Extraordinary stability of anisotropic femtosecond direct-written structures embedded in silica glass

Erica Bricchi and Peter G. Kazansky

Optoelectronics Research Centre, University of Southampton, Southampton SO17 1BJ, UK

Abstract

In this letter we report the different response to temperature displayed by isotropic femtosecond written structures (type I_fs), and anisotropic ones (type II_fs), which are characterized by the presence of a self-assembled sub-wavelength periodic structure within the irradiated volume. We observe that the anisotropic structures display an extraordinary annealing behavior, namely, their photo induced change in refractive index increases with the annealing temperature. We explain our experimental results with a theoretical model.

In recent years, femtosecond lasers have proved to be a tool for micromachining optical transparent materials[1]. The ability to process the material in three dimensions and in one single step, as opposed to traditional lithography, makes the femtosecond direct writing an alluring fabrication technique. Moreover, since the physical mechanism inducing a refractive index change in the irradiated material is based on nonlinear absorption, taking place at the focus of a converging beam, requirements on photosensitivity are greatly reduced. Hence, complex structures can be directly written in materials, such as pure silica, that are traditionally challenging for standard direct laser processing. Furthermore, depending on the laser intensity and the material utilized, different features with either positive or negative index change, or voids, can be realized in the bulk of the irradiated material, thus targeting numerous applications such as waveguides[2], Bragg gratings[3], diffraction optics[4], micro-fluidic channels[5], and data storage[6].

It has been shown that femtosecond laser writing in wide band-gap materials can induce an optically isotropic positive index change[1] as high as 3×10^{-2} (type I_fs). However, when the material is irradiated above a certain intensity threshold (which depends on the material, laser wavelength and pulse duration) we observe that the femtosecond written structures are characterized by anisotropic scattering[7], anisotropic reflection[8], strong birefringence and average negative index change[9], due to the formation a self-assembled periodic nanostructures[10]. During the energy absorption process, tunneling, multiphoton and avalanche ionization produce free electrons within the focus of the ultrashort pulsed laser[11]. Our observations suggest that, over a certain intensity threshold, the interference between a longitudinal electron plasma wave and the laser light leads to the formation of nano-sized gratings with a pitch as small as 150 nm[10]. These periodic structures are ruled in the direction parallel to the polarization of the writing laser[9] and consist of thin regions of index of refraction n_1, characterized by a strong oxygen deficiency[10], surrounded by larger regions of index n_2 (Fig. 1). Such a periodic assembly behaves as a uniaxial form-birefringent material, whose optical axis is parallel to the direction of the polarization of the writing laser. It has been shown that the local refractive index change can be as high as -0.1 with respect to the unprocessed material[9], making these self-assembled structures the strongest laser written nano-gratings ever observed. We define as type II_fs the anisotropic femtosecond written structures which are distinguished by the presence of these self-assembled nano-gratings within the irradiated volume, as opposed to the directly written structures of type I_fs, characterized by a positive index change and optically isotropic properties.

It has already been reported that the femtosecond direct written structures of type I_fs have a stability at elevated temperatures comparable to the strongest UV laser induced refractive index changes[12,13]. In this letter, we show the different response to increased temperature displayed by the femtosecond laser written structures of type I_fs and type II_fs, with particular attention to the extraordinary behavior of the structures of type II_fs, whose refractive index change increases with temperature.

An amplified, mode-locked Ti: Sapphire laser operating at a wavelength of 800 nm, with 200 fs pulse duration and 100 kHz repetition rate, was utilized to fabricate the structures to be tested. The laser beam was linearly polarized and focused with a 10× objective. The femtosecond written sample consisted of an array of six square regions of side length of 100 μm, embedded in the bulk of fused silica (Herasil 1). The sample was mounted upon a computer controlled linear motor translation stage, which could move in the three directions with a spatial resolution of few nanometers. To be able to find the transition between the structures of types I_fs and II_fs, we wrote each zone with a different pulse energy (E_1= 80 nJ, E_2=0.4 μJ, E_3=0.8 μJ, E_4=1.2 μJ, E_5=1.6 μJ, E_6=2.14 μJ as illustrated in Table I). Each square was written utilizing a dedicated computer program, which controlled the translation stage and an electronic shutter used to regulate the irradiation time. The sample was moved along the direction of the laser polarization for 100 μm at a constant speed of 60 μm/s while the shutter was open, and then translated in the orthogonal direction for 1 μm with the shutter closed; this process was iterated 100 times.

