Optical properties of infrared femtosecond laser-modified fused silica and application to waveguide fabrication

Arnaud Zoubir and Martin Richardson

College of Optics and Photonics, Center for Research and Education in Optics and Lasers and Florida Photonics Center of Excellence, University of Central Florida, P.O. Box 162700, Orlando, Florida 32816

Lionel Canioni, Arnaud Brocas, and Laurent Sarger

Centre de Physique Moléculaire Optique et Hertzienne, Université de Bordeaux 1, 351 Cours de la Libération, 33405 Talence Cedex, France

Received October 20, 2004; accepted January 10, 2005

We investigate the changes in the optical properties of fused silica exposed to intense infrared femtosecond pulses. The laser-induced absorption spectrum reveals the creation of color centers inside the glass matrix, comparable with those observed in ultraviolet-exposed fused silica. The laser-induced absorption is associated with a laser-induced refractive-index change, which can be used for waveguide fabrication. The change in third-order susceptibility in such waveguides is measured by third-harmonic-generation microscopy as a function of the irradiation parameters. © 2005 Optical Society of America

OCIS codes: 160.4670, 140.3390.

1. INTRODUCTION

Direct laser writing using infrared (IR) ultrafast lasers has become a promising fabrication route for waveguides inside optical materials. This technique allows reliable, cost-effective and single-step prototyping of photonic devices, without the design and fabrication of a mask, in contrast to the most standard fabrication techniques. A large number of photonic devices, including channel waveguides and Y couplers,[1] directional couplers,[2,3] tubular waveguides,[4] and active waveguides,[5] have been successfully fabricated by using this technique. Furthermore, the ultrafast lasers used for the writing operate at photon energies far below the material bandgap energy. The material is essentially transparent to the writing wavelength, allowing volumetric processing to depths limited only by the working distance of the focusing element. Hence, three-dimensional waveguides can be produced.[6]

Fused silica is a key material in laser-assisted waveguide fabrication. Although fused silica modified by ultraviolet (UV) radiation has been extensively studied, there is currently no precise model explaining the photosensitivity of fused silica to intense IR radiation. Furthermore, the changes in its nonlinear optical properties have not been studied yet. The potential fabrication of active devices used for all-optical switching and wave-mixing applications relies on a solid understanding of how the nonlinear properties of the source material are modified by the irradiation process. In this paper we investigate how exposure to an IR femtosecond (fs) beam affects the linear and nonlinear optical properties of fused silica. Postmortem absorption and photoluminescence spectroscopy are used to determine the nature of the defects induced by irradiation in the glass matrix. The refractive-index change that accompanies the formation of such defects is exploited for the fabrication of waveguides inside the volume of the fused-silica sample, and the waveguides are characterized. Finally, the change in the third-order susceptibility is measured by third-harmonic-generation (THG) confocal microscopy for different pulse energies.

2. EXPERIMENTAL DETAILS

In this study, irradiation parameters such as the laser pulse energy and spot size and sample translation speed are varied, and their impact on the material properties depending on these parameters is measured. To compare results obtained with different writing conditions within this paper and in future studies, we propose a definition for the energy dose D received by the material in terms of the pulse energy E_p, the laser repetition rate f, the spot area A (equal to $\pi\omega_{1/e^2}^2$ for a circular Gaussian beam), and the sample translation speed v:

$$D = \frac{E_p f}{A v}. \tag{1}$$

Note that D, in units of energy per volume, is the three-dimensional counterpart of the fluence, commonly used to quantify exposure to optical radiation in planar waveguide fabrication.

In the first part of the experiment, we studied the changes occurring in the absorption spectrum of fused silica following fs pulse irradiation. The irradiation was performed by using a laser system consisting of a fs Ti:sapphire oscillator and a regenerative amplifier producing 100 fs pulses at 800 nm at a 1 kHz repetition rate.

