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Enhanced photosensitivity in silicate optical fibers by thermal treatment

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Enhanced photosensitivity using thermal treatment has been observed on several silicate optical fibers. The effect of the treatment on fibers with different dopants has been tested via Bragg grating inscription. The presence of Ge or Sn atom has been established to be fundamental for the effect to occur. To explain the main features a model involving defect dynamics is proposed. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2714096]

Since its discovery,[1] fiber Bragg gratings have been investigated and used in several applications ranging from dispersion compensators to filters, fiber lasers, cavity mirrors, and optical fiber sensors. The core of standard single mode telecommunication fibers contains a small level of photosensitive compounds, thus showing a small modulation change in the refractive index ($\Delta n_{\mathrm{mod}} \leqslant 10^{-4}$) when exposed to UV radiation. Two different approaches have been used to increase fiber photosensitivity: codoping optical fibers with elements sensitive to UV radiation (such as B,[2] Sn,[3] Sb,[4] Ce,[5] Pb,[6] or rare earths[7]) or postfabrication methods (such as hydrogen/deuterium loading,[8] hydrogen flushing,[9] or flame brushing[10]). We have recently investigated an alternative postfabrication method which increases fiber photosensitivity of germanosilicate fibers by thermal treatments.[11] The method consists in exposing the fiber to CO_2 laser radiation before Bragg grating inscription. As a consequence of the exposure the obtained refractive index modulation for the Bragg grating is a few times higher than in untreated (i.e., unexposed to CO_2 laser radiation) fibers. In this study we extend the technique to other dopants (e.g., Sn, B, Ce). A model based on defects can explain the main features of this photosensitivity enhancement technique, thus envisaging its applicability to a wider range of material compositions with respect to those covered in this study.

Uncoated fibers were left in a fiber drawing furnace at 1800 °C for 1 min and subsequently quickly taken out from the furnace in order to rapidly cool them down to room temperature. The furnace (Heathway Ltd.) consists of a graphite resistive heating element in an inert argon atmosphere and it operates within the temperature range of 1000–2400 °C. A pyrometer provides the feedback to a computer which stabilizes the temperature within $\sim 1°$ by controlling the current crossing the graphite element and the Ar flowing within the furnace. Fiber photosensitivity was then tested via grating writing. The experimental setup to write and characterize gratings is presented in Fig. 1. Gratings at 1.55 μm were written using a phase mask and a 248 nm KrF excimer laser. The refractive index modulation (Δn_{mod}) in the fibers was derived using conventional formulas over the whole reflection spectrum.[12] The fibers used in these experiments are reported in Table I together with their numerical aperture (NA), dopants, and cut-off wavelength (λ_c). The germanosilicate fibers used in Ref. 11 (samples A and B) are also reported in the table as a reference. Gratings were written by exposing the treated and untreated fibers to excimer laser pulses at 20 Hz and $I_p \sim 300$ mJ/cm^2.

Fibers with other dopants have been studied to investigate whether photosensitivity enhancement is exclusively associated with germanosilicate fibers. Gratings 2.4 mm long were written in samples of germanium-free fiber (sample C) by exposing the fiber to 3000 pulses at ~0.1 mJ/pulse and 20 Hz. Compared to the untreated fiber, the grating written in the treated fibers provided higher reflectivity (Fig. 2). As previously observed in samples A and B, thermal treatment enhances the natural photosensitivity of fiber C. Δn_{mod} for the treated and untreated fibers were estimated to be 1.62×10^{-4} and 1.28×10^{-4}.

Samples D–I were treated according to the same thermal treatment experienced by fiber C. Gratings were written in treated and untreated samples and results are presented in Table II. Samples C–F clearly show that photosensitivity enhancement has been detected in all samples containing Ge or Sn. In contrast, four different trials performed on sample G did not reveal any significant enhancement in Ce-doped fibers. Fibers which are usually insensitive to KrF laser irradiation have been treated to CO_2 laser to investigate whether thermal treatment could induce some sort of photosensitivity (samples H and I). No gratings were detected in any of the treated samples.