After fabrication, the sample was positioned between two crossed polarizers and viewed under an optical microscope, in transmission mode, to verify the presence of laser-induced birefringence in the laser-processed regions. This optical inspection revealed that only the squares written at the highest energy levels (#5 and #6) transmit light and hence are birefringent. The laser-induced extraordinary ($\Delta\phi_e$) and ordinary ($\Delta\phi_o$) phase retardation was measured with a phase-stepping interferometric technique, (see reference 9 for experimental details). After measuring the thickness, t_p, of each directly written structure, in the direction of the propagation of light, using calibrated microscope images, the modification of the refractive index in the irradiated regions was calculated from

$$\Delta\phi = \frac{2\pi}{\lambda} t_p \Delta n \,, \tag{1}$$

where λ is, in this case, the wavelength of the probing He-Ne laser utilized in the interferometric setup (633 nm). From the experimental data, presented in Figure 2, showing the refractive index change versus increasing pulse energy (and reported in Table I), it may be noticed that no index change is observed in the first structure (#1), then Δn grows monotonically with the pulse energy until a maximum positive value of $+2.2\times10^{-3}$. From #5 the structures are observed to be birefringent and the extraordinary index change becomes strongly negative, reaching a minimum value of -4.9×10^{-3} in #6, which, as an absolute value, is the largest index modification induced in this silica sample. On the contrary, the ordinary index change, which is still positive in #5 becomes negative in #6, reaching a minimum value of -0.2×10^{-3}. Indeed, the relative measurement of the refractive index confirmed the optical observations, showing that the first four structures of the sample (#1, #2, #3 and #4) are optically isotropic (type I_fs); whereas in the last two structures (#5 #6) significant birefringence is measured. In addition, it should be noted that, an abrupt change in the sign of the laser-induced index modification arises at the same threshold as the birefringence. The behavior of the refractive index change, in the femtosecond directly written structures of type II_fs, was investigated and justified in a previous publication, and can be ascribed to the onset of self-assembled nanostructures within the irradiated volume[9].

In order to investigate the stability of the anisotropic structures of type II_fs in comparison with the non-birefringent ones of type I_fs, an annealing experiment was performed. The sample of six directly written regions was heated at a rate of 3 ^{o}C per minute, kept at 200 ^{o}C for one hour and cooled to room temperature at 1 ^{o}C per minute. The treatment was then repeated up to maximum temperatures of 500 ^{o}C, 800 ^{o}C, 1100 ^{o}C and 1400 ^{o}C, and after each annealing step the sample was removed and the index change measured, except for the final case T=1400 ^{o}C, where the sample crystallized during the operation. Our results therefore refer to the steady state value assumed by the modified structures after being heated and then cooled back at room temperature (Fig. 2).

It is observed that the index change of all the structures was unaltered up to a temperature of 500 ^{o}C, but above this temperature the isotropic structures belonging to type I_fs (#1, #2, #3 and #4) behaved very differently to the anisotropic structures of type II_fs (#5 #6). In agreement with previously reported results[12], the index change of the isotropic non-birefringent structures decreased by a factor of ~0.4, with respect to the initial value after heating to 800 ^{o}C, and finally disappeared after annealing at 1100 ^{o}C. On the contrary, the birefringent regions were still clearly visible under an optical microscope even after annealing at 1100^{o}C. Rather unexpectedly, however both the ordinary and extraordinary index change in the birefringent structures becomes more negative with respect to the unprocessed silica (Fig. 2). This behavior is more obvious in Figure 3 (a), where the normalized extraordinary index change, measured after each annealing step, is plotted versus the maximum temperature. It should be noted that, while for the structures of type I_fs the index change decreases after 500 ^{o}C, for the two structures of type II_fs, an increase is measured. Our observations lead to the surprising conclusion that, in the anisotropic structures of type II_fs the absolute value of the modification of the refractive index induced by the laser, increases with the annealing temperature. Yet, the birefringence of the structures $\beta=|n_e-n_o|$ decreases with the temperature (Fig. 3 (b)). Using the experimental measurement of the extraordinary and ordinary refractive index modification of the directly written regions (Δn_e and Δn_o respectively), the values of the local index change in the nano-gratings $\Delta n_1=n_1-n_{bg}$,. and $\Delta n_2=n_2-n_{bg}$ were calculated from[14]

