Femtosecond laser induced rotated 3D self-organized nanograting in fused silica

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Abstract: Formation of rotated 3D self-organized nanograting inside fused silica is demonstrated by using a femtosecond pulse laser. The difference of birefringence signal of non-reciprocal writing lines indicates that the excited pulses may possess a finite tilt of intensity front, which produces an electric field vector parallel to the incident direction to modulate the excited electron plasma. We suggest that the orientation of nanograting depends on the correlation between the polarization plane azimuth and the tilted intensity front based on previous investigations. The result provides an opportunity to control the rotation of self-organized nanograting in three-dimensional space.

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References and links

1. Introduction

Femtosecond (fs) pulse laser demonstrates an irreplaceable writing ability for three-dimensional (3D) structural modification in transparent materials due to its ultrashort pulse duration and ultrahigh peak intensity [1, 2]. Especially in some micro/nano-structures induced by moderate energy fs laser pulse, anisotropic scattering of light, i.e. birefringence, has been observed in the modified region [3–6]. In terms of this phenomenon, Shimotsuma et al. in 2003 reported a periodically distributed oxygen-deficient nanostructure (SiO$_{2-x}$) perpendicular to the incident light polarization in the modified region, which was interpreted as an interference modulation of electron plasma concentration by the incident light field [7]. Shortly afterwards, another research group found that this periodic nanostructure could further develop long-range order planar nanocracks within a continuous writing process, and a nanoplasmonics model was proposed to explain underlying mechanism of this self-organized structure [8, 9]. According to their opinion, the inhomogeneous distributed defects in glass could act as nanoplasmonics, which preferentially absorbs pulse energy due to local field enhancement effect, and as a result, the ionization rate of the materials is increased substantially [10]. The initially spherically-shaped plasma will perform an asymmetric growth in a direction perpendicular to the laser polarization, finally, the expanding nanoplasmas self-organized into periodic planar nanocracks. Although there seems to be an argument in the formation process of self-organized nanograting, it has been well acknowledged that the physical origin of this structure resulted from an ordered array of the induced glass defects during laser irradiation [7–11]. As a type of artificial periodic nanostructure, it contributes many optical and chemical performances in contrast to the original glass. For example, the resulting nanograting has demonstrated strong optical birefringence which has been used for anisotropic microreflectors [6] or rewritable optical storage [12]. Also, the different chemical etching rate for the locally modified and unmodified region provides alternative way to anisotropic microreflectors [6] or rewritable optical storage [12]. Also, the different chemical

reverse of the writing direction was also reported to be capable of triggering a significant
effect on the nanograting structure [19–21]. That so-called “Quill Pen Effect” possibly
depends on the correlation between the beam scanning and the pulse front tilt (PFT) of the fs
laser, which is the first time to present the PFT as a potential parameter to control structural
modification in transparent materials [19].

In this paper, we report that self-organized nanograting written by fs laser pulses can be
orderly rotated in 3D space inside fused silica through controlling the laser polarization
direction. As the observed non-reciprocal writing phenomenon indicates that the incident
pulses possess front tilt, we think that the incident electric field can project a sub-vector along
the light propagation direction, and this sub-vector may force an oscillation in the excited
plasma wave. The result means that the PFT may provide a particular contribution to the
periodic modulation of bulk electron plasma when an fs laser is used to space-selectively
process transparent materials.

2. Experiments

A regeneratively amplified mode-locked Ti:sapphire laser system (Coherent: RegA9000)
delivers 150 fs laser pulses with a repetition rate of 250 kHz at a centre wavelength of 800 nm
(photon energy 1.55 eV). A Glan polarizer and a λ/2 waveplate were used to adjust the light
pulse energy and polarization plane azimuth, respectively. Then a linearly polarized laser
beam was tightly focused via a 100 × (Olympus, 0.8 N.A.) microscope objective at normal
incidence and with a depth of about 50 µm below the sample surface. The fused silica glass
used here was a commercial one (Hefei Kejing Materials Technology) with a size of 10mm ×
10mm × 1mm, which was mounted onto a computer-controlled XYZ translation stage (Prior
Scientific Instruments: H101A ProScan model.). Its XY repeatability and resolution is 0.75
µm and 0.01 µm respectively.

We wrote a series of lines with different polarization directions in this glass. For each line
the pulse energy after microscope objective was fixed at 2 µJ that was independent on the
orientation of light polarization. The scanning speed was 50 µm/s and each line was written
with only one pass. After the lines were written, microscope images were captured using back
illumination, then the glass was mechanically polished to expose the transversal cross section
of each line. In order to obtain a clear etching pattern, the polished glass was soaked in 1
mol% hydrofluoric (HF) aqueous solution to be etched for 2 min at room temperature. Then
the transversal cross-sectional morphology of the modified regions could be observed using a
scanning electron microscope (SEM) (JEOL JSM-6700F).