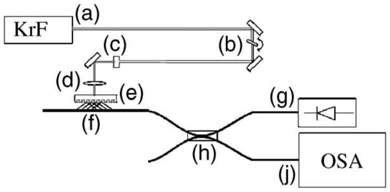

FIG. 1. EMG-150 MSC Lambda-Physik KrF excimer laser (a) delivers 20 ns pulses at 248 nm which pass through a homogenizer (b) and an aperture (c). After a few reflections the beam reaches the cylindrical lens (d) where it is focused 60 mm after the phase mask (e). The fiber (f) is placed in contact to the phase mask. Light emitted by a broadband white-light source (g) is launched into the fiber (f), is reflected by the grating, and after going through a coupler (h) is collected by an HP70950 optical spectrum analyzer (g).

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TABLE I. Composition, NA, and cut-off wavelength (λ_c) of the fibers thermally treated.

Fiber	Dopants	NA	λ_c (μm)
A	Ge	0.27	1.36
B	Ge	0.30	1.26
C	Sn	0.1	1.38
D	Ge/B	0.12	1.25
E	Sn/P	0.2	1.31
F	Ge/Sn	0.3	1.35
G	Ce/Ag/Na	0.12	1.25
H	P	0.17	1.30
I	Er/Yb	0.12	1.25

TABLE II. Photosensitivity in fiber samples treated with a thermal cycle in a furnace at 1800 °C and pristine. L, $\Delta n_{\text{treated}}$, and $\Delta n_{\text{untreated}}$ represent the grating length and Δn_{mod} in treated and untreated fibers, respectively. $R=\Delta n_{\text{treated}}/\Delta n_{\text{untreated}}$.

Fiber	L (mm)	$\Delta n_{\text{treated}}$ ($\times 10^{-4}$)	$\Delta n_{\text{untreated}}$ ($\times 10^{-4}$)	Ratio
C	2.4	1.62	1.28	1.27
D	0.55	12.2	7.72	1.58
E	1.9	2.48	2.18	1.14
F	3.3	14.8	10.2	1.45
G	2.2	1.32	1.29	1.02
H	16	⋯	⋯	⋯
I	16	⋯	⋯	⋯

In Ref. 11 the effects of thermal treatment on the absorption spectrum of thin preform slices were investigated and a model involving germanium-oxygen deficient centers (GODCs) was developed. The GODC concentration was explained on the basis of thermodynamic equilibrium of defects, the proportions of which depend on two competing reactions: the creation of GODCs from the glass network [Eq. (1)] and their destruction to produce other defects [Eqs. (2) (Ref. 13) and (3) (Ref. 14)],

$$\mathrm{SiO_3-O-GeO_3=GODC+O_{(int)}}, \tag{1}$$

$$\mathrm{GODC=Ge}E'+\mathrm{SiO_3^+}+e^-, \tag{2}$$

$$\mathrm{GODC+GeO_4=GEC+Ge(2)}, \tag{3}$$

where $\mathrm{O_{(int)}}$ represents an interstitial oxygen in the glass network and GEC is the German Electron Centre.

Two types of GODC with absorption in the 242 nm region have been identified:[15,16] The first one, also called neutral-oxygen monovacancy, is observed for exposures at low UV intensities and is believed to be responsible for the creation of most of GeE' centers [reaction (2)];[13,14] the other, called neutral-oxygen divacancy, evolves into GEC centers [reaction (3)] and is observed only at high intensities.[14]

A temperature increase shifts the reaction balance of Eqs. (1) and (2) to the right and of Eq. (3) to the left, meaning that GODCs are formed in Eqs. (1) and (3) (Ref. 15) and destroyed in Eq. (2) (Ref. 15). At low temperature reactions (1) and (3) have a lower yield than reaction (2) and the overall GODC concentration is reduced, whereas at high temperatures the opposite is true. Thermal treatment allows the formation of high concentrations of defects that are then freezed in the network when the fiber is cooled to room temperature.[11]

