Extraordinary anisotropy of ultrafast laser writing in glass

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Abstract: The unusual dependence of femtosecond laser writing on the light polarization and direction of raster scanning is demonstrated in silica and chalcogenide glasses. Two different mechanisms contributing to the observed anisotropy are identified: the chevron-shaped stress induced by the sample movement and the pulse front tilt of ultrashort light pulse. Control of anisotropies associated with the spatio-temporal asymmetry of an ultrashort pulse beam and scanning geometry is crucial in the ultrafast laser machining of transparent materials.

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The ability to directly process the material with a submicron resolution turns femtosecond laser direct writing into an attractive technique for numerous applications including laser surgery [1], three-dimensional nanostructuring [2] and optical data storage [3]. Depending on the experimental parameters (repetition rate, writing speed, numerical aperture, pulse energy and duration) different types of structural changes can be induced. In particular, three distinctive types of silica glass modifications have been observed with the increase of irradiation fluence: isotropic refractive index increase [4], self-assembled nanostructures [2] and microvoids [5]. Recently birefringent optical elements, in particular polarization diffraction gratings and radial polarization beam converters, have been produced by self-assembled nanostructuring [6,7].

The nanostructures are responsible for the form birefrigence [8], and behave like a negative uniaxial crystal. Two parameters of the birefringent modification, retardance and the azimuth of the slow axis [7], can be independently controlled during the writing process as the slow axis is defined by the polarization and the retardance as a function of the laser fluence. Retardance depends also on the laser wavelength, the pulse duration and the number of pulses transmitted through the modified region [8–10]. Moreover, it is affected by the orientation of the polarization plane with respect to the writing direction. As the direction of the slow axis is varied during the writing process, the angle between the laser polarization and the writing direction is changing accordingly, which couples the induced retardance with the polarization direction. The difference in modification for 0° and 90° angles of polarization with respect to the writing direction is known for metals [11]. Recently, a similar effect was reported for laser processing of dielectrics [12]. However, it is important to keep the retardance value independent on the light polarization for the fabrication of variant polarization optical elements, including beam converters and 5D optical memory [13,14]. Such polarization dependence is explained by the boundary conditions. The absorption is stronger for light polarized perpendicular to the interface, as described by the Fresnel coefficients. Thus the polarization parallel to the writing direction, which is absorbed more efficiently at the front kerf, is commonly used in metal cutting. For the perpendicular polarization, the light is absorbed more efficiently at the sidewalls. As an alternative, circularly or radially polarized light is used, which is equally absorbed at the front and sidewalls of the kerf [15]. The polarization dependence also arises due to the spatio-temporal properties of the ultrashort pulse laser beam quantified by the pulse front tilt (PFT) [16,17]. The PFT produced by temporal and spatial chirps in femtosecond laser pulses [18] can lead to the quill writing [14] and the anisotropic photosensitivity phenomena [19]. When the laser pulse approaches the focal point, the beam diameter is shrinking and the pulse front tilt is proportionally increasing. Thus even negligible pulse front tilt is strongly enhanced in the vicinity of the focus.
In this Letter, we demonstrate other extraordinary anisotropic properties of the femtosecond laser writing in transparent materials. Two new types of writing polarization dependences and related writing direction asymmetries, which are not directly connected with the boundary conditions, are observed. Characterization of the optical anisotropy induced in fused silica and germanium sulphide glass revealed the chevron-shape stress, which leads to the polarization dependence when adjacent laser written tracks are partially overlapping. Another polarization dependence, which is related to the anisotropic photosensitivity produced by the pulse front tilt, is observed for single line writing.

The experiments were performed with two different laser systems. The first was PHAROS Yb:KGW (Yb-doped potassium gadolinium tungstate) laser system (Light Conversion Ltd.) operating at 1030 nm with the pulse duration stretched from 300 fs to 800 fs using an internal pulse stretcher-compressor. The laser repetition rate was set to 200 kHz. The linearly polarized laser beam was focused with an aspheric lens (NA = 0.16) 300 μm below the surface of a fused silica sample. The polarization of the laser beam was controlled with the zero order half-wave plate placed just before the focusing optics. Writing speed was in the range from 0.2 to 5 mm/s or effectively 160-4000 pulses per dot.

Fig. 1. The dependence of retardance on pulse energy for four different polarizations of laser. Strongest difference is between 45° and −45° polarization. Writing speed of structures was 200 μm/s.

