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Formation of Void Array Inside Transparent and Absorptive Glasses by Femtosecond Laser Irradiation

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We demonstrate self-fabrication of void arrays in a fused silica transparent in the visible and a color-filter borosilicate glass strongly absorptive at 800 nm using tightly focused Ti-sapphire femtosecond laser pulses at 1 kHz without scanning. The period, the size, the number of voids, and the length of the aligned void structure were controlled by changing the laser pulse energy, and the position of the focal point inside two materials. The void arrays were observed by an optical microscope and also estimated by an optical diffraction experiment. The void size and period were smaller in the absorptive glass than in the transparent glass. The submicrometer-sized void was observed by a scanning electron microscope. The smaller and clearer void arrays were formed in the color filter than the fused silica glass. With increasing the laser focal depth, the void-array length increased in the fused silica and decreased in the color filter.

Keywords: Femtosecond Laser, Void Array, Fused Silica, Color Filter Glass.

RESEARCH ARTICLE

1. INTRODUCTION

Femtosecond laser processing has been considered as a powerful tool for inducing nonlinear optical effects or microscopic modifications inside transparent materials because of their high power density.[1,2] Such a process has been mainly used for fabricating various micrometer-scale optical components in the bulk materials, including waveguides, couplers, gratings and so on.[3–6] In general, the change in the refractive index due to defect formation and compaction is very small.[7,8] However, photonic crystals are periodic optical nanostructures with high refractive index modulation that affect the light propagation. The fabrication for photonic crystals requires the precise formation of voids with a periodic arrangement.[9] Recently, Kanehira et al.[10] reported a method of forming periodic nanovoid structures inside glasses. In this technique, the femtosecond laser was focused at one point, and the quasi-periodical voids were self-formed along the propagation direction of the laser beam during the irradiation process without any delicate interference experimental setup.[11] Free electron density at a focal point rapidly increases through a multiphoton ionization or tunneling ionization followed by avalanche ionization[12] because of highly intense optical field. The energy absorbed by the electrons then is transferred to the lattice and this heated lattice induces a void. For fs-laser-induced filamentation in glasses, it has been found that the dynamic competition between Kerr self-focusing and the plasma-induced defocusing effect can form multiple foci when focusing a fs laser pulse into the dielectrics. The distance between two adjunct foci is usually on the order of tens of microns.[13] In contrast, the period of the fs-laser-induced void array is only on the order of a few microns or even submicron in other glass and crystals.[14–17] The formation of a periodic void array in the direction of laser propagation is still not clearly understood because of the lack of a good physical understanding, although some approaches were reported.[10,18] Besides, the application of this novel method in absorptive materials is not reported yet as far as we know.

In this paper, we demonstrate the self-organization of a void array by tightly focusing fs-laser pulses inside a transparent fused silica glass and a color filter glass absorptive at the fs-laser wavelength. We compare the dependence of the period, the diameter, and the array length of the void array on pulse energy and focal depth in two materials. Based on the experimental results, we discuss the choice

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of materials and laser irradiation conditions for a good quality of void array structure.

2. EXPERIMENTAL DETAILS

In our experiments, we used a commercially available fused silica (1 mm in thickness) and a band-pass color filter (2 mm in thickness, Thorlabs, Schott glass FGS900). The optical absorption spectra were measured by a spectrophotometer (Genesis 6). A regeneratively amplified 800-nm Ti:sapphire laser (Cyber Laser, IFRIT) that emits 180 fs, 1 kHz, mode-locked pulses was employed in our experiments. The glass sample was put on an xyz-stage, which was controllable by a personal computer, and a laser beam in Gaussian mode was focused through a 100× objective lens with a numerical aperture (NA) of 0.7 in the interior of the glasses. The pulse energy of the fs-laser at the sample location was approximately controlled in between 10 and 40 uJ by using neutral density (ND) filters inserted between the fs laser and the microscope objective. An electronic shutter was used to control the number of pulses of the laser beams. The 125 pulses were focused inside the samples, unless otherwise noted. We observed the aligned void structure from a direction perpendicular to the incident laser beam through an optical microscope (Olympus, JP/BX51) with a 150× objective lens and a confocal laser scanning microscope (Carl Zeiss, TCS SP2 AOBS). The morphology of the periodic voids and their surroundings was analyzed with higher resolution using a scanning electron microscope (FE-SEM, Carl Zeiss, LEO-1530) after the glass was cut to get the surface to see the voids.