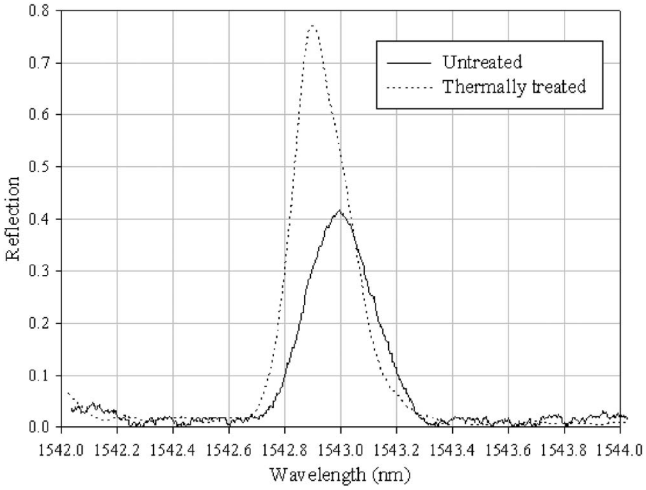

FIG. 2. Example of reflection spectra of gratings written in samples of fiber C.

Likewise, although the overall photosensitivity process in Sn-doped fibers seems to involve a small-medium-range structural reorganization initiated by defect dynamics,[17] a mechanism similar to the one observed in Ge-doped fibers can be used to explain the defect dynamics initiating the photosensitivity enhancement observed in these experiments. It has been recently shown[18] that Sn atoms are found in substitutional position in the silica network and generate the same oxygen-deficient centers (SnODCs) and E' defects as Ge.[17–20] Figure 3 shows UV spectra of preforms used to fabricate samples A, C, and F. While preform A (Ge-doped silicate) shows the absorption at 242 nm typical of GODC, in preforms C and F (Sn-doped and codoped silicates) the absorption at 252 nm associated with SnODC (Ref. 21) can be observed. More than one type of SnODCs has also been reported in tin silicate glasses[22] and their concentration has been shown to increase with thermal treatment[22] [in a similar way to the concentration of GODC (Ref. 11) in germanosilicate glasses]. Likewise to the case of Ge-doped fibers, in Sn-doped fibers the thermal treatment might alter the equilibrium balance of reactions involving SnODC: the number of SnODC could be increased at high temperature and then be frozen in the glass network when the fiber is cooled down.

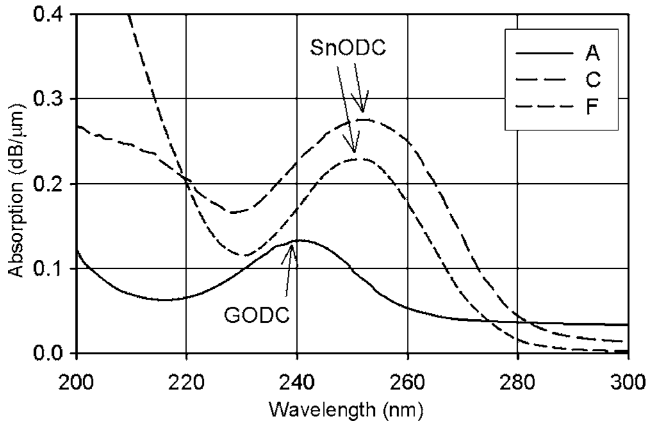

FIG. 3. UV absorption spectra of samples A (Ge-doped silicate), C, and F (Sn-doped silicate).

On the contrary, Ce-doped fibers did not show any considerable photosensitivity enhancement. In Ce-doped glasses, photosensitivity is supposed to be induced by a change in the valence of Ce atoms (from Ce^{3+} to Ce^{4+}).[23] The indifference of photosensitivity to thermal treatment can be explained by constant Ce^{3+} and Ce^{4+} concentrations. Finally, fibers doped with P and rare earths did not show any induced photosensitivity after thermal treatment. No grating has been detected in any of these fibers, possibly because thermal treatment did not generate any defect with absorption at 248 nm.

A dependence on the water content was observed in the treated fibers. Although the photosensitivity enhancement in fibers containing several ppm of–OH is considerably greater than that in fibers with low water content, nonetheless the effect was also observed in this latter case.

In conclusion, thermal treatment of optical fibers before grating inscription has been shown to significantly increase photosensitivity. Tests on different fiber core compositions have shown that a fundamental requirement for photosensitivity enhancement is the presence of either Ge or Sn as dopants. In germanosilicate fibers this effect has been related to an observed increase of GODC defects due to thermal effects. A similar effect involving SnODC defects has been suggested to explain the enhancement in Sn-doped fibers.

