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RESEARCH ARTICLE

Micromachining soda-lime glass by femtosecond laser pulses

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The physical process of forming a modified region in soda-lime glass was investigated using 1 kHz intense femtosecond laser pulses from a Ti: sapphire laser at 775 nm. Through the modifications induced by the femtosecond laser radiation using selective chemical etching techniques, we fabricated reproducible and defined microstructures and further studied their morphologies and etching properties. Moreover, a possible physical mechanism for the femtosecond laser modification in soda-lime glass was proposed.

Keywords ultrafast processes, glass, laser ablation

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1 Introduction

Glass is widely used as an optical material with a high transparency in the visible spectrum. Laser modification [1] could lead to optoelectronic devices such as optical waveguides [2] embedded in glass substrates without cracking. In the past decade, a femtosecond laser has been used to fabricate microchannels [3, 4] through wet chemical etching. In addition, the morphology and etching properties of the femtosecond-laser-induced modification were extensively studied, providing scientific support for the production of various glasses with different functions [5].

Significant efforts have contributed to the discovery of the fundamental mechanisms for the localized modified structure inside bulk glasses using femtosecond-laser pulses. Experimental results from fused silica demonstrated that laser irradiation could induce densification within the focal volume [6–9]. An increase in the reactivity resulted in greater etching in the densified zones compared to the unmodified zones, and the corresponding densification profiles suggested femtosecond-laser-induced structures in silica glass [10–12]. In addition, the main structural modification of some multicomponent glasses led to an expansion of the focal volume accompanied by a lower local density [13, 14]. However, Vega *et al.* reported that the local densification in the glass occurred within the entire laser-modified region [15]. Bhardwaj *et al.* produced arrayed planes of laser-modified material and presented a nanoplasmonic model [16]. Recently, Cheng group discussed the threshold effect on the formation of a nanograting upon femtosecond laser irradiation in porous glass [17]. Despite the above achievements in this field, the detailed morphology of the modified area still requires further studies.

Herein, we investigate the morphological characteristics of the modified microstructure in soda-lime glass after femtosecond laser irradiation. The irradiated samples are etched in a hydrofluoric-acid solution to show the topography of the modified region. A possible physical mechanism for the femtosecond laser modification in soda-lime glass is proposed.

2 Experimental

In our experiments, a commercial femtosecond laser (UMW-2110i, Clark-MXR Inc.) was used to deliver linearly polarized laser pulses with a duration of 130 fs at a center wavelength of 775 nm and a repetition rate of 1 kHz. The maximum pulse energy was 1 mJ. A long working-distance objective lens with a numerical aperture of 0.40 was applied to further focus the laser pulses. The sample used in this study was a commercially available soda-lime cover glass plate with a thickness of 170 μm. The sample was mounted on a high-precision translation stage with a resolution of 150 nm. The sample surface was perpendicular to the laser beam, and the reflected laser beam from the sample was monitored using a CCD camera. Figure 1 shows the schematic of the longitudinally written laser lines (detail in Ref. [18]). The sample was moved parallel to the laser beam at a constant speed of 10 μm/s through the glass slab. Because damage to the surface of the sample would scatter the incident laser, the laser focal spot was moved from the lower surface to the upper surface. After writing, the glass samples were immersed into a static bath of hydrofluoric acid (5% HF by volume) at room temperature for 0.5 h and then cleaned and examined with an SEM (Philips XL30ESEM).

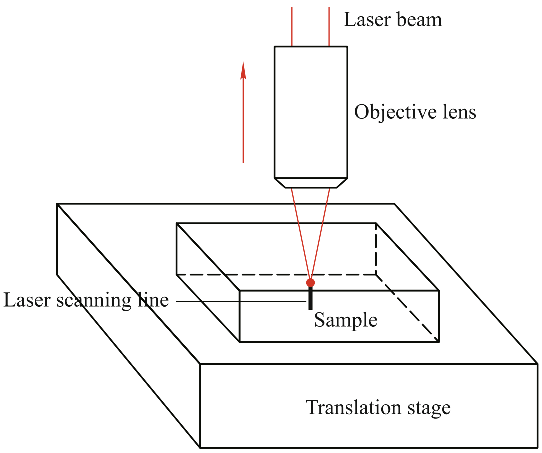

Fig. 1 The schematic of fs laser parallel writing, red arrow show the direction of laser scanning.