The writing photon energy (1.55 eV) is much smaller than the bandgap of silica (8.9 eV), allowing the laser beam to penetrate deep down inside the material and produce volumetric defects. To resolve these changes with a standard spectrophotometer, we produced a rather large defect volume inside the sample by using a 5 cm focal-length cylindrical lens to focus the IR beam. The cylindrical lens produces a filamentlike focus spot approximately 1 mm in length and perpendicular to the direction of propagation. The sample is then translated along 1 mm transversely and perpendicularly to the filament to produce a 1 mm-by-1 mm damage area, buried approximately 1 mm inside the sample. The confocal parameter of the lens was calculated to be around 200 μm, but the plasma created inside the glass sample seemed slightly longer, owing to self-focusing effects. The pulse energy used in these experiments was 700 μJ, and the translation speed was varied from 0.2 to 10 μm/s.

In the second part of the experiment, we fabricated waveguides by focusing the laser beam in the fused-silica samples by using a 0.25 N.A. 10× microscope objective. The sample is moved along the laser beam direction at 10, 20, and 50 μm/s with a computer-controlled translation stage. The pulse energy is maintained below 5 μJ to avoid inhomogeneous defects that would increase the waveguide loss. The samples are typically 5 mm thick and were cut in 10 mm-by-10 mm cubes. All samples were obtained commercially and have optical-quality polished surfaces on both sides.

3. STUDY OF THE LASER-INDUCED DEFECTS

Laser-induced defects have been extensively studied in the case of UV exposure, in which the photon energy is above the material bandgap. They are usually associated with the formation of color centers, consisting of an unpaired electron on a silicon atom, accompanied by oxygen vacancy, leading to a well-known increase of optical absorption.[7,8] However, the mechanisms underlying multiphoton photosensitivity in the IR are still not fully understood. Davis *et al.* associated IR laser-induced defects with Si E′ centers measured by electron-spin resonance in fused silica.[9] In Ref. 10, no color-center absorption in the visible region was observed in fused silica at irradiances up to the laser damage threshold, although color centers were observed in other silicate glasses. Finally, Streltsov and Borrelli concluded that the thermal stability of the color centers is not consistent with that of the observed induced refractive index.[11] We used UV absorption spectroscopy to identify the type of defects induced during the irradiation process. Figure 1 shows the change in the absorption spectrum measured by a Cary 500 spectrophotometer (Varian) after IR fs exposure at room temperature (D=0.312 GJ/cm^3 and D=3.12 GJ/cm^3). As we increase the energy dose by changing the translation speed, the spectrum exhibits an increase in absorption in the 3–7 eV range. More precisely, two bands appear in the absorption spectrum at 4.8 and 5.8 eV. In the UV irradiation case, the 4.8 eV peak was attributed to the formation of a nonbridging oxygen hole center (NBOHC), an oxygen dangling bond ≡Si—O•.[7] The 5.8 eV peak was attributed to the generation of Si E′ centers after high-power UV laser irradiation. Such defects have also been observed after x-ray, electron, and neutron irradiation.[12–15]

Time-resolved absorption spectroscopy reveals that these UV laser-induced absorption bands are transient in nature.[16] The recovery time of the induced optical absorption is explained as a conversion from E′ centers to nonabsorbing states of the E′ center that have been linked to the OH content of the glass. Although high-OH samples tend to exhibit rapid recovery, low-OH compositions can have recovery times that are several orders of magnitude longer. We measured the evolution of the IR fs laser-induced absorption bands shown in Fig. 1, as a function of time over several hours at 25 °C and after a 2 h annealing process at 200 °C. As can be seen in Fig. 2, the amplitude of both the 4.8 and the 5.8 eV peaks exhibits an exponential decay at room temperature, with a calculated

