Femtosecond laser-induced microstructure in Foturan glass*

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We report on the microstructure formation in Foturan glass, induced by 1 kHz, 120 femtosecond laser irradiation. It is found that the line-shaped filamentation, not void array tends to be formed in this glass. This is different from our previous experimental results in fused silica and BK7 glasses. A possible mechanism Ag^+ captures the free electrons generated by laser, is proposed to explain the observed phenomena.

Keywords: femtosecond laser, line-shaped filamentation, Foturan glass, mechanism
PACC: 4262, 4262A, 4270G

1. Introduction

Femtosecond laser pulses can be used to micromachining a variety of surface/internal mirostructures in transparent materials, which include ripples, voids, gratings, waveguides and so on.[1−6] Among these phenomena, the formation of different types of voids attracted much attention because of its potential application in photonic devices. At the beginning, a single void was produced at the focal point by focusing a femtosecond laser beam, and periodic void array was achieved by translating the sample.[7] Later on, it is found that periodic array could be formed spontaneously along the propagation direction of laser with a period of several micrometers when focusing a single femtosecond laser beam.[2] This is a simple method to fabricate void array. Based on this, many groups,[2,8,9] including us investigated the influences of different laser irradiation condition, including laser intensity, incident pulse number, and focusing depth, on the shape and period of void array. It has been a common belief that a single pulse tends to form the line-shaped structure, while multiple pulses are prone to form periodic void array. Periodic void array has a large refractive index change because of gas phase filled in the void. In contrast, the line-shape structure is an almost uniform line from top to bottom, and like a filamentation. It has a greater potential application for optical devices than periodic void array, for example, to reflect the optical beam or be used as a wavelength filter.[8] However, up to now, it is confined to obtain the line-shaped structure owing to the single-shot request. Therefore, it is interesting to find a new fabrication way or popular material for line-shaped structure formation.

In this paper, we investigate the line-shape structure formation in Foturan glass induced by 1 kHz, 120 fs laser pusles, and the mechanism responsible for the observed phenomenon is discussed. Foturan glass is chosen, since it exhibits large third-order nonlinear susceptibility, good chemical and biocompatibility, and has been used extensively on the microfabrication.[10] Moreover, the irradiated area by femtosecond laser can turn to yellow after subsequent heat treatment, which is a great indicator for microfabrication process. Foturan glass is composed of lithium aluminosilicate glass and doped with a little bit of silver, cerium, and antimony. When exposure to femtosecond laser, the Ce^{3+} ion release an electron to become Ce^{4+}, while Ag^+ captures the free electrons and forms Ag atoms. These Ag atoms will diffuse and agglomerate further to form clusters in the femtosecond laser irradiated area after subsequent heat treatment at about 500 °C.[1] Lastly, the femtosecond laser irradiated area appears yellow in colour.

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2. Experiments

A regenerative amplified Ti: sapphire laser was used in our study, which emits 120 fs, 1 kHz, mode-locked pulses at wavelength of 800 nm. The Foturan glasses were placed on a three-dimensional translation stage controlled by computer. For the detailed experimental setup you can refer to Ref. [9]. We focused the pulses inside samples to generate structural changes using a 100× objective lens (NA=0.8). The spot size of the focused beam was approximately 1.5 μm in diameter at the focus. An electronic shutter was used to control the exposure time. The laser pulse energy could be varied continuously by using a neutral filter.

Before the experiments, the glass samples were cut into small sizes of 4 mm×4 mm×2 mm and then six-sided polished. After irradiation, the samples were further annealed. The temperature was first ramped from room temperature to 520 °C at 5 °C/min, and then held at 520 °C for 3 hours duration. Finally, the samples were naturally cooled down to room temperature.

