Self-organized void strings induced in $SrTiO_3$ crystal by a femtosecond laser

Juan Song (宋 娟)[1,2], Haiyi Sun (孙海轶)[1], Xinshun Wang (王新顺)[1,2], Jian Xu (徐 剑)[1,2], Jianrong Qiu (邱建荣)[1,3], and Zhizhan Xu (徐至展)[1]

[1] *State Key Laboratory of High Field Laser Physics, Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800*

[2] *Graduate School of the Chinese Academy of Sciences, Beijing 100039*

[3] *State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027*

Densely-aligned void arrays of the length of hundreds of micrometers are fabricated in $SrTiO_3$ crystal by tightly focusing multiple femtosecond (fs) pulses and fixing the focal point at a certain depth of $SrTiO_3$ crystal without translation. The effect of the laser energy and the laser irradiation time as the well as entrance crystal plane on the induced structures is investigated. It is possible to control these factors to achieve the desirable void strings. This kind of self-fabrication method combined with the high linear refractive index of $SrTiO_3$ (2.30 at 800 nm) largely extends the fabrication scope which is generally limited by the short working distance of the high numerical aperture (NA) objective lens in scanning fabrication mode. The possible formation mechanism is also discussed.

OCIS codes: 160.4670, 190.4400, 210.4810, 220.4000, 230.4000.

Compared with the conventional long-pulse laser fabrication, femtosecond (fs) laser micromachining has some unique characteristics, such as contactless fabrication, selective treatment, small heat-affected zone, high precision and high reproducibility. These advantages of femtosecond laser pulses are even more pronounced in laser processing of dielectric materials because of highly nonlinear absorption and reduced heat diffusion as compared to metals, allowing the generation of well-defined microstructures with high quality and reproducibility[1]. Fabrication of periodic microstructures in dielectrics is very attractive research subject for their potential applications in photonic crystal device. Conventional methods, such as multiple-beam interference, three-dimensional translation of single-beam direct writing, holographic technology[2−4] and so on, are time consuming and relatively complex. Kanehira et al. reported that, by fixing the laser focal point at a certain depth beneath the entrance surface without translation, a line of periodic nanovoids formed spontaneously along the laser propagation direction in borosilicate glasses[5]. This novel method is more efficient in generating periodic voids and is applied to micromachining some other glasses like fused silica[6]. In this paper, we applied this novel method to fabricate $SrTiO_3$ crystal, which belongs to the perovskite-structured transition metal oxide. The factors that have influence on the induced voids, are investigated. They can guide us to induce controllable void string formation.

The experimental setup is shown in Fig. 1. 800-nm mode-locked pulses from a regeneratively amplified Ti: sapphire laser, with 120 fs pulse length and 1 kHz repetition rate, were tightly focused in the bulk of $SrTiO_3$ crystal by a high numerical aperture (NA) microscopic objective (e.g. $100 \times \text{NA} = 0.9$ or $50 \times \text{NA} = 0.8$). The pulse energy could be adjusted by a neutral-density filter and be monitored by an energy meter. The pulse number could be controlled by an electric light shutter. Charge coupled device (CCD) captures the optical micrographs of the sample, and transmits them to the monitor where the fabrication process is displayed.

As shown in Fig. 2, quasi-periodically-aligned voids were induced at the focal depth of 200 μm beneath the sample surface by tightly focusing 8 fs pulses through 100× microscope objective lens (NA=0.9). From left to right, the pulse energy increased from 37.9 to 40.0 μJ and to 43.4 μJ, and the same energy was repeated twice. Noticablely, the pulse energy employed here is far larger than the critical self-focusing power of $SrTiO_3$ crystal ($P_{\text{cr}} = 3.77\lambda^2/(8\pi n_0 n_2) = 0.2$ MW), so the self-focusing

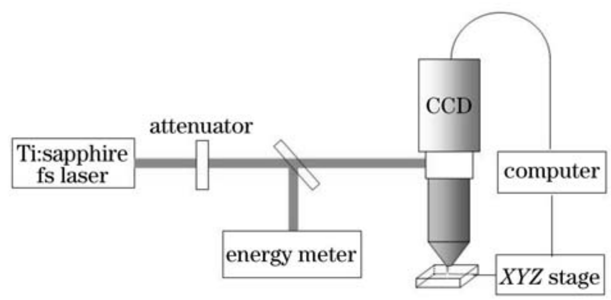

Fig. 1. Experiment setup for laser fabrication.