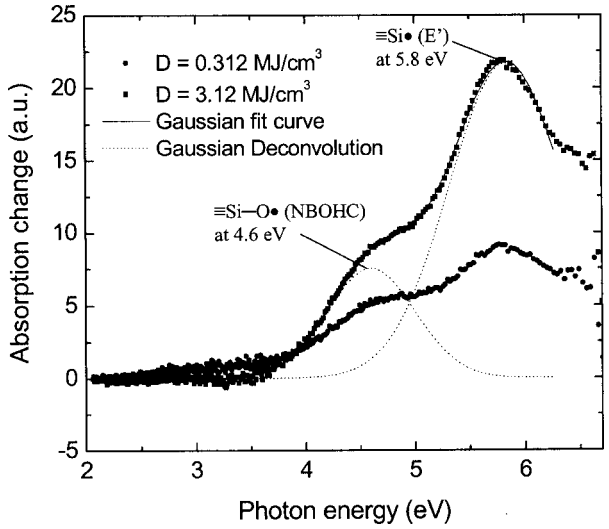

Fig. 1. Absorption change spectra after irradiation to IR fs pulses measured for two different energy doses (i.e., translation speeds) in fused silica.

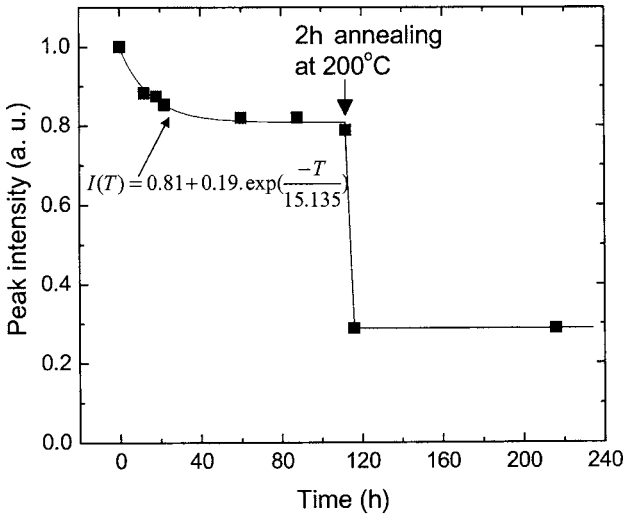

Fig. 2. Evolution of the 5.8 eV peak intensity as a function of time at 25 °C and after a 2 h annealing process at 200 °C.

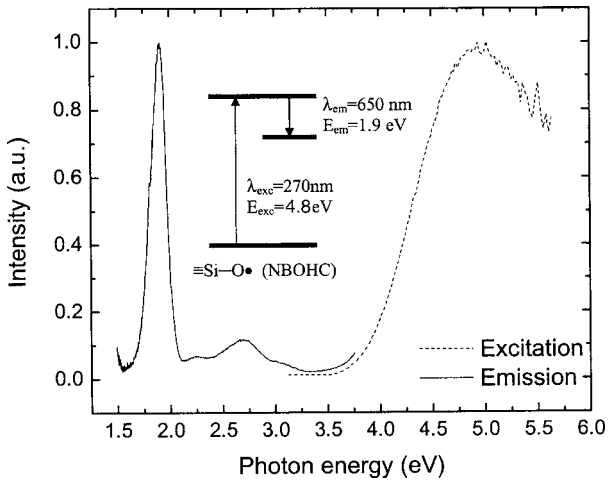

Fig. 3. Excitation and emission spectra of defects in fused silica induced by IR fs pulses.

decay-time constant of approximately 15 h. The 2 h annealing interrupted the decay process and resulted in a significant decrease of the induced absorption, although the material did not completely recover.

