High damage threshold birefringent elements produced by ultrafast laser nanostructuring in silica glass

GHOLAMREZA SHAYEGANRAD,* XIN CHANG, HUIJUN WANG, CHUN DENG, YUHAO LEI, ∗ AND PETER G. KAZANSKY

Optoelectronics Research Centre, University of Southampton, Southampton, SO17 1BJ, UK
*g.shayeganrad@soton.ac.uk

Abstract: Birefringent patterning by ultrafast laser nanostructuring in silica glass has been used for space-variant birefringent optics with high durability and high optical damage threshold. We demonstrate that the oblate-shaped birefringent modification (type X) with ultrahigh optical transmission has higher optical damage resistance, comparable to pristine silica glass. The lower damage threshold of nanogratings based modification (type 2) following thermal annealing at 900 °C for an hour is improved from 0.96 J/cm² to 1.62 J/cm² for 300 fs laser pulses and approaches the optical damage threshold of type X (1.56 J/cm²). This opens the door to utilize these optical elements for high power laser applications where optical transmission and damage threshold are the key parameters. The lower damage threshold of type 2 modification is related to the relatively high concentration of defects, such as E’ centers and oxygen-deficiency centers (ODCs).

1. Introduction

Femtosecond (fs) laser writing has emerged as a technologically attractive method for creating birefringence patterns through the fabrication of polarization-controlled self-assembled lamella structures (nanogratings, referred as type 2 modification) in various transparent bulk materials (silica glass in particular) and thin films as well [1–7]. The success of using fs-lasers in 3D nanostructuring stems from the nonlinear nature of interaction where the change is confined to material at the focal volume with high-precision and minimal collateral damage [8]. Various geometric phase optical elements (GPOEs) [9] and cylindrical vector beam converters (S-waveplates) [10] have been fabricated by polarization controlled optical axis orientation of form birefringence of nanograting based modifications. Silica glass is an ideal optical material due to its wide transmission window, high durability and high optical damage threshold [11]. Compared to the plasmonic meta-surface and liquid crystal elements, optical elements based on fs-laser induced nanogratings in silica glass with higher optical damage threshold found their applications in high power laser systems. However, the reduced transmission in the visible and ultraviolet range, stemming from the fluctuation of the periodicity of nanogratings, hinders their further applications. More recently, a new type of birefringent modification with ultra-high transmission (referred as type X modification) was demonstrated in silica glass by ultrafast laser writing [12]. Such anisotropic nanopores based modification has been utilized to fabricate GPOEs and polarization converters with almost 100% efficiency in the visible range [12]. However, the optical damage threshold of type X modification has not been investigated and whether it can be used for high-power laser applications is still an open question.

Here, we demonstrated that the optical damage threshold (1.56 J/cm²) of anisotropic nanopores based type X modification, comparable to pristine silica glass (∼ 2 J/cm² [13]), is 1.6 times
higher than that of the nanograting-based type II modification (0.96 J/cm$^2$) by the irradiation of 300 fs laser pulses. It indicates that optical elements with high damage threshold and high optical transmission can be realized with type X modification and they are suitable for high power laser applications. The lower damage threshold of type 2 modification can be attributed to the relatively high-density defects, such as the E’ centers and oxygen-deficiency centers (ODCs). Following annealing at 900°C for one hour, the optical damage threshold of type 2 modification was improved and approached type X damage threshold. We also found that the damage threshold fluence of the type X nanostructures increased with the increasing duration of laser pulses, which is consistent with previous experimental studies with pristine silica glass [13].