The separate tracks were imprinted in Ge_{25}S_{75} glass with the second laser system, regeneratively amplified Ti:Sapphire laser delivering 150 fs light pulses at 800 nm wavelength and operating at 250 kHz repetition rate. The tracks were inscribed with 0.55 NA objective 200 μm below the surface at the scan speed of 200 μm/s. After the irradiation, the samples were inspected with a quantitative birefringence measurement system Abrio (CRi Inc.).

First, a set of structures was written in silica glass with four different polarization orientations with respect to the scanning direction (perpendicular, parallel and ±45°). The tracks, comprising of 1 × 1 mm squares, were imprinted by translating the sample in the direction perpendicular to the laser light propagation. The tracks separated by 1 μm were partially overlapping (the estimated spot size was about 4 μm). The pulse energy was increased in steps from 0.8 to 1.5 μJ. All samples after irradiation exhibited strong birefringence produced by self-assembled nanostructures in the range of retardance values 50-250 nm. The retardance revealed strong polarization dependence for all pulse energies (Fig. 1). The difference in modifications written with 0° (parallel) and 90° (perpendicular) polarization plane angles, with respect to the writing direction, could be explained by the effect of the polarization dependent Fresnel reflection at the boundaries of an induced...
structure [15]. The difference was also observed between +45° and −45°, which is unexpected and counterintuitive from the point of anisotropic laser light interaction at the boundary. Moreover, the difference for +45° and −45° (more than 20% of the retardance value) was stronger than for 0° and 90° (less than 10% difference at its peak). In contrast to the metal cutting, where the light polarized parallel to the writing direction is the most efficient, in our experiments we observed that the light polarized at +45° with the writing direction produced the highest retardance.

In order to understand the influence of the +45° polarization on the strength of the induced retardance, several squares were written with various combinations of the polarization orientation, track writing and raster scanning directions (Fig. 2). One can clearly see that all three parameters affected the induced structures. Throughout this paper, only the strength of retardance is compared, as this parameter can be easily measured. However, the difference in obtained structures could be also observed under an optical microscope as the areas with the stronger birefringence exhibited slightly stronger scattering. Recently, Raman spectroscopy revealed higher density of 3-tetrahedra rings for the longitudinal polarization compared to the transversal polarization [16].

Very interesting case is illustrated by the structure number 8 (Fig. 2) where two parts were written with the same angle between the light polarization and the writing direction but with the different raster scanning direction. As a result, raster scanning in one direction, from the bottom to the top, resulted in higher retardance than for scanning from the top to the bottom.

The laser induced stress was investigated as possible reason for this phenomenon. To evaluate the effect of laser induced stress, we investigated several glasses where nanogratings are not produced and thus only stress birefringence is observed. For the stress birefringence, the relation between the retardance \( R \) and stress \( \sigma \) is defined as:

\[
R = C_{pe} \cdot \sigma \cdot d,
\]

where \( C_{pe} \) is the photoelastic coefficient, \( d \) is the thickness of the birefringent region. The larger photoelastic coefficient is, the stronger retardance is induced by stress. For the experiments, we selected glasses with different photoelastic coefficients: chalcogenide glass (germanium sulphide), borate glass and phosphate glass (Fig. 3). The chalcogenide glass
(germanium sulphide \((\text{Ge}_{25}\text{S}_{75})\)) has a photoelastic coefficient 50 times higher \((2.2 \times 10^{-12}\ \text{Pa}^{-1})\) than fused silica \((0.4 \times 10^{-12}\ \text{Pa}^{-1})\) [20]).

![Fig. 3. Microscope images of the femtosecond laser written tracks in chalcogenide, borate and phosphate glasses respectively. On the left images are taken without polarizers and the right with crossed polarizers. The highest birefringence is induced in glass with the highest photoelastic coefficient.](image)