Photoluminescence spectroscopy was performed on the induced defects. Both the fluorescence emission and the excitation spectra of the irradiated sample were measured. As shown in Fig. 3 (dashed curve) the excitation spectrum confirmed the presence of defects absent from unexposed glass, having an absorption band around 4.8 eV, previously revealed by the UV absorption spectrum. The 5.8 eV band was too far in the UV to be resolved by our fluorescence spectrometer. In the emission spectrum, we observed a strong emission peak at 1.9 eV (650 nm) and a weaker peak at 2.7 eV (460 nm) corresponding to the fluorescence emission of the laser-induced defects, as shown in Fig. 3 (solid curve). The 1.9 eV peak corresponds to the red luminescence of the NBOHC, whereas the 2.7 eV peak is attributed to the twofold coordinated silicon.[17] Here again, these results are fully consistent with the results reported for UV-irradiated fused silica and confirm the multiphotonic nature of the mechanisms leading to the creation of defects following IR fs laser irradiation.

4. WAVEGUIDE FABRICATION

In this experiment, the sample was translated along the writing laser direction, in a longitudinal writing scheme. The translation speed was adjusted to find a compromise between speed of processing and good homogeneity of the waveguide walls. The optimum speed was found to be 20 μm/s. During the writing process, a weak plasma arising from multiphoton ionization was observed at the focal spot within the material. Part of the writing laser beam was coupled to the channel waveguide while it was being written. Observation of the beam profile in the far field during the writing process showed that, as the waveguide was fabricated, light was progressively confined within a volume of smaller N.A. than that of the microscope objective. The writing pulse energy was varied from 0.8 μJ ($D=3.18$ MJ/cm^3) to 5 μJ ($D=19.89$ MJ/cm^3) for which different waveguide morphologies were obtained, as illustrated in Fig. 4. Outside this energy range, no guiding could be obtained in the produced structures, probably owing to insufficient index change below 0.8 μJ and to high scattering loss above 3 μJ ($D=11.94$ MJ/cm^3). In the energy range in which waveguides were successfully fabricated, we estimated the refractive-index change Δn by measuring the N.A. of the waveguide output by using the relation: N.A.$=\sqrt{n_1^2-n_0^2}$, where n_1 and n_0 are the refractive indices of the core and cladding, respectively (Fig. 4). The value of Δn increases with increased pulse energy, then reaches a maximum value of 0.005 at 2 μJ ($D=7.96$ MJ/cm^3) and, surprisingly, slowly decays as the pulse energy is increased further. This decay was also observed by Streltsov and Borrelli,[11] and its origin remains unclear.

In a standard step-index fiber with core radius a and core and cladding indices n_1 and n_0, the number of guided modes is determined by the V number, as defined by Eq. (2), which must be less than 2.405 for the fiber to be single mode[18]:

$$V=\frac{2\pi}{\lambda}a\sqrt{n_1^2-n_0^2}. \tag{2}$$

Below 2 μJ, the waveguides are single mode for 633 nm radiation, with a clean mode profile corresponding to the LP_{01} mode (first inset in Fig. 4). From the measured size and refractive index of these waveguides, and in the step-index approximation, the calculated V number is <2.107, which is consistent with the observation that the waveguides are single mode. Waveguides fabricated with energies greater than 2 μJ result in the next higher-order mode (LP_{11}) being generated (second inset in Fig. 4). This observation is also consistent with the measured waveguide parameters, which lead to a V-number value >3.626.

5. THIRD-ORDER SUSCEPTIBILITY MEASUREMENT

Until now, only passive waveguide structures have been fabricated by laser direct writing. Producing active three-dimensional devices would considerably increase the

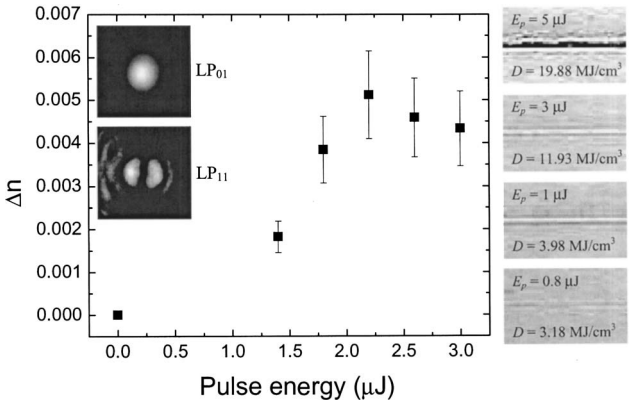

Fig. 4. Refractive-index change and waveguide morphology for different writing pulse energies. The insets show the mode profiles at 633 nm corresponding to the LP_{01} and LP_{11} modes at the waveguide outputs.