3. RESULTS AND DISCUSSION

We investigated the effect of the absorption at laser wavelength, the number of incident pulses, laser pulse energy, and the focal position on the period and number of generated voids in a fused silica and a doped borosilicate glass color filter). Figure 1 shows the absorption spectra of the fused silica and the color filter. The fused silica does not show any absorption at 800 nm and 400 nm.

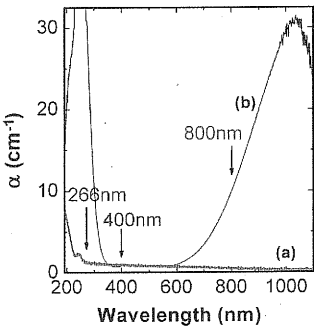

Fig. 1. Absorption spectra of the fused silica (a) and the color filter (b).

Even at 267 nm corresponding three-photon absorption wavelength, the linear absorption coefficient is less than 0.5 cm^{-1}. It implies that the voids are formed at least by four photon absorption process. In contrast, the color filter has the less band gap energy and much larger absorption at 800 and 267 nm. Thus, we expect more effective photoionization in the color filter glass because three-photon ionization process includes a resonant level at 800 nm. The absorption at the laser wavelength indicates the role of typically doped semiconductor in color filters. Figure 2 shows the microscopic images of the void arrays fabricated at 500 μm from the incident surface in two materials with various pulse energies. We chose one hundred and twenty five laser pulses after we measured the dependence of void array formation on the number of 30 μJ pulses. The void size, the period, and the array length increased with pulse energy in both materials. In the fused silica, the maximum array length is 130 μm.

The fused silica shows three different featured parts after 10 μJ laser pulses. The initial part consists of a few voids with large void diameters and intervals because of high intensity. The middle part shows a long quasi-periodic void array with a small void diameter and interval. However, the last part looks like a waveguide. With 20–40 μJ laser pulses, a long crack or irregular damage was observed just below the focal point. In contrast, the color filter shows clear void arrays with the maximum length of 118 μm. It also shows the smaller void size and intervals than in the fused silica. From the absorption spectra in Figure 1, we can expect more effective photoionization in the color filter than the fused silica, producing the higher density of electron plasma at the focal point with the same intensity of laser pulse. The smaller size and the clearer boundary of the voids with the higher plasma density may be related to the role of dopants in the color filter, because quantum dots in glass were reported to have a high Kerr coefficient.[19] Thus, the color filters can be better candidates for self-formation of void-arrays, although further investigation is necessary to clarify the mechanism. Figure 3(a) shows that the diameter increases

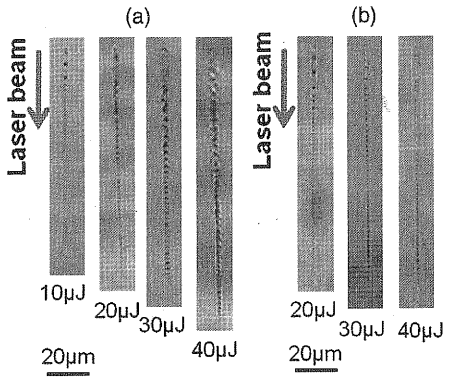

Fig. 2. Optical microscope images of void arrays in fused silica (a) and color filter (b) formed by 125 fs-laser pulses with 30 μJ pulse energy at focal depth of 400 μm with various pulse energies.

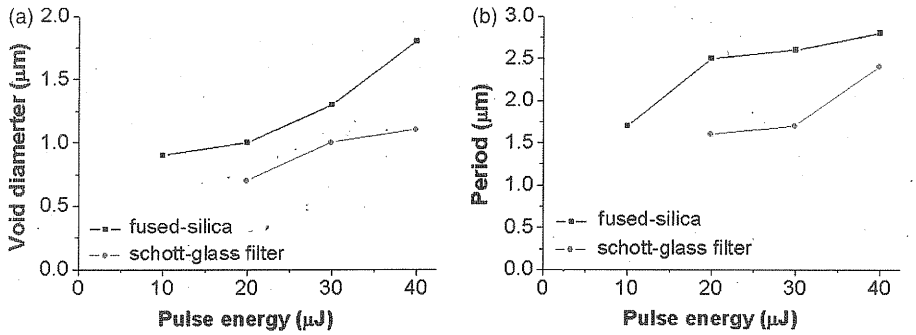

Fig. 3. Dependence of the void diameter (a) and the period (b) on the laser pulse energy in the fused silica and the color filter.

from 900 nm to 1.8 μm and the period also increases from 1.7 to 2.8 μm in the fused silica. Figure 3(b) shows that the average diameter increases from 700 nm to 1.1 μm, and the period also increases from 1.6 to 2.4 μm in the color filter. The effective length of void array with the constant period is larger in the color filter, which is a better feature for photonic crystal application.

