $\alpha(5.8\text{ eV})(t)$ (full symbols) and $\alpha(4.9\text{ eV})(t)$ (open symbols) as a function of time t. The origin of the time scale corresponds to the end of the irradiation session. Inset: $\alpha(5.8\text{ eV})(0)$–$\alpha(5.8\text{ eV})(t)$ plotted against $\alpha(4.9\text{ eV})(t)$–$\alpha(4.9\text{ eV})(0)$. The full line ($r = 0.97$) was obtained by linear fitting data corresponding to $t < 2000$ s.

inset confirms this result, while evidencing possible small deviations at long times from anticorrelated time dependencies.

Finally, we performed a set of experiments aimed at investigating the effect of repeated irradiations: a sample which had been irradiated with 10^4 pulses of 100 MW cm^{-2} intensity was irradiated again ~1 h after the end of the first irradiation session by using a laser intensity $I_2 = 75$ MW cm^{-2}. By performing in situ OA measurements on the fiber being re-irradiated it turns out that the second irradiation bleaches the absorption at 4.9 eV grown during the post-irradiation stage. As a matter of fact, we observe a progressive reduction (Fig. 3) of α(4.9 eV) during the second irradiation, the bleaching being almost complete after a few 10^3 laser pulses. This effect is also accompanied by a regrowth of the 5.8 eV band which will not be dealt here. The efficiency of this bleaching process can be estimated by the initial annealing rate $\Gamma = \alpha^{-1}(d\alpha/\mathrm{dN})_{N=0}^{E=4.9eV}$, i.e. the initial decrease slope of α(4.9 eV), as estimated by a linear fit on the first ~10 points in Fig. 3, normalized for the absorption coefficient at 4.9 eV at the beginning of the re-irradiation experiment. By repeating the re-irradiation experiment as a function of I_2 we found out that the dependence of Γ on laser intensity is approximately linear (inset of Fig. 3). Preliminary data show, instead, that the intensity dependence of the induced 5.8 eV band is quadratic, in agreement with the previous finding on fused SiO_2 samples,[27] where this result was interpreted as an evidence of the E' centers being generated by a two-step process.

4. Discussion

The growth of the 5.8 eV band due to laser-induced E' centers is commonly observed as the main outcome of UV laser irradiation of bulk SiO_2 for intensities in the MW cm^{-2} range, as demonstrated by several previous works [1–7,13]. The efficiency of defect generation observed in the fiber (Fig. 1), 2.5×10^{16}cm^{-3} defects after 10^4 pulses, turns out to be one or two orders of magnitude higher than previously observed in bulk high-purity synthetic silica for comparable laser intensity levels [2,5,7]. On the other side, it is close to that typical of fused SiO_2 materials, where it was shown that UV-induced damage processes are assisted by two-step processes via inter-band electronic levels provided by impurities [27]. Still, the native absorption coefficient of the fiber material, $2\times10^{-3}cm^{-1}$ at 200 nm, is much lower than that of fused SiO_2, where impurity-related absorption is of the order of 1 cm^{-1} in the UV spectral range [27]. On one side, a precise quantitative comparison is hindered by the fact that we cannot exclude an enhancement of the defect generation efficiency in this experiment due to partially focusing of the laser beam inside the material due to the cylindrical profile of the fiber. On a qualitative basis, however, such results suggest that SiO_2 in the form of an optical fiber, although being very pure from the chemical point of view, is intrinsically much more sensitive to laser-induced generation of point defects than bulk SiO_2 due to stresses accumulated in the material during the fiber drawing process leading to the formation of high concentration of precursor sites for the formation of defects, e.g. oxygen vacancies or strained Si – O – Si bonds [11–13].