The measured value of retardance in the chalcogenide glass was 200 nm for 0.6 \(\mu\)J pulse energy. This is very close to the typical retardance values of form birefringence observed in fused silica. The subsequent thermal annealing at 310°C (glass transition temperature is 305°C) completely removed this birefringence confirming that it is induced solely by stress. Compared to chalcogenide glass, the laser exposed regions showed a much weaker birefringence in borate glass, with the \(C_{pe}\) reduced to the value of \(4.35 \times 10^{-12}\ \text{Pa}^{-1}\) (Fig. 3). In phosphate glass, with a \(C_{pe}\) value of \(0.42 \times 10^{-12}\ \text{Pa}^{-1}\), which is about 50 times smaller than in chalcogenide glass, no birefringence was detected. We also tried measuring the stress induced birefringence in silica glass. However, the direct measurement was not possible due to strong form birefringence in this glass. Recently the stress induced by ultrashort light pulses was characterized by an indirect measurement method, where the stress has been measured via deflection of glass machined cantilevers [19]. The maximum induced stress was about 300 MPa, thus using a photoelastic coefficient for fused silica we estimate the stress-induced retardance of about 35 nm.
The slow axis distribution of imprinted tracks in chalcogenide glass revealed the presence of chevron-shaped stress along the scanning direction (Fig. 4). The orientation of slow axis did not depend on the polarization of the writing beam confirming that the observed birefringence is related to mechanical forces exerted on the glass matrix and not to subwavelength structures. Material expansion produces stress in glass surrounding the light effected zone. The stress pattern is circularly symmetric in stationary conditions. The chevron-shaped stress distribution can be induced by multiple laser pulses delivered at a high repetition rate. We speculate that when the sample is moving the material is displaced by the thermal gradient and the front of modification is under higher strain than the back. Then the stress is annealed at the front and is frozen at the back of the modified region, leading to chevron-shaped stress distribution. It is worth to mention, that chevron-shaped structures were also observed in lithium niobate crystal [21] and on the silica glass surface [17].
If the chevron-shaped stress is indeed responsible for the observed directional dependence, the strength of the produced retardance should depend on the polarization angle with respect to the stress induced by a previous track (Fig. 5(a,c)). As a result, the effect should depend on the direction of the track writing and raster scanning.

This assumption was confirmed by images taken during the writing procedure, which reveal the influence of the induced stress on the interaction of laser irradiation with the material (Fig. 6). When the distance between laser written tracks is sufficiently large, they can be treated as being separate (Fig. 6(a)). As a result, the front of the track is perpendicular to the writing direction. In this case, the light polarized at 0° to the writing direction (perpendicular to the front) would produce stronger modification than the light polarized at 90° [12]. While the light polarized at 45° should have identical conditions as the light polarized at −45° and thus produce identical modification. If the distance between tracks is small and the track written by the laser overlaps with a region under strain, the situation is completely different. The front of the written track becomes tilted (Fig. 6(b)). As a result, the strongest modification is induced by polarization, which is at 45° to the writing direction and perpendicular to the front of the modification. The strength of the modification depends on the mutual angle between the polarization and the front of the modification. This observation clearly explains the observed retardance dependence on polarization (Fig. 1).

Also in the experiment, the correlation of the strength of retardance with the angle between the laser polarization and the stress induced by the previous track (also front of modification) was observed. The retardance was much stronger for the polarization perpendicular to the induced stress (front of modification) than for the parallel. By choosing the correct scanning algorithm, the observed polarization dependence could be eliminated. For instance in the structure number 3 of Fig. 2, the uniformity was achieved by changing the polarization orientation with the writing direction in such a way that it was always parallel to the chevron-shaped stress. The polarization dependence can be also compensated by the bidirectional raster scanning (Fig. 2, structure number 9). However, this produces double periodicity in the imprinted structure as a result of every second track having a different birefringence than the previous one [6]. Additionally, such type of scanning is not applicable for the fabrication of certain structures such as spirals.
The importance of the observed unusual polarization dependence can be clearly seen in the writing of the polarization converter (Fig. 7 [Media 1]) [7]. In this experiment, the laser beam is drawing spiral trajectories with polarization azimuth rotating in a certain manner. As the polarization plane orientation was changing with respect to the writing direction, the white light emission intensity was oscillating with the maximum (corresponding to $+45^\circ$) 5 times larger than minimum. Surprisingly, despite the relatively small retardance value difference (less than 10%), the strong corresponding variation in white light emission was observed.

As the polarization dependence is related to a previously written track, it should disappear with increasing the separation between tracks (Fig. 5(d)). The structures number 2 and 3 shown in Fig. 2 were written with the distances between tracks ranging from 0.5 $\mu$m to 3 $\mu$m. The dependence of retardance on the light polarization (the structure number 2 in Fig. 2) disappeared at the track separation of 3 $\mu$m (Fig. 8, left). Taking into account that the estimated laser spot diameter was about 4 $\mu$m, we can assume that at 3 $\mu$m, tracks effectively do not overlap, supporting the explanation based on the stress produced by the neighboring track.

Another type of anisotropy was observed in the structures, which did not exhibit the dependence of retardance on polarization at a small track separation (the third in Fig. 2). Unexpectedly, at a larger track separation, the structures displayed the polarization dependence (Fig. 8, right). This indicates that the polarization-stress interaction is not the only mechanism responsible for the retardance dependence on the polarization. Indeed, the strength of modification can also depend on the angle between the pulse front tilt (PFT) and...
polarization [22]. The pulse front tilt can be introduced either by the angular dispersion or by the combination of spatial and temporal chirps [18]:

$$p = p_{ad} + p_{sc} = k_0 \beta + \varphi^{(2)} \nu,$$

where $k_0$ is a wavenumber, $\beta$ – the angular dispersion, $\varphi^{(2)}$ is the group-delay dispersion and $\nu$ is the spatial frequency gradient.