Figure 4 shows the microscope images of the voids fabricated in two materials with 125 pulses with a 30 μJ pulse energy at various depths from the entrance surface. The indicated depth is the laser focal position without the sample. With the deeper focal points, we obtained the longer void array in the fused silica. Because the focal point at 600 μm without a sample corresponds to 800 μm from the surface, the filament reached the bottom of the fused silica. The length of void array increases from 50 to 170 μm as the focal depth increases from 100 to 550 μm in the fused silica. In case of the large focal depth, the long optical path from the surface produces a large amount of self-focusing to the propagating fs pulse. This self-focusing causes a localization of the pulse energy at the focal point and the high intense pulse proceeds a longer distance than the small focal depth case. In contrast, the void-array length decreases dramatically from 100 to 30 μm as the focal

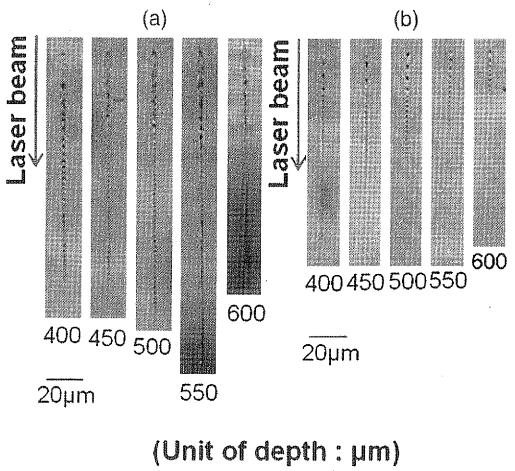

Fig. 4. Optical microscope images of void arrays in fused silica (a) and color filter (b) formed by 125 fs-laser pulses with 30 μJ pulse energy with different focal depths.

depth increases from 400 to 600 μm. The pulse energy decreases only by 20% from 400 μm depth to 600 μm if we consider the linear absorption at 800 nm. Thus, three photon absorption processes cannot explain this large reduction. The reduced array length in case of focusing at deep positions may be caused by the less plasma mobility or saturable absorption of quantum dot in the color glass.[20] A few voids near the focal point in the fused silica are large and merged each other. However, the color filter shows relatively clear and small void image even around focal points. Figure 5 shows that the overall features of the void array self-formed at different focal depths in two materials. The void size decreases from 1.3 μm to 800 nm and the void period also decreases from 2.8 to 2.3 μm as the focal depth increases from 400 to 550 μm in the fused silica. The color filter also shows that the average size decreases from 900 to 800 nm and the period changes from 2 to 1.7 μm.

We performed the diffraction experiment for the void array formed in the fused silica to check the uniformity of the void period. Figure 6(a) is the void array formed by 125 pulses of a 30 μJ pulse energy at 500 nm below from the surface of the fused glass. The arrays are separated by 20 μm. Figure 6(b) is the diffraction pattern obtained with a 633 nm HeNe laser. The horizontally distributed spots indicates the 20 μm interval of the arrays. The vertically distributed pattern indicates the interval of voids. The strongest diffraction pattern gives the 2.6 μm interval and the other weak patterns are originated from the initial voids formed close to the focal points and the tail voids of the arrays.