3. Results

We investigated the influences of the exposure time, laser intensity and the focusing depth on the generated microstructures. The chosen geometrical focusing depths were 200 and 400 μm below the sample surface. Shown in Fig. 1(a) are the side views of typical microstructures. Figure 1(b) is the magnification of the left six in Fig. 1(a) (red square frame). At fixed exposure time and laser intensity, we repeated the experiments twice. One can see that line-shaped filamentation along the laser propagation direction is formed. This is different from our previous experimental results (void array) carried out in fused silica and BK7 glasses.[9] Line-shaped filamentation shows dark or light yellow coloration after subsequent heat treatment. When a short exposure time, such as 1/32, 1/64, and 1/125 s is used, the whole filamentation appears uniform light yellow. Yellow colour comes from Ag atoms aggregation. The shade of yellow colour depends on the aggregated Ag atom concentration which is determined by incident laser intensity if the same heat treatment condition is used. Larger laser intensity facilitates more Ag atoms to aggregate in the process of heat treatment, and the irradiated area by laser will show dark yellow, in the contrast, the irradiated area by smaller laser intensity shows light yellow. Therefore, uniform yellow colour appeared in the condition of short exposure time indicates uniform laser intensity distribution along the line-shaped filamentation. This is easily to understand, since multiple pulses induced accumulation effect during the short exposure time can not be well reflected.

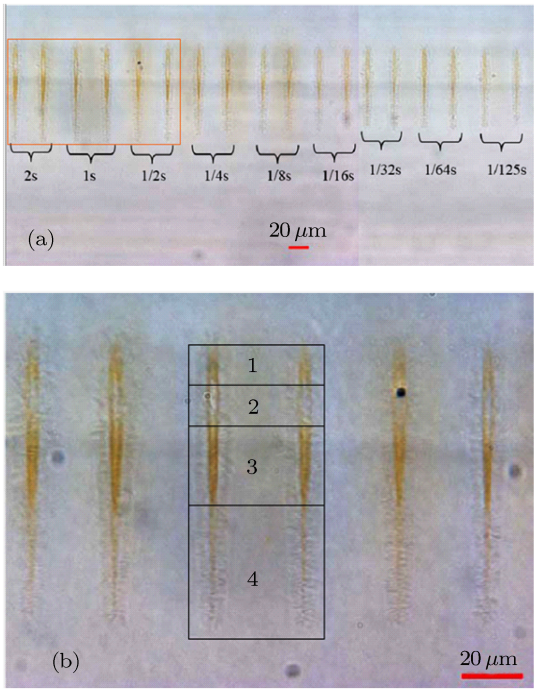


Fig. 1. (colour online) Side views of microstructure in Foturan glass when irradiated by a 100× object lens (NA=0.8) with incident laser energy of 4 μJ focused 200 μm beneath the sample surface. (b) is magnification of the left six in (a) (indicated by red square frame). Laser was incident at the top of the images.

With an increase of exposure time, the line-shaped filamentation demonstrates an inhomogeneous structure. We classify the whole filamentation into 4 sections as shown in Fig. 1(b); (1) the area before the focus with a colour of light yellow, (2) the focus area with a transparent centre and two yellow edges, (3) the area after the focus with a colour of dark yellow, and (4) the tail area with a colour of much lighter yellow. In contrast, yellow colour in section 3 is much darker than that in section 1, which indicates laser intensity after the focus is much larger than that before the focus. The laser intensity in the tail area is the smallest, and this area appears much lighter yellow. The laser intensity in the focus area is the largest (Section 2), and so this area demonstrates a unique structure. This is probably caused by Ag ion diffusion away from the focus. It has been testified that glass network modifiers such as alkaline earth ions and

rare-earth ions would migrate away from the laser focal region after femtosecond laser irradiation.[11−13] The high-intensity laser distribution in the focus area produces a large temperature/pressure gradient making central Ag ions migrate to the two sides, and appears the above-mentioned structure. The focus area can even be damaged when higher laser intensity is used (such as 2 s, 1 s in Fig. 2(a)). In addition, it is found that the focusing depth has no obvious effect on the structure of line-shaped filamentation except the much longer filamentaion is observed in 400 μm focusing depth as shown in Fig. 2.