functionality and integration of such devices, opening new pathways toward the fabrication of three-dimensional integrated optical circuits. A number of laser-written passive waveguide devices have already been demonstrated, such as directional couplers, and could potentially be engineered as active elements for optical routing, or wave mixing, making use of the nonlinearity of the substrate material. In one configuration, they could be designed such that a 2π nonlinear phase shift is created for a given optical power propagating along the interaction length of the device.[19] Another solution proposed for all-optical switching and routing operations utilizes the properties of two-dimensional discrete soliton networks in waveguide arrays.[20] Recently, Pertsch *et al.* demonstrated the direct-write fabrication of matrices of closely coupled waveguides in which discrete diffraction occurred by evanescent coupling from adjacent waveguides.[21] These waveguide structures could potentially be suitable for the propagation of two-dimensional discrete solitons to perform complex all-optical signal processing. In both cases, the switching mechanism relies on the nonlinear optical properties of the sample material. To operate at practical optical power levels in ~1 cm long devices, the nonlinear material must exhibit a large n_2 value. We have shown in Section 4 that, as the material structure is changed by the writing process, so are its linear optical properties. It is therefore possible to also expect a slight change in the nonlinear properties of the processed material. We investigate, for the first time to our knowledge, the nonlinear property changes of IR fs laser-written waveguides by using THG confocal microscopy. This technique measures the third-harmonic signal generated from laser-exposed fused silica. More details concerning this technique can be found in Ref. 22. Third-harmonic generation has also been used to determine the $\chi^{(3)}$ coefficient.[23] In a confocal microscope configuration, it can be shown that the third-harmonic signal intensity $I_{3\omega}$ is expressed by[22]

$$I_{3\omega} = K\frac{1}{\omega^4}\frac{P_\omega^3}{\tau_p^3}|J|^2, \tag{3}$$

where ω is the beam waist, P_ω is the fundamental beam average power, τ_p is the pulse duration of the fundamental wave, J is the effective interaction length, and K is a parameter depending on sample properties and experimental conditions, which can be expressed as[22]

$$K = \frac{|\chi^{(3)}|^2}{48\pi c\epsilon_0 F}, \tag{4}$$

where F is the laser repetition rate. As a result, the change in the third-order susceptibility $\Delta\chi^{(3)}/\chi^{(3)}$ can be expressed by

$$\frac{\Delta\chi^{(3)}}{\chi^{(3)}} = \left(\frac{I_{3\omega}^{\mathrm{ex}}}{I_{3\omega}^{\mathrm{un}}}\right)^{1/2} - 1, \tag{5}$$

where the superscripts un and ex refer to unexposed and exposed material. Hence, by measuring the intensity of the THG signal created at the interface between air and both the exposed and the unexposed material, it is possible to measure the change in $\chi^{(3)}$ for the exposed region. Furthermore, thanks to the high spatial resolution of the system (~1 μm), it is also possible to have an accurate measurement of the waveguide diameter. Both the change in third-order susceptibility and the change in waveguide diameter are measured as a function of the pulse energy. As shown in Fig. 5, the modified region diameter shows a linear dependence with the pulse energy. This behavior is indicative of the threshold nature of the material modification process. The material is affected only by the most intense region in the spatial writing beam profile, which increases as the pulse energy increases. The third-order susceptibility change quickly decreases with increased irradiation energy and saturates for pulse energies above 3 μJ (D=11.94 kJ/cm^3), which roughly corresponds to the threshold for inhomogeneous damage, as illustrated by the waveguide micrographs in Fig. 4. The material responds as if laser radiation produces a transition from its initial phase to another that has different optical properties. The induced change is independent of deposited energy above a specific value, indicating a phase change that has a specific energy threshold. This result is consistent with the saturation of the waveguide properties, such as the refractive index and the Raman peaks' intensity associated with laser-induced photostructural changes, observed by several groups at higher energies.[1,11,24]