3 Results and discussion

3.1 Laser line written in a parallel direction

The sample was moved parallel to the laser beam at a constant speed of 10 μm/s from the lower surface to the upper surface. Figure 2 shows an SEM image of a typical pattern on the end of a soda-lime glass plate that was exposed to a laser power of 5 mW. Two features could be discovered: one is a dome-like bump in the center, which has a diameter similar to the focal spot of the laser, and the other one is a bright annulus around the bump, which has a diameter of about 30 μm. Bhardwaj reported similar surface swelling by femtosecond laser modification in glass [19]. A well-known phenomenon is that the thermal expansion in the radial direction that results from a micro explosion within the material during laser exposure, leading to a reduction in the density at the center of the modified region. The compression induced by the expansion of the central region results in a structural change in the surroundings, i.e., the formation of a densified region [8, 15, 20]. However, in the axial direction, the surface protrudes when the focal spot of the laser arrives at the surface, the stress is released, and a surface bump is formed. The crater at the center of the bump region indicates that the surface ablation threshold is less than the modification threshold of the bulk. Additionally, a bright white annulus appears at the periphery of the bump region. This is the results from the secondary electron image obtained by SEM. As secondary electron emission is a surface process, it is strongly influenced by slight modifications in the material surface [21]. Qiu group discovered that after femtosecond laser irradiation, the elements composing the glass are concentrated in the surrounding part to form ring-shaped regions [22]. Moreover, the properties of the glass were affected by modification of the Si–O bonds due to the presence of metal atoms [23]. Therefore, after femtosecond laser exposure, the concentrations of the metal elements lead to a weakening of the glass structure. The weakening of the glass structure improves the secondary electron yield; thus, this region appears white in the SEM image.

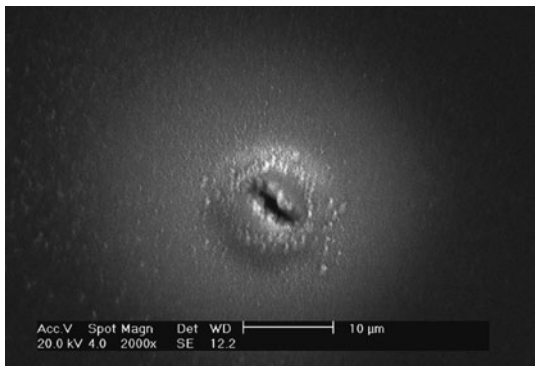

Fig. 2 SEM image of the exit face of the modified region written by fs laser pulses.

3.2 Chemical etching of laser-modified sample

The laser-processed samples were immersed into a static bath of diluted hydrofluoric acid (5% HF) and kept inside for 30 minat room temperature. The samples were then cleaned for further study of the topographies of the modified structures.

Figure 3 shows the SEM images of the modified region written under the same conditions after etching, indicating that their structures were densified inside the laser-processed volume. Only a pillar (under the surface swelling region) remained at the central part of the laser-modified region in the sample, and the pillar surface was approximately in the same plane as the undamaged region [Fig. 3(a)]. This indicates that the etching rate for the surface of the protrusion region was equal to that of the undamaged region, i.e., the surface density in the

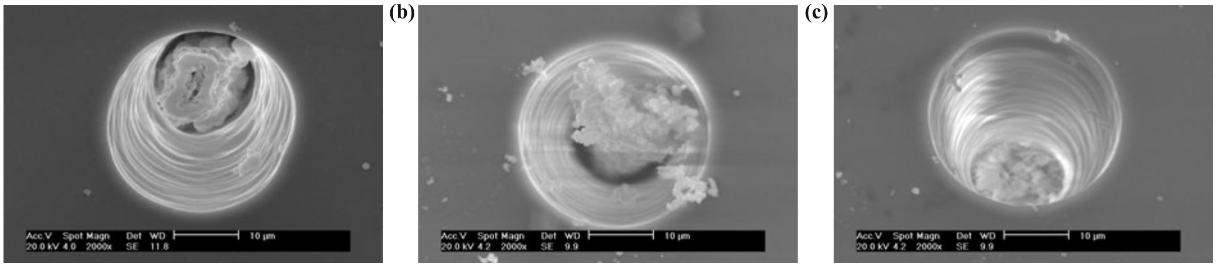

Fig. 3 SEM images of the modified region written by the same conditions after etching. **(a)** The whole pillar, tilting view; **(b)** the collapsed pillar; **(c)** the bottom of etching hole, tilting view.