To better measure the actual void size, we cleaved the fused silica along the void array, and polished and etched it in a HF solution. Figure 7(a) shows a confocal microscopic image of the void arrays with a 4 μm interval fabricated by 30 μJ pulses at 500 μm focal depth. The SEM image in Figure 7(b) shows the smallest void with a diameter of about 700 nm. According to the SEM observation, the fabricated voids and void array are found to consist of a gas phase. The diameter of the voids inside the glass is much smaller than that at the focal point, presumably due to the weaker laser intensity and self-focusing effect. The self-formation of void arrays was explained by competing process between self-focusing due to nonlinear

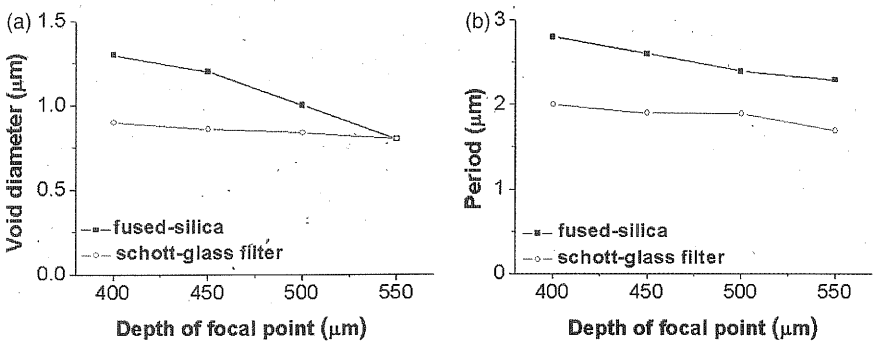

Fig. 5. Dependence of the void diameter (a) and the period (b) on the focal depth in the fused silica and the color filter.

effect and defocusing due to diffraction[14] and plasma diffusion. When the laser pulses propagate deeply into the glasses, the losses of the pulse energies due to diffraction will reduce the laser intensity, leading to the reduction of electron plasma density, forming a large density gradient. Thus, the plasma wave is reflected and then interfere with the forward-traveling electron wave, creating a standing-wave pattern.[14] Because the wavelength of the electron plasma wave is inversely proportional to the electron density, the void period decreases at the ending part of the array. Recently, the spherical aberration was reported as another important factor for the formation of periodic void arrays because it changes the laser intensity distribution.[18] Our results show that the quantum-dot doped glass filter may improve the photo-ionization efficiency via a resonant absorption level at the irradiation wavelength and also influence on the electron plasma density distribution because semiconductor quantum dots can provide the higher electron mobility than dielectrics.

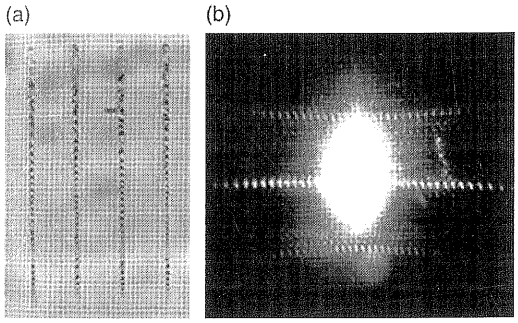

Fig. 6. (a) Optical microscope images of void arrays in fused silica formed by 125 fs-laser pulses with 30 μJ pulse energy (b) Diffraction pattern with a 633 nm HeNe laser.

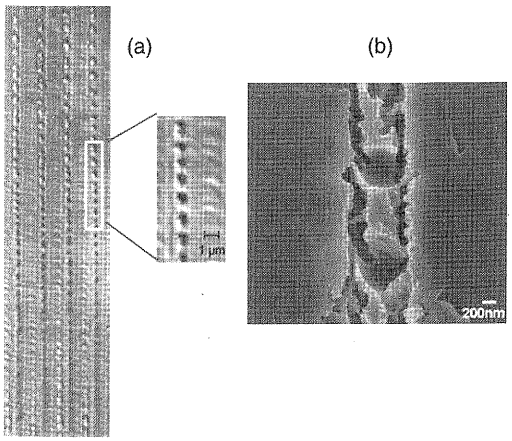

Fig. 7. Confocal microscope image (a) and SEM image of the sub-μm sized void array formed by 30 μJ pulses at focal depth of 500 um in the fused silica. The array interval is 4 μm.

4. CONCLUSIONS

We report that void structures of the length of hundreds of micrometers can be self-fabricated in fused silica and color filter glass by tightly focusing femtosecond laser pulses without translation. The laser intensity and the depth of the focal position from the fused-silica surface are important parameters for the void size, the period and the lenghth of void arrays, because self-focusing affects the focused laser propagation. Materials with a high Kerr coefficient will be able to decrease the void fabrication threshold energy. Thus, the color filter which is doped with quantum-dot can be a good candidate for photonic crystal devices and high-density 3D optical data storage.

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