$$\begin{aligned}\Delta n_e &= \left[\sqrt{\frac{n_1^2 n_2^2}{f n_2^2+(1-f)n_1^2}}-n_{bg}\right],\\ \Delta n_o &= \left[\sqrt{f n_1^2+(1-f)n_2^2}-n_{bg}\right]\end{aligned} \qquad (2)$$

where n_{bg} is the refractive index of silica, n_1 and n_2 are the local refractive indices of the nano-grating, $f=t_1/\Lambda$ is the filling factor, $\Lambda=t_1+t_2$ is the period of the nano-grating, and finally, t_1 and t_2 are the width of the regions with index n_1 and n_2 respectively (Fig.1). The value of the filling factor, f=0.3, was chosen from our previous experimental measurements of the period of the nano-grating, created in various structures, which were written under similar conditions to the test sample here.

Indeed, as it might be expected, both values of the local index change in the nano-gratings (Δn_1, and Δn_2) decrease, in their absolute values, with increasing temperature (Fig. 4), hence the grating becomes weaker and, consequently, the value of the birefringence reduces, as shown in Figure 3 (b). However, since n_2 anneals more rapidly than n_1, the relative weight in (2) is such that the absolute values of the ordinary and extraordinary index change increase.

We speculate that the different annealing rate within the nano-grating, which we deduce from the calculation of the local refractive indices versus increasing temperature, is related to the different local composition of the periodic regions of refractive index n_1 and n_2. The results reported in reference 10, indeed revealed that the thin regions of width t_1, characterized by a strong negative index change with respect to silica (up to -0.1[9]), are oxygen-deficient regions. However, such a structural modification is not detected in the regions of width t_2, which are characterized by a positive index change.

Although the mechanisms responsible for the creation of the femtosecond induced index change are still under investigation, it is believed that the positive index change, measured in the structures of type I_fs, is associated to volume change, photoelasticity and to the modification of the absorption spectrum due to the presence of defects[15].

This type of modification eventually anneals at elevated temperatures[15]. We believe that the regions of index n_2 have a similar thermal behviour, whilst the strong structural modification of the regions of index n_1 prevents them from disappearing.

In conclusion, we have reported the first experiment related to the annealing of femtosecond directly written structures of type II_fs, which showed extraordinary thermal stability. The unexpected behavior displayed by these structures, namely a growth of the absolute value of the ordinary and extraordinary refractive index change with the temperature increase, was justified considering the periodical structure formed by the femtosecond laser in the irradiated volume. Non-birefringent regions started degrading at 800° C; whereas the femtosecond written structures of type II_fs could not be annealed, making them an attractive candidate for embedded polarization sensitive photonic applications.

References

[1] K. Miura, J. Qiu, H. Inouye, T. Mitsuyu, and K. Hirao, Appl. Phys. Lett. **71,** 3329 (1997).

[2] G. Cerullo, R. Osellame, S. Taccheo, M. Marangoni, D. Polli, R. Ramponi, P. Laporta, and S. De Silvestri, Opt. Lett. **27,** 1938 (2002).

[3] Y. Kondo, K. Nouchi, T. Mitsuyu, M. Watanabe, P. G. Kazansky, and K. Hirao, Opt. Lett. **24**, 646 (1999).

[4] E. Bricchi, J. D. Mills, P. G. Kazansky, B. G. Klappauf, and J. J. Baumberg, Opt. Lett*.* **27,** 2200 (2002).

[5] Y. Bellouard, A. Said, M. Dugan, and P. Bado, Opt. Express **12**, 2120 (2004).

[6] E. Glezer , M. Milosavljevic, L. Huang, R. J. Finlay, T. H. Her, J. P. Callan, and E. Mazur, Opt. Lett*.* **21** 2023 (1996).

[7] P. G. Kazansky, H. Inouye, T. Mitsuyu, K. Miura, J. Qiu, K. Hirao, and F. Starrost, Phys. Rev. Lett. **82**, 2199 (1999).

[8] J. D. Mills, P. G. Kazansky, E. Bricchi, and J. J. Baumberg, Appl. Phys. Lett. **81,** 196 (2002).