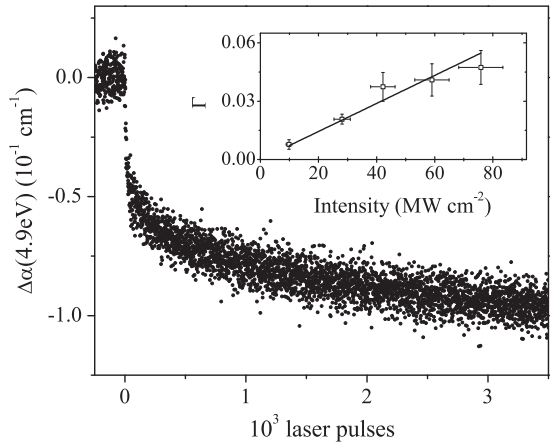

Fig. 3. Variations of the absorption coefficient at 4.9 eV observed during irradiation with 75 MW cm^{-2} laser intensity of a sample which had been previously irradiated with 10^4 pulses of 100 MW cm^{-2} intensity. Inset: normalized annealing rate Γ of the absorption coefficient at 4.9 eV as a function of laser intensity, least-square fitted by a linear function.

Post-irradiation decay of E' centers on a time scale of a few hours has been previously interpreted as a consequence of its chemical reaction with diffusing H_2 [6,7,20–25]:

$$\equiv Si^{\bullet} + H_2 \Rightarrow \equiv Si{-}H + H \qquad (1)$$

where H_2 required for reaction (1) to take place may be already present in the native fiber or be itself a consequence of irradiation via breaking of Si – OH or Si – H bonds. An important difference between present results and previous findings both on fibers and on bulk SiO_2 is our evidence of a 5.3 eV band growing in the post-irradiation stage concurrently to E' centers decay. Data in Fig. 2 show that the growth kinetics of the 5.3 eV band is quite closely correlated to that by which E' centers are annealed by diffusing H_2. This leads to assumption that the center responsible for the 5.3 eV band is formed by fast trapping on some pre-existing precursor of very mobile diffusing hydrogen atoms made available by the main reaction (1): in fact, within this scheme the two kinetics would be strongly anticorrelated being both governed by rupture of H_2 on E' defects acting as dissociation centers. The small deviations from a strict correlation observed at long times are likely due to a minor additional annealing process of E' that is not hydrogen-related. As a consequence of this reasoning, the defect absorbing at 5.3 eV is expected to contain a hydrogen atom in its chemical structure. In the following, the defect absorbing at 5.3 eV is referred to as 5.3 eV-center.

Data in Fig. 3 yield information on the response of the 5.3 eV-center to UV laser light. Indeed, re-irradiation of a sample in which the 5.3 eV-centers have already formed in the post-irradiation stage leads to the rapid annealing of the absorption band associated to these defects. This demonstrates that 5.3 eV-centers can be destroyed by laser light at 4.7 eV photon energy. Also, the linear dependence of the annealing rate on laser intensity (inset of Fig. 3) shows that annealing is triggered by a single photon process. Being the laser photon energy 4.7 eV within the band at 5.3 eV, the photo-induced annealing of the defect can be interpreted as arising from the fact that absorption is due to a transition from the ground electronic state to an unstable excited state from which the defect has a significant dissociation probability. The slope Λ obtained by linear fitting data in the inset of Fig. 3 is proportional to the photo-dissociation cross section of 5.3 eV-centers, $\sigma_d = \Lambda\tau^{-1}h\nu \sim 1\times10^{-19}cm^2$. The ability of 4.7 eV photons to destroy 5.3 eV-centers also explains why they grow only after the end of irradiation, as their formation during the irradiation session is contrasted by their concurrent annealing photo-induced by each laser pulse. Further studies are needed to get more detailed information on the nature of this photochemical annealing process. It is worth noting, however, that σ_d is comparable with typical photo-dissociation cross sections measured for other defects in SiO_2, e.g. the H(II) center which is formed by H trapping on twofold coordinated Ge impurities [28,29].