One can obtain another estimation of the changes in the nonlinear properties of the laser-modified material by measuring the spectral broadening of pulsed laser light propagating in the fabricated waveguide.[25] Pulses from a Ti:sapphire laser centered at 780 nm were end coupled in 4 mm long waveguides, by using the 0.25 N.A. 10× microscope objective. The spectrum recorded at the waveguide output exhibits significant spectral broadening due to self-phase modulation occurring during the propagation. Characterization of this self-phase modulation can provide estimations of the waveguide's nonlinear optical properties. Although this technique does not allow a precise measurement of the nonlinear refractive index, as it relies on accurate knowledge of the pulse temporal amplitude and phase, an estimation of the nonlinear phase shift can be obtained by assuming a given pulse shape $E(z,t)$ and fitting the measured spectrum with the calculated spectrum $S(z,\omega)$ by using

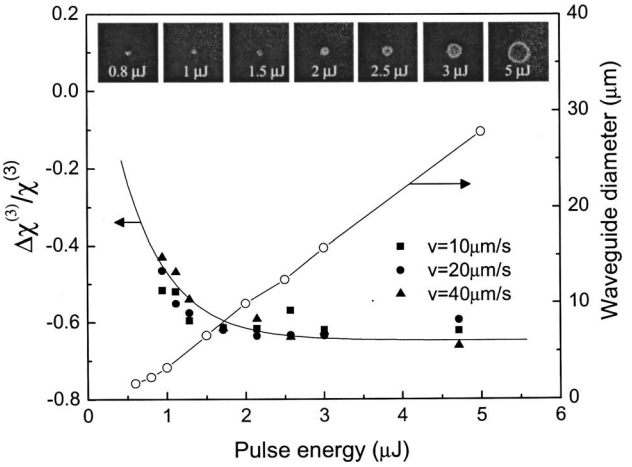

Fig. 5. Waveguide diameter and third-order susceptibility changes as a function of pulse energy for different translation speeds. The insets are the corresponding THG micrographs.

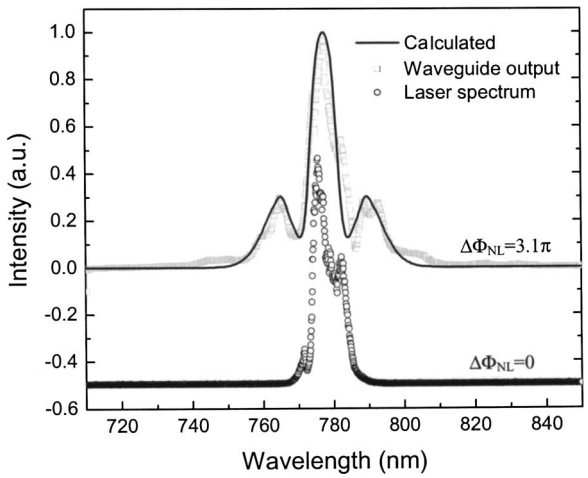

Fig. 6. Comparison of the input laser spectrum, the broadened spectrum of the coupled light, and the calculated spectrum corresponding to a nonlinear phase shift of 3.1π due to self-phase modulation.

$$S(z,\omega) \propto |\tilde{E}(z,\omega)|^2 = \left| \int_{-\infty}^{\infty} E(0,t)\exp[i\Delta\phi^{\mathrm{NL}}(z,t) + i(\omega-\omega_0)t]\mathrm{d}t \right|^2 . \quad (6)$$