Fig. 2. Periodic void arrays induced by tightly focusing 8 fs laser pulses with different energy at the focal depth of 200 μm.

1671-7694/2007/S1S218-04

is believed to occur, Figure 2 shows that, with the increase of the pulse energy, the diameters of the induced voids vary little and are all about 700 nm, which is far beyond the diffraction limit of the used microscope objective ($2\omega_0 = 1.22\lambda/\mathrm{NA} = 1.22$ μm). The total lengths of the void strings present a increasing tendency from 84.7, 77.2 μm to 96.5, 95.3 μm and then to 102.3, 107.9 μm, which is about 30 times the Rayleigh length of the focused laser beam ($z_{\mathrm{R}} = n\pi\omega_0^2/\lambda$ equal to 3.4 μm). As depicted in Fig. 1, the initial position of the void string moves toward the entrance surface as the pulse energy increases, and this can be qualitatively interpreted by employing Marburger's formula $1/z_{\mathrm{NL}}(P) = 1/f_{\mathrm{L}} + 1/z_{\mathrm{cr}}(P)$, $z_{\mathrm{cr}} = 0.367ka^2/\{[(P/P_{\mathrm{crit}})^{1/2} - 0.852]^2 - 0.0219\}^{1/2}$, where z_{cr} is the focal length of self-focusing, f_{L} is the focal length of the external lens. The self-focusing occurs earlier and the beginning of the filament moves toward the incident surface as the pulse energy increases[7]. It is worth note that the void array not only moves toward the entrance surface, but also extends along the laser propagation direction and makes the void string even longer. This may be explained in terms of fs-pulse self-guided propagation. The self-propagation distance is determined by the range where the Kerr-effect induced self-focusing counteracts the dominating defocusing effect caused by the plasma. When the focal depth is fixed, the increased pulse energy means that the light intensity in more space around the focal point goes beyond the multiphoton ionization threshold, which finally triggers the exponential growth of plasma. The generation of plasma prevents the further collapsing of the focused beam and elongates the modified structure. We performed a statistical measurement about the relationship of the length of the induced void string with the pulse energy, as shown in Fig. 3. It is noticeable that the void string length tends to be saturated in a exponential way. This result is similar to the results of the filament formed inside BK7 optical glass and the fused silica[8]. We believe that the fact that the scattering and absorption effects of the plasma become stronger as the pulse energy increases is responsible for the saturation action. From Fig. 2, we can see that, the process that tens of submicrometer-sized voids of the length of hundreds of μm formed spontaneously and periodically along the laser propagation axis is completed in a short timescale of 1/125 s without any assisting translation. This method is very attractive in high-speed large-scale laser micromachining.

We also did research on the dependence of the void strings on the pulse number. Figure 4 shows the microstructures fabricated by tightly focused fs-laser pulses with the energy of 41.7 μJ at the focal depth of 100 μm beneath the entrance surface through a 100× objective lens. The two structures on the left side were induced by 125 pulses, while the other two ones on the right side are induced by 500 pulses. We can see that those microstructures all begin with a heavily-damaged head and then end with a relatively longer and narrower well-aligned void strings. The results in Fig. 4 indicate that although

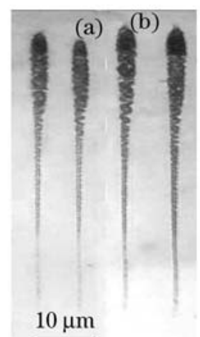

Fig. 4. The void array induced by tightly focusing (a) 125 pulses and (b) 500 pulses at the focal depth of 100 μm. The pulse energy of 41.7 μJ is used.