While the identification of the microscopic structure of the 5.3 eV-center cannot be conclusively addressed here, tentative models can be put forward based on comparison of present data with literature. H(I) center (═Si$^{\bullet}$ – H), consisting in a Si atom bonded to two oxygen atoms and one hydrogen and hosting an unpaired electron, was shown to be destroyed by absorption of UV light [24], although no satisfactory reconstruction of the shape of its absorption band in this spectral region is available in the literature. Additionally, H(I) is supposedly formed by trapping on twofold coordinated Si precursors (═Si$^{\bullet\bullet}$) of H atoms made available by rupture of H_2 on paramagnetic centers such

as E' [24,30], with this being consistent in principle with the scheme proposed here. However, ESR measurements (not reported) on the irradiated fiber samples reveal E'-type signals but do not show the characteristic 7.4 mT doublet associated to H(I) [30].

Another point defect in SiO_2 proposed to have similar characteristics to those discussed here for the 5.3 eV-center is E'_β, a variant of the E' center distinguishable from the more common E'_γ center by its electron spin resonance (ESR) properties [11,15,31]. E'_β was demonstrated to grow in X-irradiated samples as a consequence of the reaction of H atoms with some unknown precursor [11,15,31]. The most commonly accepted formation process of E'_β is trapping of H atoms on pre-existing oxygen vacancies ($\equiv Si - Si \equiv$) [11,31]:

$$\equiv Si{-}Si\equiv + H \Rightarrow \equiv Si{-}H \ldots \equiv Si^{\bullet}\left[E'_\beta\right] \quad (2)$$

The proposed structure of E'_β comprises a silicon dangling bond and a nearby ≡Si – H group. The latter is assumed to be sufficiently far from the dangling bond that no hyperfine interaction between the proton and the unpaired electron can be revealed by ESR. This model proposed for E'_β is essentially identical with that developed for the E'_2 center in crystalline α-SiO_2 [11]; as E'_2 was associated to an absorption band at 5.4 eV [15], one could expect an absorption band with similar characteristics to be measured also for the hypothetically isostructural E'_β embedded in amorphous SiO_2. Hence, these evidence are consistent with the tentative identification of the 5.3 eV-centers with E'_β forming on pre-existing oxygen vacancies in the fiber material. The absence of absorption data for the fiber in the vacuum-UV range hinders us from verifying the presence of the 7.6 eV absorption band associated to oxygen vacancies [11], which should be expected in the system for process (2) to be meaningful.

On the other side, this attribution cannot be considered a definitive one at the moment, since neither the structural model of E'_β nor the reaction responsible for its formation has been conclusively clarified. Indeed, other possibilities aside from Eq. (2) have been proposed. According to one of them [32], E'_β may consist in an isolated silicon dangling bond structure (i.e. $\equiv Si^{\bullet}$) formed by reaction of H atoms with Si – H impurities, that is by the inverse of reaction (1). This would require reaction (1) to be endothermic and its inverse to be exothermic. This remarkably contrasts with several experimental evidence (including those of Fig. 1 in the present paper) in favor of reaction (1) taking place only from left to right at temperatures >200 K [6,7,20–25], although requiring an activation energy of ~0.4 eV which provides the main bottleneck limiting the reaction rate [25].

5. Conclusions

We investigated by in situ optical absorption measurements the modifications induced in a commercial multimode optical fiber by exposure to pulsed UV laser light. The major absorption band induced by laser irradiation is that at 5.8 eV associated to E' centers, which are generated by laser exposure of the fiber and partially destroyed in the post-irradiation stage due to their chemical reaction with diffusing hydrogen. The generation efficiency of E' centers in the fiber is much higher than that typically observed in high purity bulk SiO_2, likely due to the abundance of defect precursors formed during the fiber drawing process. Post-irradiation decay of E' centers is accompanied by the concurrent formation of another center absorbing at 5.3 eV supposedly driven by diffusion of H atoms produced as a side effect of the reaction between E' and H_2. This defect is tentatively proposed to be E'_β, formed by trapping on oxygen vacancies of H atoms produced as a side effect of the reaction between E' and H_2. Independent of its microscopic structure, the 5.3 eV-absorbing defect turns out to be photosensitive that it can be photochemically destroyed by absorption of 4.7 eV photons with a $\sim 10^{-19} cm^2$ cross section.

Acknowledgements

We are grateful to the members of the LAMP group (http://www.fisica.unipa.it/amorphous) for support and enlightening discussions.