3. Results and discussion

Figure 1 shows a classical image of birefringence of fs laser written lines in fused silica. The
written lines demonstrated obvious optical anisotropy whether the laser scanning direction is
along \( S \) or \( S' \). In Fig. 1(a), a linear polarization light source was used to be the back
illumination for all of the lines written by continuous scanning. The lines varied gradually
from bright to dark depending upon polarization plane azimuth \( \theta \). This implies that the
difference \( \Delta n \) between the ordinary and extraordinary indices of refraction will change from
positive to negative. Moreover, the cross-polarized image in Fig. 1(b) presents a near-perfect
symmetric distribution of the birefringence signal on both sides with the center at 90°. It
seems to agree very well with the previous conclusions that the birefringence in the modified
region results from an embedded self-organized nanograting perpendicular to the laser
polarization, and its orientation and the associated \( |\Delta n| \) will further alter with the rotation of
the polarization plane azimuth \( [12, 13, 22] \). However, when we carried out a measurement
about the birefringence signal by quantifying the transmission (the panel (c) of Fig. 1), we
found that there always had an intensity variation between two lines with opposite scanning
directions in each group. Here we excluded the stage movement as the cause by confirming
an incidence at normal direction and keeping the stage in the horizontal plane. Therefore, this
phenomenon should attribute to the non-reciprocal writing effect of fs pulse laser in isotropic
medium, which introduces the PFT into the formation process of self-organized nanograting [19, 21, 23].

Fig. 1. Optical microscope images of the written lines with varied polarization plane azimuth. Two lines of each group were independently written with opposite scanning directions. (a) The illumination was linear polarization light. (b) Cross-polarizer images recorded the birefringence phenomenon in the same region in (a). (c) The intensity variation of birefringence signal from the written lines with varied polarization plane azimuth.

In Fig. 2, SEM images of the transversal cross sections of the lines with varied polarization plane azimuth revealed some interesting results for the written nanograting. Figure 2(a) exposes a periodic nanograting elongated along the light propagation direction $k$ with scanning direction along $S$ and polarization plane azimuth $\theta = 120^\circ$. Meanwhile, we found a longer and more complete nanograting written along the $S'$ scanning direction, which may be responsible for the stronger birefringence signal as shown in Fig. 1. But the orientation of nanograting does not show any dependence on the scanning direction.

Fig. 2. SEM images of self-organized nanogratings in the transversal cross section of written lines with varied polarization plane azimuth. The writing direction of line was along $S$ in (a), and along $S'$ in (b). The red bar denotes the orientation of nanograting. (c) The pulse energy was increased to 2.2 $\mu$J to get a better pattern and the writing direction of line was along $S'$.

More surprising results can be found from Fig. 2(b). When the polarization plane azimuth of the incident pulse increases from 0° to 80°, the periodic nanograting rotates counterclockwise in the plane of the transversal cross section, while those ones on the other side turns clockwise following the azimuth from 180° to 100°. This indicates that this rotation is a chiral phenomenon with the center at 90°. Besides, we also found another periodic rotation of the formed nanograting occurring in the plane perpendicular to the incident light propagation direction, which has been intensively studied in past years [7–9].

We plotted the dependence of the average gap ($d$) between the adjacent nanocracks on the polarization plane azimuth $\theta$ in Fig. 3. The result fits well to the relation $d = \lambda/(2n\sin\theta)$ ($\lambda =$...
800nm and n = 1.45 for fused silica) except two special cases at θ = 0° or 180°. In fact, as far as the two rotations are concerned, the etched pattern can be taken as the projection on two mutual orthogonal planes for a rotated 3D periodic nanostructure. This hypothesis is strongly associated with its 3D polarization dependence in the writing process, and offers the favourable configuration to support the birefringence. But in the cases of θ = 0° or 180°, there should have been formed a smooth sheet without any periodic trace in the laser modified region, but now appeared an extra period (Fig. 2(c)) of about 1100nm, which is of the incident wavelength 800nm. Therefore we think an additional electric oscillation along the light propagation direction possibly worked on the trapping electron plasma. We will further discuss this phenomenon later. On a closer observation, it is found that the alignment of nanocracks is altered in different parts of single nanostructure, especially in the end part, e.g. the nanostructure of θ = 80°. That slight variation may result from anisotropic trapping of electron plasma by the ponderomotive force in the presence of intensity gradients by the PFT. In the wavefront of the pulse, the self-focusing effect defines the boundary of the modified region where the intensity distribution may well be locally twisted or displaced due to the interface reflection or refraction, therefore the ponderomotive force will reorient the electron plasma oscillation.