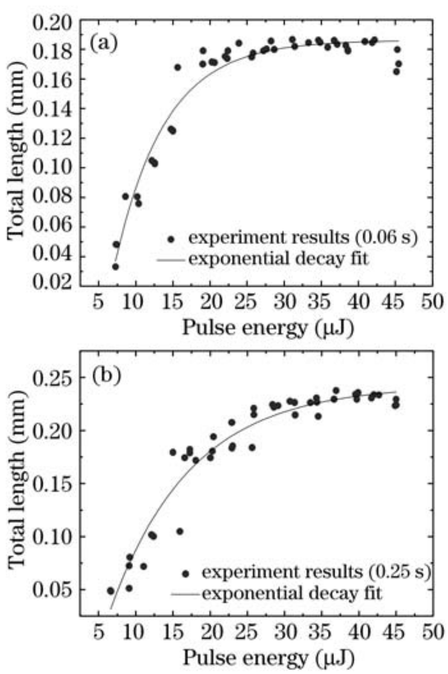

Fig. 3. Total length of the induced microstructures for different irradiation time versus the pulse energy.

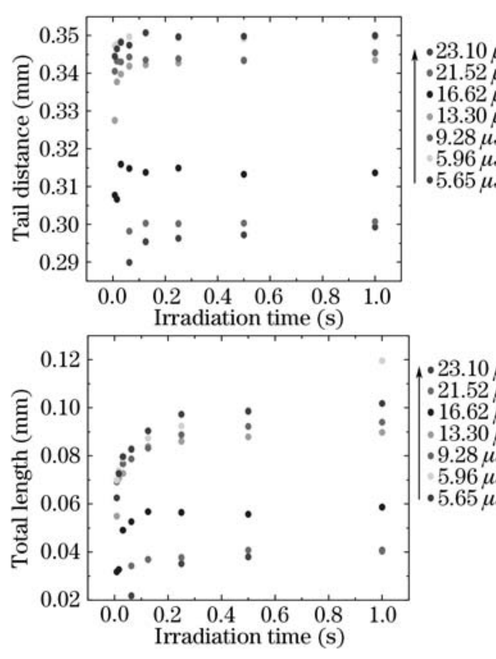

Fig. 5. Parameters of induced microstructures versus pulse number.

the increased pulse number makes the head of the structures shift toward the entrance surface and makes the whole structure even longer, the additional pulses make little contribution to extending the void strings and even have negative effect on forming the desired void string structures by destroying the previously regular void array head. We also notice that the increased pulse number changes the diameters of the void strings and the intervals between them vary little.

We also did detailed research on the dependence of the structures' parameters on the pulse number to further verify the results described above, as shown in Fig. 5. From the statistical results for different pulse energy, it is obvious that, whatever the pulse energy is, the tails of the microstructures nearly all stop extending along the laser axis at the pulse number of 63. The influence of the pulse number on the induced structures may be explained as follows: generally, the pulse number imposes influence on the induced structures mainly through thermal accumulation and thermal self-focusing. Thermal accumulation can make more and more region out of the focal point reaching the melting point and finally enlarge the modified region by fs pulses[9]. But the thermal self-focusing, which mainly results from the Gauss distribution of the thermal refractive index change caused by thermalrefractive coefficient $\mathrm{d}n/\mathrm{d}t$ [10] will make the focal length become shorter. As $SrTiO_3$ crystal has no linear absorption at 800 nm, so the transfer of energy to $SrTiO_3$ is nearly neglectable unless the pulse does not reach the focal point. Therefore, thermal self-focusing should not be the reason why the damage head moves toward the entrance surface with the increased pulse number. So slightly increase of the induced void string with the increase of the pulse number from 8 to 63 may be attributed to the reason that before and after the visible modified region, defect state or refractive index change invisible under optical microscope was created by the preceding pulses and these defects absorbed more energy leading to the onset of the abruptly increasing plasma and the following microexplosion. In our experiment, the laser pulse repetition is 1 kHz, which means that the time interval between the neighboring pulses is 1 ms. Taking into account the thermal property of $SrTiO_3$ (thermal conductivity (100 C): K = 12 W/mK, specific heat (300 K): C = 0.544 J/(g $\cdot$ K), density: ρ = 5.175 g/cm^3) and the focal condition (NA=0.9), the characteristics time required for heat to diffuse out of the focal volume of $SrTiO_3$ can be calculated in terms of $t_c = \omega^2 C\rho/4K$ as 1 μs. Hence, the interval time from shot to shot far exceeds the time for heat diffusion and then the focal volume as well as the region around it returns to room temperature before the next pulse arrives, and makes the propagation of the following pulse never affected by thermal accumulation. This may explain the little change of the void diameters.