The input laser pulse was assumed to have a super-Gaussian temporal distribution ($m=2$), which is the shape that yielded the best fit (Fig. 6). The nonlinear phase shift $\Delta\phi^{\mathrm{NL}}$ was estimated to 3.1π for peak intensity of 40 GW/cm^2 inside the waveguide. The nonlinear refractive index n_2 is related to $\Delta\phi^{\mathrm{NL}}$ by

$$\Delta\phi^{\mathrm{NL}} = k_0 n_2 I_0 L . \quad (7)$$

With expression (6), the nonlinear refractive index n_2 inside the waveguide is estimated to be 1.9×10^{-16} cm^2/W. It should be emphasized that the combined error on the measurement of the pulse width, mode profile, and nonlinear phase shift is significant, and this calculation should be considered only an estimate. However, it indicates, along with the results obtained by the THG confocal microscopy experiment, that the n_2 value of IR fs laser-irradiated fused silica is reduced in comparison with the reported n_2 value of pure fused silica (2.6×10^{-16} cm^2/W).

6. CONCLUSION

We have identified and characterized defects produced by an IR femtosecond laser in fused silica by absorption spectroscopy and photoluminescence spectroscopy. The defects exhibit characteristics that are similar to the defects induced by UV radiation, previously described in the literature. These defects are accompanied by an increase of refractive index, and translation of the glass samples allowed the fabrication of volume waveguides. Our experimental results reveal that good-quality waveguides can be obtained only within a narrow pulse energy range. Furthermore, they suggest that the third-order susceptibility of fused silica is altered by the irradiation process. This is confirmed by the nonlinear phase shift produced by self-phase generation measured for pulses propagating inside the waveguides. These results are relevant for the design of active waveguides using the nonlinear properties of the material.

ACKNOWLEDGMENTS

The authors thank Thierry Cardinal for the use of his equipment and technical expertise in photoluminescence spectroscopy. This research was supported by National Science Foundation contract DMR-9912975 and by the state of Florida.

The corresponding author, M. Richardson, can be reached by e-mail at mcr@creol.ucf.edu.

REFERENCES

1. A. Zoubir, M. Richardson, C. Rivero, A. Schulte, C. Lopez, K. Richardson, N. Hô, and R. Vallée, "Direct femtosecond laser writing of waveguides in As_2S_3 thin films," Opt. Lett. **29**, 748–750 (2004).
2. D. Homoelle, S. Wielandy, A. L. Gaeta, N. F. Borrelli, and C. Smith, "Infrared photosensitivity in silica glasses exposed to femtosecond laser pulses," Opt. Lett. **24**, 1311–1313 (1999).
3. A. M. Streltsov and N. F. Borrelli, "Fabrication and analysis of a directional coupler written in glass by nanojoule femtosecond laser pulses," Opt. Lett. **26**, 42–43 (2001).
4. A. Zoubir, C. Lopez, M. Richardson, and K. Richardson, "Femtosecond laser fabrication of tubular waveguides in poly(methyl methacrylate)," Opt. Lett. **29**, 1840–1842 (2004).
5. R. Osellame, S. Taccheo, M. Marangoni, R. Ramponi, P. Laporta, D. Polli, S. De Silvestri, and G. Cerullo, "Femtosecond writing of active optical waveguides with stigmatically shaped beams," J. Opt. Soc. Am. B **20**, 1559–1567 (2003).
6. S. Nolte, M. Will, J. Burghoff, and A. Tuennermann, "Femtosecond waveguide writing: a new avenue to three-dimensional integrated optics," Appl. Phys. A **77**, 109–111 (2003).
7. K. Kajihara, Y. Ikuta, M. Hirano, and H. Hosono, "Power dependence of defect formation in SiO_2 glass by F_2 laser irradiation," Opt. Lett. **81**, 3164–3166 (2002).
8. L. Dong, J. L. Archambault, L. Reekie, P. St. J. Russell, and D. N. Payne, "Photoinduced absorption change in germanosilicate performs: evidence for the color-center model of photosensitivity," Appl. Opt. **34**, 3436–3440 (1995).
9. K. M. Davis, N. Sugimoto, and K. Hirao, "Writing waveguides in glass with a femtosecond laser," Opt. Lett. **21**, 1729–1731 (1996).
10. O. M. Efimov, K. Gabel, S. V. Garnov, L. B. Glebov, S. Grantham, M. Richardson, and M. J. Soileau, "Color-center generation in silicate glasses exposed to infrared femtosecond pulses," J. Opt. Soc. Am. B **15**, 193–199 (1998).
11. A. M. Streltsov and N. F. Borrelli, "Study of femtosecond-laser-written waveguides in glasses," J. Opt. Soc. Am. B **19**, 2496–2504 (2002).
12. M. A. Stevens-Kalceff, A. Stesmans, and J. Wong, "Defects induced in fused silica by high fluence ultraviolet laser pulses at 355 nm," Appl. Phys. Lett. **80**, 758–760 (2002).
13. Z. Lin, V. A. Mashkov, and R. G. Leisure, "Multiple interconversions of the E′ and oxygen-hole defect centers in high-purity amorphous silica during anneal-interrupted x irradiation," Phys. Rev. Lett. **74**, 1605–1608 (1995).