[9] E. Bricchi, B. G. Klappauf, and P. G. Kazansky, Opt. Lett. **29**, 119 (2004).

[10]. Y. Shimotsuma, P. G. Kazansky J. Qiu and, K. Hirao, Phys. Rev. Lett*.* **24**, 2474051 (2003).

[11] C. B. Schaffer, A. Brodeur, and E. Mazur, Mater. Sci. Tech. **12,** 1784 (2001).

[12]. S. J. Mihailov, C. W. Smelser, D. Grobnic, R. B. Walker, P. Lu, H. Ding, J. Unruh, J. Lightwave Tech. **22**, 94 (2004).

[13] P. G. Kryukov, Yu. V. Larionov, A. A. Rybaltovskii, K. A. Zagorulko, A. Dragomir, D. N. Nikogosyan, and A. A. Ruth, Microelec. Eng. **69**, 249 (2003).

[14] M. Born and E. Wolf. Principles of optics. Cambridge University Press, Cambridge, 1999.

[15] J.W. Chan, T. Huser, S. Risbud, and D.M. Krol, Opt. Lett. **26**, 1726 (2001).

Table I. Fabrication details of the sample

Energy (μJ)	Square identifier	Δn_e [a)] ($\times 10^{-3}$)	Δn_o [a)] ($\times 10^{-3}$)
0.08	#1	+0.0±0.2	+0.0±0.2
0.40	#2	+1.6±0.2	+1.2±0.2
0.80	#3	+2.2±0.2	+2.2±0.2
1.20	#4	+1.9±0.2	+2.3±0.2
1.60	#5	-2.8±0.2	+0.9±0.2
2.14	#6	-4.9±0.2	-0.2±0.2

a) Before annealing

Figure Captions

Fig.1

Schematic of the self-assembled nano-grating formed in the irradiated volume of the directly written structures of type II_fs. n_{bg}: refractive index of silica. n_1, n_2: local refractive indices of the nano-grating. $f=t_1/\Lambda$: filling factor, $\Lambda=t_1+t_2$: period of the nano-grating. t_1, t_2: width of the regions with index n_1 and n_2 respectively.

Fig.2

Measure of the laser induced index change of each directly written region versus the energy after each annealing step. (left): Δn_e (right) Δn_o.

Fig.3

(a): Extraordinary index change normalized to the value measured before annealing, versus the temperature. (b): Birefringence versus the temperature.

Fig.4

Δn_1 and Δn_2 versus temperature rise and normalized to their initial value (before annealing).