References

[1] T.E. Tsai, D.L. Griscom, Phys. Rev. Lett. 67 (1991) 2517.
[2] K. Arai, H. Imai, H. Hosono, Y. Abe, H. Imagawa, Appl. Phys. Lett. 53 (1988) 1891.
[3] H. Nishikawa, R. Nakamura, Y. Ohki, Y. Hama, Phys. Rev. B 48 (1993) 15584.
[4] N. Fukata, Y. Yamamoto, K. Murakami, M. Hase, M. Kitajima, Appl. Phys. Lett. 83 (2003) 3495.
[5] K. Kajihara, Y. Ikuta, M. Hirano, H. Hosono, J. Non-Cryst. Solids 322 (2003) 73.
[6] F. Messina, M. Cannas, J. Phys. Condens. Matter 17 (2005) 3837.
[7] M. Cannas, F. Messina, J. Non-Cryst. Solids 351 (2005) 1780.
[8] R.K. Brimacombe, R.S. Taylor, K.E. Leopold, J. Appl. Phys. 66 (1989) 4035.
[9] P. Karlitschek, G. Hillrichs, K.F. Klein, Opt. Commun. 155 (1998) 376.
[10] K. Saito, M. Ito, A.J. Ikushima, S. Funahashi, K. Imamura, J. Non-Cryst. Solids 347 (2004) 289.
[11] G. Pacchioni, L. Skuja, D.L. Griscom (Eds.), Defects in SiO_2 and Related Dielectrics: Science and Technology, Kluwer Academic Publishers, USA, ISBN: 0-7923-6685-9, 2000.
[12] H.S. Nalwa (Ed.), Silicon-based Materials and Devices, Academic Press, USA, ISBN: 0-12-513909-8, 2001.
[13] L. Skuja, H. Hosono, M. Hirano, Proc. SPIE 4347 (2001) 155.
[14] G.P. Agrawal, Fiber-Optic Communication Systems, third editionJohn Wiley & Sons INC9780471215714, 2002.
[15] D.L. Griscom, J. Ceram. Soc. Jpn. 99 (1991) 899.
[16] G. Buscarino, S. Agnello, F.M. Gelardi, Phys. Rev. Lett. 94 (2005) 125501.
[17] G. Buscarino, S. Agnello, F.M. Gelardi, Phys. Rev. Lett. 97 (2006) 135502.
[18] D.L. Griscom, J. Non-Cryst. Solids 349 (2004) 139.
[19] S. Girard, IEEE Trans Nucl Sci 54 (2007) 4.
[20] Z. Li, S.J. Fonash, E.H. Poindexter, M. Harmatz, F. Rong, W.R. Buchwald, J. Non-Cryst. Solids 126 (1990) 173.
[21] A.A. Bobyshev, V.A. Radtsig, Kinet. Katal. 31 (1990) 931.
[22] H. Imai, K. Arai, H. Hosono, Y. Abe, T. Arai, H. Imagawa, Phys. Rev. B 44 (1991) 4812.
[23] N. Kuzuu, Y. Komatzu, M. Murahara, Phys. Rev. B 44 (1991) 9265.
[24] V.A. Radtsig, V.N. Bagratashvili, S.I. Tsypina, P.V. Chernov, O. Rybaltovskii, J. Phys. Chem. 99 (1995) 6640.
[25] F. Messina, M. Cannas, J. Phys. Chem. C 111 (2007) 6663.
[26] Avantes Catalog, http://www.avantes.com/2006–2007.
[27] F. Messina, M. Cannas, J. Phys. Condens. Matter 20 (2008) 275210.
[28] F. Messina, M. Cannas, R. Boscaino, J. Non-Cryst. Solids 351 (2005) 1770.
[29] M. Cannas, F. Messina, J. Non-Cryst. Solids 345 (2004) 433.
[30] L. Skuja, J. Non-Cryst. Solids 239 (1998) 16.
[31] D.L. Griscom, J. Non-Cryst. Solids 68 (1984) 301.
[32] D.L. Griscom, J. Appl. Phys. 58 (1985) 2524.