2. Experimental details

Laser re-irradiation of the anisotropic nanostructures induced by linearly polarized focused fs laser pulses in silica glass was performed to investigate the optical damage behaviour of the modifications with different writing conditions that is crucial in high power laser applications. The schematic diagram of the experimental setup is shown in Fig. 1(a). A regeneratively amplified Yb:KGW laser (PHAROS, Light Conversion Ltd.), operating at a centre wavelength of 1030 nm and a bandwidth of $\Delta \lambda \approx 13$ nm (TEM$_{00}$-mode, $M^2 \leq 1.07$) with a repetition rate set to 200 kHz and a pulse duration tuneable in the range of 165-900 fs (FWHM) was employed. The laser pulses were focused $\sim$170 µm beneath the synthetic silica glass sample surface with an aspheric lens of 0.16 numerical aperture (NA) for bulk nanostructuring. The spot radius was $\sim$2.7 µm at 1/e$^2$ intensity, measured with a knife-edge technique in air. The sample was mounted on a computer-controlled XYZ stage (Aerotech Ltd.) that allows precise adjustment of the focal-plane and translation parallel or perpendicular to the laser propagation axis. The laser power was measured after the aspheric lens with Gentec optical power meter and laser pulse width measured by a commercial autocorrelator (APE PulseCheck).

![Fig. 1.](image)

Fig. 1. (a) Schematic diagram of the experimental setup used for writing/overwriting of birefringent nanostructures in silica glass. (b) Birefringent images of the inscribed nanostructure patterns before (top) and after (bottom) laser overwriting in the center (see text for detail). Pseudo-colour (inset) indicates the orientation of the slow axis of the birefringent modification. EOM is an electro-optic modulator, QWP is a quarter waveplate, and CCD is a charge coupled device.

Transverse writing configuration with translation perpendicular to the laser propagation axis was used. The laser energy is varied using a calibrated attenuator (Altechna, Watt Pilot). The
combination of a linear polarizer, an electro-optic modulator (EOM) and a quarter-wave plate (QWP) was used to control the azimuthal angle of the laser beam polarization. Thermal annealing was performed in an oven (Nabertherm GmbH) in the ambient air atmosphere. The retardance and slow axis azimuth of the induced nanostructures were quantitatively analysed with an Olympus BX51 optical microscope equipped with a birefringence measurement system (CRi Abrio imaging system) and a white light illumination source propagates through a bandpass filter operating at 546 nm wavelength. The optical path difference (OPD) was measured by a wavefront sensor (SID4-HR GE, PHASICS Inc.).

Several experimental parameters have been identified to be important for the deposition of energy in the bulk silica glass and subsequently controlling anisotropic nanostructures by focusing high intensity fs-laser radiation [14]. Apart from the laser wavelength and the laser beam polarization, the major key parameters are the laser fluence (energy density in J/cm²), laser pulse width, and number of pulses applied to the same laser spot. Here, we conducted the writing experiment by changing intensity and scanning speed to control the accumulated fluence. Material modification is confined to a volume where the intensity exceeds the material modification threshold. For pulse durations of 300 fs and 600 fs, the threshold of single pulse bulk damage (threshold of nonlinear absorption) is measured to be \( \sim 2.3 \text{ J/cm}^2 \) and \( \sim 2.8 \text{ J/cm}^2 \), respectively, with a 0.16 NA aspheric lens [14], comparable with the threshold of single-pulse with 300 fs pulse width induced catastrophic damage on surface of silica glass (\( \approx 2.1 \text{ J/cm}^2 \)) [13]. Note that damage on the surface significantly depends on the surface quality, such as surface roughness and presence of cracks, created in the manufacturing processes [15], suggests that laser induced surface damage can be improved by the reduction of surface roughness, imperfections and defects [16].

To study the damage threshold of fs laser induced anisotropic nanostructures in silica glass, firstly, fused silica samples were irradiated with focused linearly polarized fs laser pulses (parallel to y-axis, Fig. 1(a)) to write squares of type X and type 2 modifications (100×100 \( \mu \text{m}^2 \)) with slow axis azimuth at 0° along x-axis (Fig. 1(b), top). The scanning direction was along x-axis. During the writing procedure, the sample was moved at uniform velocity of 0.2 mm/s and 10 mm/s, respectively, for type 2 and type X modifications; corresponding to 1000 and 20 pulses/\( \mu \text{m} \) at 200 kHz. Energy and width of the pulses were set to (0.8 \( \mu \text{J} \) and 600 fs) and (0.74 \( \mu \text{J} \) and 300 fs) corresponding to 5.8 TW/cm² and 10.8 TW/cm² for type X and type 2 modifications, respectively, with nonlinear absorption approximately 8% and 15% [14]. Here, we have chosen 300 fs laser pulses to generate smooth type 2 with optical transmission about 90% compared with type 2 rough with optical transmission of about 70% which can be produced by 600-fs laser pulses. The critical power for self-focusing of silica glass at 1030 nm to be 5 MW [17]; for our 300 fs and 600 fs laser pulses, corresponds to a pulse energy of 1.5 \( \mu \text{J} \) and 3 \( \mu \text{J} \), respectively. Therefore, for both types of modification, self-focusing is negligible.