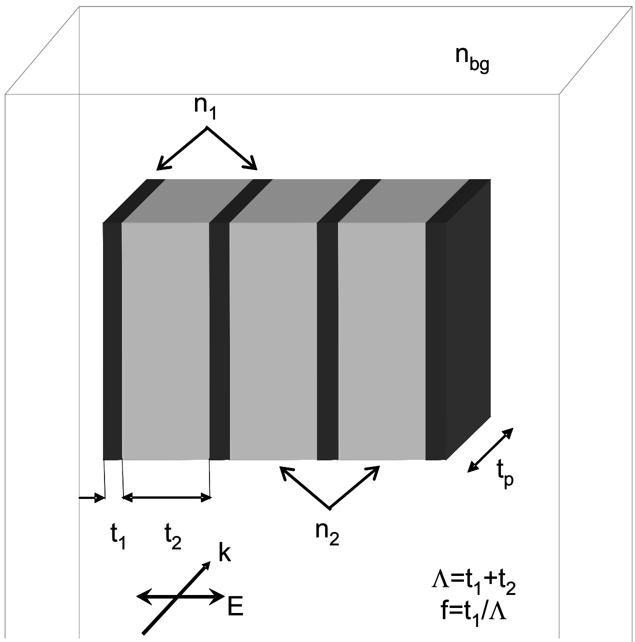
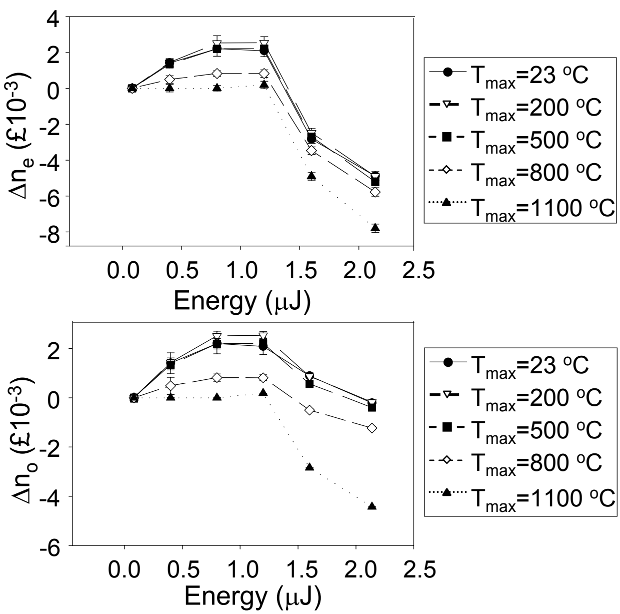
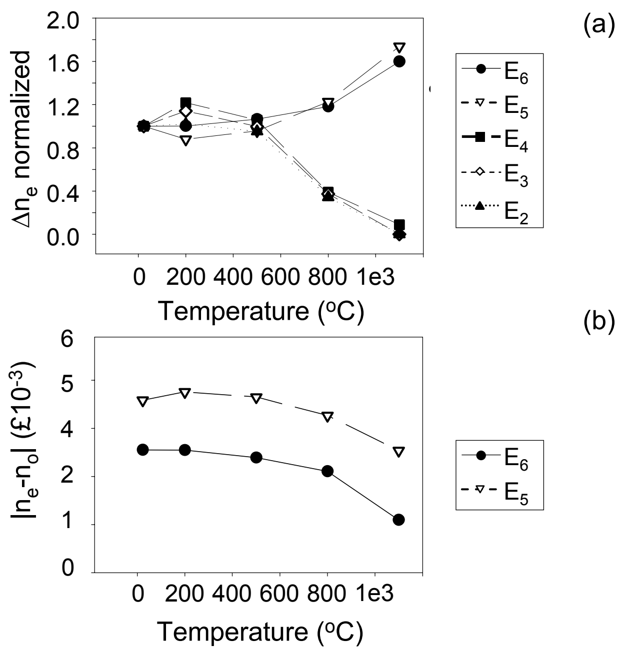


Figure 1



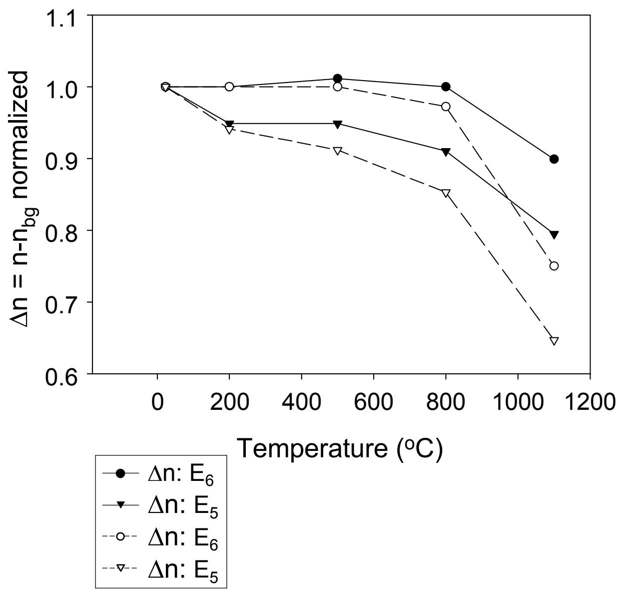
Δn_e (£10^-3)
Energy (μJ)
Δn_o (£10^-3)
Energy (μJ)
T_max=23 ºC
T_max=200 ºC
T_max=500 ºC
T_max=800 ºC
T_max=1100 ºC

Figure 2



(a)
2.0
1.6
1.2
0.8
0.4
0.0
Δn_e normalized
0 200 400 600 800 1e3
Temperature (oC)
E6
E5
E4
E3
E2
(b)
6
5
4
3
2
1
0
|n_e-n_o| (£10-3)
0 200 400 600 800 1e3
Temperature (oC)
E6
E5

Figure 3



1.1
1.0
0.9
0.8
0.7
0.6
Δn = n-n_bg normalized
0
200
400
600
800
1000
1200
Temperature (oC)
Δn: E6
Δn: E5
Δn: E6
Δn: E5

Figure 4