![Figure 3. The dependences of the gap d between two adjacent nanocracks (■) and the transversal length of the written traces (○) on the polarization angle θ of incident light pulse. Solid line corresponds to a λ/(2nsinθ) fit of the measured data. The error bars come from a calculation of mean square root (MSR) error.](image)

Figure 3 also describes the dependence of the nanostructure length on the polarization plane azimuth. The aspect ratio variation of these written traces indicates an underlying anisotropic photosensitivity of isotropic homogeneous medium, which is caused by light pulses with a finite tilt of intensity front. This mechanism is firstly proposed by Kazansky et al. [24] to explain a cosine-like dependence of absorbance and phase shift in the focus area on the laser polarization. According to their viewpoint, the ponderomotive forces associated with anisotropic intensity gradients will remove defects more effectively from the beam path for the light polarized along the pulse front tilt, which reduces photon losses; therefore we think that the structure length variation should have resulted from the anisotropic modification of the light-matter interaction. Besides, we find the etching rate varying for different nanostructures—specifically, the closer the angle is to 90°, the clearer and narrower the...
etched nanograting is. This result proves that the induced defect concentration per unit area is adjustable by varying the laser polarization, and has been applied for fabrication of 3D microchannels in bulk material [13–15].

Fig. 4. (a) Schematic of the experiment using tilted fs pulses. $\mathbf{k}$ represents a wave vector of incident light, and $\phi$ is the angle between the wave vector $\mathbf{k}$ and the Poynting vector $\mathbf{p}$. (b) A resolution of the incident electric vector ($\mathbf{E}$) for two sub-vectors ($\mathbf{E}_//$, $\mathbf{E}_\perp$). $\theta$ is the polarization plane azimuth. (c) The formation of periodic nanostructures in the traversal cross section of the writing lines are demonstrated at $\theta = 0^\circ$ or $90^\circ$. The lines are written along $+y$ or $-y$ direction.

As the laser beam used here was close to being Gaussian spatial profile and focused into the glass with the normal direction, the most possible reason causing an electric field vector along the light propagation direction is the PFT, which commonly suffers from spatio-temporal distortions due to group-velocity dispersion when fs pulses propagate in dispersive medium, e.g., transparent dielectrics or microscope objective, and moreover, the PFT magnitude will be significantly increased in the focus area [25]. Recently there are some evidences that anisotropic modification in glass could be written by fs laser with PFT [21, 24], but the PFT has not been proposed as a parameter to modulate nanograting in 3D space by controlling of laser polarization. Figure 4 shows the schematic of current experiment. The scanning direction is along $+y$ or $-y$ direction, $\theta$ and $\phi$ are respectively the polarization plane azimuth and the angle between the wave vector $\mathbf{k}$ and the Poynting vector $\mathbf{p}$ (i.e. the intensity front normal of light pulse). In order to simplify the model, the plane consisting of $\mathbf{k}$ and $\mathbf{p}$ is set to parallel to the $y$-$z$ plane. Therefore, we can resolve the incident electric vector $\mathbf{E}$ into two orthogonal sub-vectors, $\mathbf{E}_//$, $\mathbf{E}_\perp$, as shown in Fig. 4(b). Thus, the rotation of the formed nanograting in $x$-$z$ plane will depend mainly on $\mathbf{E}_//$, while the other rotation in $x$-$y$ plane is dominated by $\mathbf{E}_\perp$. Furthermore, $\phi$ is fixed at a small angle, the strength of $\mathbf{E}_//$, is actually determined by the polarization plane azimuth according to the relation $\mathbf{E}_// = \mathbf{E} \cdot \cos \theta \cdot \sin \phi$. When $\theta = 0^\circ$ or $180^\circ$, $\mathbf{E}_//$ has maximum strength to force the electron plasma to perform the additional oscillation along $\mathbf{k}$ together with the nanoplane array perpendicular to the incident electric field $\mathbf{E}$ (Fig. 4(c)), therefore the periodic structure with wavelength level of gap is horizontal in the traversal cross section of the lines, as shown in Fig. 2(c). In previous studies, a few papers have reported a longitudinal periodic structure with the period
of the wavelength of light in the head of induced nanostructure, and the authors considered them as a result of the interference between plasma waves and plasma oscillation [16, 19]. But in our case, the period is so large as to be out of the relation $d = \lambda/(2\sin\theta)$, so these nanocracks at $0^\circ$ or $180^\circ$ may originate from a mixed array of cross-sections of different electron plasma oscillation planes. According to our model, we speculate that the gap between the adjacent nanocracks should be $\sim\lambda/(\sin\phi)$, but it still needs more experimental proofs to confirm. From Fig. 4(c), when $\theta = 90^\circ$, $E_{\perp} = 0$, the formed nanograting rotates to its intrinsic direction perpendicular to $E$, which is a most common type of self-organized nanograting structure [8, 9, 15–17]. By the described model, we can simultaneously control two orthogonal rotations by varying polarization direction of single laser beam. This process implies that a 3D interference mechanism between the electron plasma and the incident electric field for writing and rotating of self-organized nanograting in fused silica.

4. Conclusion

In conclusion, our results show that it is possible to tune the rotation of self-organized periodic nanograting written by fs laser with PFT by changing laser polarization plane azimuth. We attribute this phenomenon to an additional modulation of electron plasma caused by the electric field along the light propagation direction. Our experiments provide the new opportunity for controlling the written nanograting from 2D plane to 3D space in isotropic medium. We believe that the anisotropic writing style by the PFT of fs laser can offer more choices in practice of biomaterial processing and fabrication of integrated optical elements.

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