The square regions were written by line scanning with 1-\( \mu \text{m} \) line separation in y-axis (Fig. 1.a). After completing the writing procedure, the centre of the squares was overwritten by a 50×50 \( \mu \text{m}^2 \) squares with focused fs laser polarization rotated 90° (parallel to x-axis) centred at 1030 nm wavelength (Fig. 1(b), bottom). The optical damage was determined by measuring the retardance of the structures following laser re-irradiation with various pulse energies and pulse durations. The damage threshold of type X and type 2 nanostructures after annealing at 900 °C for an hour was also investigated.

3. Results and discussion

The damage threshold fluence for type X and type 2 modifications was quantitatively studied by varying energy and pulse density of overwriting laser pulses with fixed pulse width of 300-fs and repetition rate of 200-kHz. The scanning speed was varied from 0.010 up to 10 mm/s to adjust the pulse density (Fig. 2(a) and 2(b)). It is noticeable that the presented results were obtained
with focused fs laser pulses centred at 1030 nm in the bulk silica glass through 0.16 NA aspheric lens, otherwise surface damage might occur first because of surface field enhancement by surface cracks, nodules, or voids. The damage threshold intensity or fluence is quantitively determined where the retardance begins to degrade. The average retardance value of type X and type 2 modifications before re-irradiation was measured to be ∼48 nm and ∼200 nm, respectively. The retardance of type X and type 2 began to decrease at intensity of 5.2 TW/cm² and 3.2 TW/cm², respectively, for 300-fs pulses and scanning speed of 0.01 mm/s. The damage threshold of 5.2 TW/cm² and 3.2 TW/cm² corresponding to fluence of 1.56 J/cm² and 0.96 J/cm² are below the threshold of single pulse induced bulk damage ∼2.3 J/cm² for 300-fs pulse width at 1030-nm wavelength. In other words, the damage threshold of type X and type 2 after 20 and 1000 shots of irradiation reduced approximately 1.5 and 2.4 times compared to the single-shot bulk damage threshold with 300-fs pulses at 1030-nm, which could be attributed to the nonlinear ionization memory.

Moreover, the damage threshold of both type X and type 2 modifications increased with increasing scanning speed as expected because of decreasing density of laser pulses or accumulated fluence. With increasing energy or intensity of the re-irradiation laser pulses, birefringence of the type X and type 2 was further decreased, and anisotropic nanostructures were transferred to isotropic modification at intensities of 5.8 TW/cm² and 7.5 TW/cm², respectively, for 0.01 mm/s scanning speed corresponding to 20,000 pulses/µm. By more increasing the intensity of overwriting laser pulses, old nanostructures were replaced with the new one with slow axis 90° orientation and the birefringence of the reproduced nanostructures was increased, in agreement with the literature [18]. After producing isotropic nanostructures, type of the created new nanostructures depends on the parameters of the overwriting laser pulses. Here, we observed that anisotropic nanostructures transferred to type 2 modification or self-assembled nanogratings independent on type of the initial modification. OPD of type 2 modification was measured following re-irradiation with scanning speed of 0.02 mm/s and different intensities (Fig. 2(c)). The nanogratings were transferred to isotropic structure at ∼7.5 TW/cm², where OPD related to vertical and horizontal polarisation light are equal (∼100 nm), consistent with the value obtained in Fig. 2(b)). It confirms that the erasure process does not return the material to its bulk form and in this case some nanopores survive, from old nanostructures that have not been completely erased [18,19], even with increasing pulse density and laser pulse intensity. The rewriting process was examined 3 times for the given scanning speeds to establish the threshold value. The relatively small error bars reflect that the difference in the damage threshold of type X and type 2 is significant and reproducible.