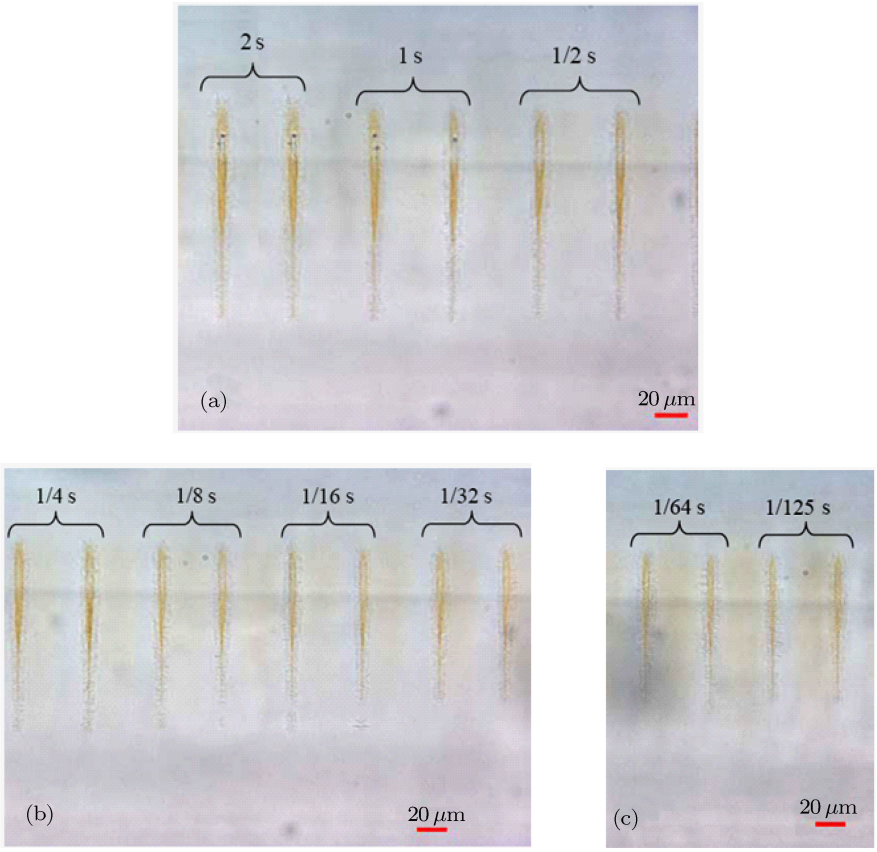


Fig. 2. (colour online) Side views of microstructure in Foturan glass when irradiated by a 100× object lens (NA=0.8) with a larger incident laser energy of 7 μJ focused 400 μm beneath the sample surface. (a), (b) and (c) are corresponding to the different exposure time, respectively. Laser was incident at the top of the images.

4. Discussion

The question confusing us is that why line-shaped filamentaion, not periodic void array is prone to be formed in Foturan glass, which is different from our previous experimental results in fused silica and BK7 glasses.[9] We compare their properties that are listed in Table 1. It is found that Foturan glass has a wider band gap compared with BK7 glass, and a larger thermal expansion coefficient than that of fused silica. On the other hand, Foturan glass also has a similar band gap to fused silica, and a close thermal expansion coefficient to BK7 glass. So we can conclude that band gap and thermal expansion are not the key factors affecting the void array formation. However, the large thermal expansion coefficient can explain the mirocrack formation in Foturan glass. In Fig. 1(b) and Fig. 3, we can see clearly that many microcracks are produced around the line-shaped filamentation. Femtosecond laser induced material damage depends on the generation of free electrons. Free electrons are generated inside glasses by a series of nonlinear optical effects including multiphoton absorption, tunnel ionization, and avalanche ionization.[24] The energy absorbed by the free electrons then transfers to the lattices by electron phonon scattering, and heated lattice causes microcracks. It can be imaged that the mirocrack is more easily induced if material has a small thermal diffusion coefficient, or large thermal expansion

coefficient. Foturan glass has the largest thermal expansion coefficient in these three glasses, which is more than 10 times than that of fused silica, and hence, microcracks are easily formed. The similar phenomenon is also found in BK7 glass because of its large thermal expansion coefficient.[15]