The pulse front tilt can be characterized by the shift of the delay axis of the FROG trace measured with a GRENOUILLE. The PFT was measured for our laser system in the horizontal (parallel to the writing direction) and vertical (perpendicular) directions for several pulse durations. At the shortest pulse duration of 250 fs, the PFT was 0.59 fs/mm and 0.18 fs/mm for horizontal and vertical axes respectively. At 800 fs, corresponding values were 0.67 fs/mm and 0.5 fs/mm. The PFT introduced by the angular dispersion does not depend on the temporal chirp. This behavior was observed for the horizontal axis, where a spatial frequency gradient was reduced by a precise pulse compressor alignment. The PFT strongly depended on the temporal chirp indicating the presence of spatial chirp for the vertical axis. The azimuth of the PFT was controlled by adding the temporal chirp and was estimated at an angle of 37° to the writing direction for the pulse duration of 800 fs.

![Fig. 9. Retardance variation for two polarizations when the structure was written at different angles. The difference in the strength of birefringence is defined by the angle between the pulse front tilt and the writing direction. Separation between tracks was 3 \( \mu \)m, fabrication algorithm as in the structure number 2 in Fig. 2. Arrows indicate laser writing direction (black) and the polarization plane direction (blue).](image)

To validate this prediction, the structures (number 2 in Fig. 2) with a 3 \( \mu \)m separation between tracks were written rotating the orientation of the scanning direction (Fig. 9, left). The polarization was rotated by the same angle as the writing direction keeping the same \(-45°\) or \(+45°\) mutual angle. The strength of induced retardance exhibited a periodic variation with the angle of writing direction. The variation for one writing direction was shifted by \( \pi \) with respect to the other direction. The biggest difference was observed for approximately 90° where the pulse front tilt was at about 45° to the writing direction. The difference completely disappeared at about 45° and 135°. The explanation of this observation can be the following. The azimuth of pulse front tilt in our experiments was at about 45° to the writing setup coordinate system (Fig. 10). If the structures were written as shown in Fig. 10 left, the polarization plane direction will be parallel or perpendicular to the pulse front tilt direction. It was demonstrated that the pulse front tilt leads to a stronger material modification for the polarization parallel to the pulse front tilt [22]. If the writing direction was aligned along the PFT, then the polarization was always directed at about 45° to the PFT and no difference in retardance was observed. It is worth mentioning that in our experiment we also observed the quill writing effect, manifesting itself as a change in retardance strength by reversing the writing direction [16,17]. As a result of this effect, the difference in retardance was larger for
polarization at 180° than at 0° (Fig. 9). Interestingly, the PFT dependence completely disappeared when the laser written tracks were partially overlapping. All previous experiments on the pulse front tilt were performed either writing single tracks [16,17] or printing separate dots [22].

Fig. 10. Schematics explaining observed polarization dependence. For the left image, the writing direction is at 45° with respect to the pulse front tilt; whereas an electric field is oriented perpendicular or parallel to the pulse front tilt. The stronger modification is induced for the polarization parallel to the pulse front tilt. For the right image, the writing direction is perpendicular the pulse front tilt and an electric field is always at 45° to it. As a result the structures are equivalent for both polarizations.

In conclusion, we have demonstrated two different sources of the polarization dependence observed in femtosecond direct writing experiments. One is related to stress induced birefringence and the other is produced by the spatio-temporal distortion of the laser pulse. Stress measurement indicates that during laser writing the material is dragged by the thermal gradient and it causes chevron-shape stress distribution. Stress induced birefringence causes tilt in the front of tracks. As a result, the light polarized at 45° to the writing direction induces the highest retardance. The polarization dependence is strongly affected by the density of laser written tracks. For overlapping tracks, this dependence is mainly defined by the stress induced birefringence. The PFT is playing the major role only for separated tracks. As a result, the effect of spatio-temporal distortion can be minimized by overlapping adjacent tracks.

Stress induced retardance as high as 200 nm was observed in germanium sulphide glass because of a large photoelastic coefficient. The strength of the stress induced birefringence is very close to the values produced by self-assembled nanogratings in silica glass. The ability to control stress-induced birefringence in glasses with high photoelastic coefficients can be explored for the fabrication of birefringent optical elements such as polarization converters.

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