The physical mechanisms responsible for damage of laser-induced nanostructures within the fs regime with photon energy below bandgap are multiphoton ionization eventually followed by impact ionization. Subsequently, the absorbed energy by electron plasma transfers to the lattice typically in a few picoseconds. It heats the lattice before the energy dissipates through diffusion or radiative recombination and degrades the nanostructures via material phase change or change in the electronic band structure. The photoexcited electrons relax into the self-trapped excitons (STE) followed by radiatively recombination or non-radiatively transformation into point defects, which facilitate nanostructures formation in silica glass [3]. The presence of fs laser induced defects leads to enhancement of the absorption and therefore the damage can be initiated at relatively lower laser fluences compared to the pristine fused silica.

The anisotropic type X modification was initiated by randomly distributed nanopores following elongation via near-field enhancement with nanopores of about ≤50 nm in diameter [12]. One possible situation for type X formation is changing the bonding structure of silica glass after interaction with fs-pulses which results in formation of defects such as É centres, ODC, and NBOHCs. All these defects create energy levels in the previously forbidden band gap as localised states which reduce the energy absorption threshold. Subsequently, new transitions with lower
Fig. 2. Illustration of the damage threshold of type X and type 2 modification in silica glass. (a) and (b) the evolution of retardance of type X and type 2 versus intensity of the rewriting laser pulses with a pulse duration of 300 fs, for several scanning speeds. Repetition rate is 200 kHz. (c) OPD measurement of type 2 modification after overwriting at 0.02 mm/s scanning speed. Top images are birefringent images measured by Abrio imaging system.
energy are available to excite the electrons. This is important because both excitation and relaxation processes may be influenced by the presence of such defect states.

For damaging imprinted nanostructures, one needs to excite electrons in defect states and/or in the valance band to the conduction band and thus it is necessary to supply enough energy for these transitions to take place. At low intensities (≤10^{11} W/cm^2), this can be achieved by absorption of a photon with energy larger than or equal to the bandgap, while, at high intensities (>10^{11} W/cm^2) multiphoton ionization (I≈10^{12} W/cm^2) or tunnel ionization (I≈10^{15} W/cm^2) dominates. Once an initial excitation electron density has been reached, it is possible to further excite the conduction band electrons through impact ionization resulting in an electronic avalanche. Superimposed multiple fs laser pulses and photoexcitation of the NBOHC through multiphoton absorption or impact ionization for pulses >250 fs by hot electrons, result in the dissociation of oxygen atom and the E_δ centres. Note that both the oxygen deficiency centres (ODCs) and E centres are detected in both birefringent modifications type X and type 2 (Fig. 3). As mentioned above, all these defects are the result of the formation of localised energy states in the previously forbidden bandgap which may influence both excitation and relaxation processes. Defect-assisted ionization lowers the multiphoton absorption order.

![Graph showing transmission (% vs Wavelength (nm))](image)

**Fig. 3.** A UV-Vis absorption spectra of type X and type 2 before and after annealing at 900 °C for an hour. The absorption related to the ODCs and E’ centers disappeared after annealing. Absorption peak of E’ centers and ODC(II) are at 214 nm 248 nm, respectively.

To understand the reason of difference between damage threshold of type X and type 2, the damage behaviour of type X and type 2 modification after annealing was investigated. It is found that, by annealing type 2 modification at 900 °C for an hour, the damage threshold of type 2 modification is improved from 3.2 TW/cm^2 to 5.4 TW/cm^2 (Fig. 4) and reached the damage threshold of type X. This demonstrates that defects, such as ODCs and E’ centres, are likely the major factor that leads to the low damage threshold of type 2, which can be bleached under thermal treatment as seen in Fig. 3, consistent with Refs. [20,21]. On the other hand, these defects can be annealed at a lower temperature for several hours, e.g., 500 °C, requiring only a more primary furnace. Note that we did not observe noticeable change on damage threshold of type X following annealing at 900 °C for an hour.
Fig. 4. Retardance of type 2 modification before and after annealing at 900 °C in air for an hour versus intensity of overwriting laser pulses. Pulse density is 10,000 pulses/µm and laser pulse duration is 300 fs.