bump region was equal to that of the undamaged region. However, the etching rate around the bump region was higher than that of the unaffected region, implying that densification occurred in that region. Bourhis *et al.* [24] reported that the local modification zones in femtosecond-laser-processed glass are not homogeneously affected by acid etching. They discovered that a composition variation between the center and ring regions led to deeper etching and left a central peak surrounded by a valley. They suggested that the concentrations of metal elements reduced the chemical resistance in the ring. Therefore, local densification and the concentrations of metal elements in the soda-lime glass could improve the chemical activity.

Figure 3(b) shows that the pillar collapsed in another sample with a large number of round particles falling apart. The formation of these particles could be explained by the nanoplasmonics model [25]. The nonlinear multiphoton absorption at defects or color centers was inhomogeneous and could result in the localized formation of ionization hot spots in the focal volume [26]. The extremely high pressures and temperatures could be reached locally, generating multiple nanoscale densifications, which are distributed randomly at the center of the laser beam. The central exposed area was segmented into separated particles by the local nanoscale densified area. Therefore, the binding affinity between the particles was weak and could lead to pillar collapse during rinsing of the sample. Figure 3(c) shows the bottom of the etching hole without a pillar. This implies that the pillar was broken at the bottom and fell apart during the cleaning process.

However, although a laser source emits linearly polarized laser pulses, the modified structures exhibit no preferred orientation phenomenon, and no planar nanostructure was found in the laser-modified area. Similar results were reported by Bourhis *et al.* [24]. A further detailed study on the modification mechanisms in different glasses is necessary.

In order to test the repeatability, a 3×2 array on a soda-lime sample was scanned using a laser power of 0.33 W and a scanning speed of 2.5 mm/s. After a chemical etching process, the microscope image of the pattern clearly showed that a 3×2 through-hole array was clearly fabricated in the glass sheet (Fig. 4), suggesting that repeatability was facile to achieve.

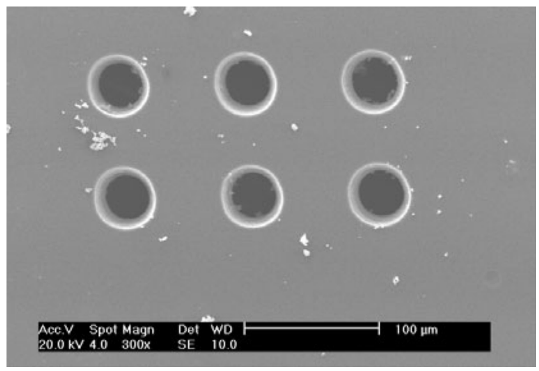

Fig. 4 SEM image of the 3×2 through hole array.

4 Conclusions

The soda-lime glass exhibited a modified microstructure after treatment with a femtosecond laser. A bump and a bright-white annulus around the bump appeared on the surface. A multiphoton absorption process, microexplosion, and nanoplasmonic process are likely involved in the modified mechanism. Local densification and the concentrations of metal elements in the soda-lime glass by femtosecond laser exposure could improve the chemical activity. After selective chemical etching, a pillar consisting of separated particles was observed in the femtosecond-laser-modified structure. Through-holes could be produced by prolonging the time for chemical etching or by increasing the laser power. The through-holes that result from the selective chemical etching and femtosecond-laser modification exhibit sharp edges and repeatability in soda-lime glass. Therefore, the use of femtosecond-laser exposure and chemical etching provides a versatile and highly precise means of micromachining inexpensive soda-lime glass.

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