Table 1. The properties of fused silica, BK7 and Foturan glasses.

property	fused silica/ BK7	Ref.	Foturan	Ref.	unit
density ρ	2.202/2.51	[16]	2.37	[17], [18]	g/cm^3
thermal expansion β	0.54/7.1	[19]	8.6	[17], [18], [20]	10^{-6}K^{-1}
thermal diffusivity α	8.4/5.17	[21]/[22]	6.47*	[17], [18]	10^{-3}cm^2/s
Yong's modulus σ	71.5/80.8	[16]	78.0	[17], [18]	GPa
nonlinear refractive index n_2	2.5×10^{-16}/3.45×10^{-16}	[23]/[24]	$(4.3\pm0.7)\times10^{-16}$	[10]	cm^2/W
band gap E_g	9.1/4.7	[21]/[25]	8.0	[10]	eV

*: This value is calculated by Ref. [15] based on the equation $\alpha = K/c\rho$, where K is thermal conductivity, c is specific heat, and ρ is density.



Fig. 3. (colour online) Top views of the left six in Fig. 1(a) (in the red square frame).

For the formation of line-shaped filamentation in Foturan glass, we can not obtain any information from the Table 1. Therefore, we can deduce that it is probably caused by material itself, that is, composition. It is well known that Foturan glass is doped with a little bit of silver, cerium, and antimony. When exposure to femtosecond laser, free electrons generate from Ce^{3+} ion oxidation reaction (Ce^{3+}+e=Ce^{4+}). According to our proposed mechanism of void array,[9] it is crucial to form a large amplitude electron plasma standing wave (EPW). The free electrons generated by the leading part of the femtosecond laser pulse then interact with the following part of the femtosecond laser pulse, forming an electron plasma wave. A difference for Foturan glass is that it is doped with Ag^+, which will capture the produced free electrons and become Ag atoms. This causes the decrease of free electron density directly. Thus, the incident laser intensity is not an effective intensity to generate free electron, and so the condition we proposed in Ref. [9] to excite a large amplitude EPW (a relativistic intensity beyond 10^{15} W/cm^2) can not be calculated by incident laser intensity. In fact, when a 120 fs laser pulse of 4 μJ (which is the minimal pulse energy used in our experiments) is focused into a focal spot size of $\sim$1.5 μm inside glasses, the peak intensity reaching 10^{15} W/cm^2 level can be satisfied. When we increase the incident laser intensity further, several voids appear near the focus as shown in Fig. 2(a) (2 s and 1 s), but it is difficult to form periodic void array in the other section of filamentation, even a much larger laser intensity is used (25.1 μJ). This can be attributed to the non-uniform distribution of laser intensity along the filamentation. To confirm our deduction, we carried out the same experiments in another doped glass, Au^+ doped silicate glass. Au^+ plays the same role as Ag^+ in Foturan glass,[26] and the similar results have been observed. Consequently, we think that the line-shaped filamentaion structure is more easily produced in some ion-doped glasses.

5. Conclusions

We investigate the microstructure formation in Foturan glass induced by femtosecond laser, and have found that the line-shaped filamentation, not void array structure is more easily produced in it. This is different from our previous experimental results observed in fused silica and BK7 glasses, which can be explained by Ag^+ doping. Ag^+ captures the generated free electrons, and decreases the practical effect of incident laser. This line-shaped filamentaion structure has potential applications in multifunctional optical devices, and Foturan glass provides such a path for this field.

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