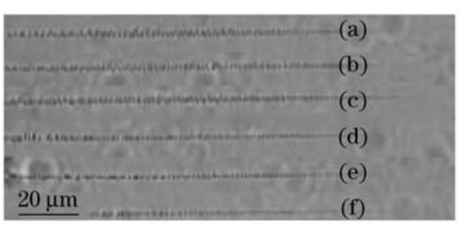

Fig. 6. Void array induced at the focal depth of 150 μm with the entrance surface of the laser beam parallel to the (010) crystal plane.

Table 1. Laser Parameters of Fig. 6

Line Number	Pulse Energy (μJ)	Pulse Number
(a)	46.8	500
(b)	46.8	250
(c)	35.6	125
(d)	24	500
(e)	18.6	1000
(f)	18.6	1000

Until now, the study on the self-organized void strings induced by femtosecond laser was mainly done in glasses, which have isotropic optical properties. Crystal, which is anisotropic, is expected to have different response to fs-pulse fabrication on its different crystal orientation. We did observe the different void morphologies while the entrance crystal plane was changed. Figure 6 shows that when the laser propagation axis is perpendicular to the (010) crystal plane other than the (001) plane used above, the induced holes are not spherical voids anymore, but are rectangular-shaped cavities with the aspect ratio of up to 2.5. Table 1 shows the corresponding laser parameters of Fig. 6. This difference may be attributed to the different mechanical strength at different crystal orientations, and the different mechanical strength against the inner pressure from a laser-induced plasma leads to different aspect ratio. As is known to all, for the manipulation of light at a subwavelength scale with artificial photonic structures two ingredients exist: shape and periodicity. And it has been theoretically predicted that combining shape and periodicity should lead to enhanced optical properties, such as an increased width of the photonic band gap[11]. So these periodically-aligned rectangular-shaped void strings and the spherical void arrays we report here will present different optical properties as photonic crystal device.

The relationship of the characteristics of induced void array with the employed pulse energy indicates that the self- focusing effect may play an important role in the induced microstructures. $SrTiO_3$ crystal has a high nonlinear refractive index n_2 of 2.08×10^{-15} cm^2/W, which is one order of magnitude larger than that of fused silica. It is reasonable that strong competition between the Kerr-effect-induced self-focusing and the plasma-induced defocusing not only stops the collapsing of the laser beam and extends the laser-affected region to tens of times the Reilaygh length, but also makes the light intensity quasi-periodically modulated by this dynamic process, and finally lead to the plasma generation at tens of positions corresponding to the localized maximum intensity. In addition to that, the high-NA microscope objective lens may play some role in the formation of the structures, because, under tightly focusing condition, the nonparaxial effect of femtosecond laser propagation is no longer to be neglected, and we think that this nonparaxial effect may replace the catastrophic focusing in the case of paraxial condition with a sequence of focusing-defocusing cycles. This role of the nonparaxial effect is under the investigation and the numerical simulation is under way. The pulse number also may make some contribution to the increasing of the induced structures by defects accumulation or refractive index change accumulation caused the proceeding pulses, other than by the thermal accumulation.

The self-assembled void-array microstructures induced by tightly focusing multiple fs laser pulses are presented. In this paper, the influence of the pulse energy and the pulse number as well as crystal planes on the induced void strings is investigated. The results show that with the increase of the pulse energy, the void strings not only shift toward the entrance surface but also extend toward the laser propagation direction. It is also worth noting that further increasing pulse number above a threshold value nearly has little positive influence on the induced void array. Holes with different aspect ratio can be obtained by just changing the entrance crystal plane. The results provide guides for choosing more proper laser parameters for generating the desired void arrays to apply to photonic devices.

This work was supported by the National Natural Science Foundation of China (No. 50672087) and the National Basic Research Program of China (No. 2006CB806000). J. Song's e-mail address is ddvsh@163.com.

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