14. M. A. Stevens-Kalceff, "Micromodification of silicon dioxide in a variable pressure/environmental scanning electron microscope," Appl. Phys. Lett. **79**, 3050–3052 (2001).
15. L. Skuja, "The origin of the intrinsic 1.9 eV luminescence band in glassy SiO_2," J. Non-Cryst. Solids **179**, 51–69 (1994).
16. N. Leclerc, C. Pfleiderer, H. Hitzler, J. Wolfrum, K.-O. Greulich, S. Thomas, H. Fabian, R. Takke, and W. Englisch, "Transient 210-nm absorption in fused silica induced by high-power UV laser irradiation," Opt. Lett. **16**, 940–942 (1991).
17. T. Mohanty, N. C. Mishra, S. V. Bhat, P. K. Basu, and D. Kanjilal, "Dense electronic excitation induced defects in fused silica," J. Phys. D **36**, 3151–3155 (2003).
18. K. Okamoto, *Fundamentals of Optical Waveguides*, Optics and Photonics Series (Academic, 2000).
19. G. I. Stegeman, E. M. Wright, N. Finlayson, R. Zanoni, and C. T. Seaton, "Third order nonlinear integrated optics," J. Lightwave Technol. **6**, 953–970 (1988).
20. D. N. Christodoulides and E. D. Eugenieva, "Blocking and routing discrete solitons in two-dimensional networks of nonlinear waveguide arrays," Phys. Rev. Lett. **87**, 233901 (2001).
21. T. Pertsch, U. Peschel, F. Lederer, J. Burghoff, M. Will, S. Nolte, and A. Tünnermann, "Discrete diffraction in two-dimensional arrays of coupled waveguides in silica," Opt. Lett. **29**, 468–470 (2004).
22. A. Brocas, L. Canioni, and L. Sarger, "Efficient selection of focusing optics in non linear microscopy design through THG analysis," Opt. Express **12**, 2317–2326 (2004).
23. R. Barille, L. Canioni, L. Sarger, and G. Rivoire, "Nonlinearity measurements of thin films by third-harmonic-generation microscopy," Phys. Rev. E **66**, 67602-1–67602-4 (2002).
24. J. W. Chan, T. Huser, S. Risbud, and D. M. Krol, "Structural changes in fused silica after exposure to focused femtosecond laser pulses," Opt. Lett. **26**, 1726–1728 (2001).
25. K. A. Cerqua-Richardson, J. M. McKinley, B. Lawrence, S. Joshi, and A. Villeneuve, "Comparison of nonlinear optical properties of sulfide glasses in bulk and thin film form," Opt. Mater. (Amsterdam, Neth.) **10**, 155–159 (1998).