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[1] K. O. Hill, Y. Fujii, D. C. Johnson, and B. S. Kawasaki, Appl. Phys. Lett. **32**, 647 (1978).
[2] D. L. Williams, B. I. Ainslie, J. R. Armitage, R. Kashyap, and R. Campbell, Electron. Lett. **29**, 45 (1993).
[3] L. Dong, J. L. Cruz, L. Reekie, M. G. Xu, and D. N. Payne, IEEE Photonics Technol. Lett. **7**, 1048 (1995).
[4] K. Oh, P. S. Westbrook, R. M. Atkins, P. Reyes, R. S. Windeler, W. A. Reed, T. E. Stockert, D. Brownlow, and D. DiGiovanni, Opt. Lett. **27**, 488 (2002).
[5] K. O. Hill, B. Malo, F. Bilodeau, D. C. Johnson, T. F. Morse, A. Kilian, L. Reimhart, and K. Oh, *Optical Fiber Communication*, 1991 OSA Technical Digest Series Vol. 1, (Optical Society of America, Washington, D.C., 1991), p. 14.
[6] X.-C. Long and S. R. J. Brueck, Opt. Lett. **74**, 2110 (1999).
[7] J. L. Blows, P. Hambley, and L. Poladian, IEEE Photonics Technol. Lett. **14**, 938 (2002).
[8] P. J. Lemaire, R. M. Atkins, V. Mizrahi, and W. A. Reed, Electron. Lett. **29**, 1191 (1993).
[9] M. Fokine, Opt. Lett. **25**, 302 (2000).
[10] F. Bilodeau, B. Malo, J. Albert, D. C. Johnson, K. O. Hill, Y. Hibino, M. Abe, and M. Kawachi, Opt. Lett. **18**, 953 (1993).
[11] G. Brambilla, V. Pruneri, L. Reekie, and D. N. Payne, Opt. Lett. **24**, 1023 (1999).
[12] G. Brambilla and V. Pruneri, IEEE J. Sel. Top. Quantum Electron. **7**, 403 (2001).
[13] J. Nishii, K. Fukumi, H. Yamanaka, K. Kawamura, H. Hosono, and H. Kawazoe, Phys. Rev. B **52**, 1661 (1995).
[14] M. Fujimaki, T. Watanabe, T. Katoh, T. Kasahara, N. Miyazaki, Y. Ohki, and H. Nishikawa, Phys. Rev. B **57**, 3920 (1998).
[15] M. Takahashi, T. Fujiwara, T. Kawachi, and A. J. Ikushima, Appl. Phys. Lett. **72**, 1287 (1998).
[16] H. Hosono, Y. Abe, D. L. Kinser, R. A. Weeks, K. Muta, and H. Kawazoe, Phys. Rev. B **46**, 11445 (1992).
[17] N. Chiodini, S. Ghidini, A. Paleari, G. Brambilla, and V. Pruneri, Appl. Phys. Lett. **77**, 3701 (2000).
[18] N. Chiodini, F. Meinardi, F. Morazzoni, A. Paleari, R. Scotti, and G. Spinolo, Phys. Rev. B **58**, 9615 (1998).
[19] N. Chiodini, F. Meinardi, F. Morazzoni, A. Paleari, R. Scotti and D. Di Martino, J. Non-Cryst. Solids **261**, 1 (2000).
[20] A. Anedda, C. M. Carbonaro, A. Serpi, N. Chiodini, A. Paleari, R. Scotti, G. Spinolo, G. Brambilla, and V. Pruneri, J. Non-Cryst. Solids **280**, 287 (2001).
[21] G. Brambilla, V. Pruneri, and L. Reekie, Appl. Phys. Lett. **76**, 897 (2000).
[22] A. O. Rybaltovskii, I. A. Kamenskikh, V. V. Mikhailin, N. L. Semenova, D. A. Spasskii, G. Zimmerer, P. V. Chernov, and K. M. Golant, Glass Phys. Chem. **28**, 379 (2002).
[23] M. M. Broer, R. L. Cone, and J. R. Simpson, Opt. Lett. **16**, 1391 (1991).