Fig. 5. Changing retardance of type X and type 2 modifications by annealing at 1000 °C for different durations of time.

The thermal stability of type X and type 2 was also demonstrated by annealing experiments (Fig. 5). Samples with different writing conditions were annealed at 1000 °C for different annealing time (1 to 8 hours). In the first hour, the retardance of type 2 structures dropped
drastrically (about 40%), due to the releasing of fs-laser pulses induced stress, and then the
decay rate decreased. In contrast, the retardance of type X modification decreased slowly with

Fig. 6. (a) Damage threshold of type X modifications versus intensity of overwriting
laser pulses for different laser pulse durations, (b) Damage threshold fluence of type X
modification and single pulse absorption of pristine silica glass versus laser pulse duration
for 1 mm/s scanning speed.
increasing annealing time. In addition, the rate of decreasing retardance in the first hour is reduced from 41.7% to 26.3% with changing pulse density from 5000 to 33 pulses/µm as expected, due to less stress accumulation with less pulse density. It indicates that birefringent elements fabricated based on type X modification has higher thermal stability and can be used in high temperature conditions.

Besides, we investigated the damage behaviour of type X versus overwriting laser intensity for different laser pulse durations (Fig. 6(a)). We observed that the damage threshold fluence of type X modification increased with increasing laser pulse duration, following the same trend of single-pulse absorption threshold of pristine silica glass (Fig. 6(b)). This shows, in the regime where we are working (<10 TW/cm²), the contribution of photoionization is more significant than the contribution of the avalanche ionization, resulting in higher electron densities at lower pulse durations. Higher electron densities for shorter pulse durations result in higher lattice temperatures and, consequently, lowering damage threshold [22]. This result is consistent with a higher breakdown threshold with increasing pulse durations reported in [13]. In addition, comparing our results for pulse duration of 165 fs and 200 pulses/µm at 200 kHz with the reported data by Altechna (∼2.3 J/cm²) for pulse duration of 212.4 fs and 10 pulses/µm at 100 Hz [23], our result is about 2 times smaller than Altechna’s report due to the difference in the definition of damage as well as difference in rewriting pulse density and pulse duration. Since the pulse repetition interval of 5-µs (200 kHz repetition rate) is larger than 1-µs thermal relaxation time of silica glass (varies with glass composition), the dependence of multiple pulse damage threshold on the repetition rate or heat accumulation is negligible. Altechna defined damage as the catastrophic shattering or a visible damage on surface or bulk, but in this article, damage is defined as gradation of retardance of the nanostructure, which indicates the actual limit for functional type 2 and type X based optical devices in high power laser applications. Moreover, the accumulation of point defects during the writing structure helps to initiate multiphoton ionization of rewriting process at lower fluences [24].

4. Conclusion

The damage threshold of type X and type 2 modifications in silica glass within femtosecond regime was demonstrated by using a simple diagnostic method of retardance measurement for different overwriting conditions. We found that damage threshold of type 2 (5.2 TW/cm² or 1.56 J/cm² for 300 fs laser pulses) is lower compared to type X (3.2 TW/cm² or 0.96 J/cm² for 300 fs laser pulses) which is attributed to the absorption enhancement by fs pulses induced defect structures. By annealing at 900 °C in air for an hour to erase defect centres like E’ centres and ODCs, damage threshold of type 2 modifications was effectively increased to 5.4 TW/cm² close to that of type X modification. In addition, the damage threshold was increased with laser pulse duration. The physical mechanisms responsible for damage of laser-induced nanostructures are multiphoton ionization followed by impact ionization. The presence of fs laser induced defects leads to enhance the absorption and therefore the damage is initiated at relatively low laser fluences compared to pristine fused silica. This study reveals that ultralow-loss photonic devices based on type X modification has a potential of application in high-fluence laser systems below ∼1.5 J/cm².

Funding. European Research Council (ENiGMA,789116).

Disclosures. The authors declare no conflicts of interest.

Data availability. The data that support the findings of this study are available from the corresponding author upon reasonable request.

References


