

Research Article

Three-Dimensional Residue-Free Volume Removal inside Sapphire by High-Temperature Etching after Irradiation of Femtosecond Laser Pulses

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We applied the femtosecond laser-assisted etching technique, that is, irradiation of focused femtosecond laser pulses followed by selective chemical etching, to volume removal inside sapphire. At room temperature, volume etching only slightly advanced while residue remained inside the volume. By increasing the etching temperature, complete volume etching without residue was achieved. Complete etching was, however, accompanied by undesirable phenomena of surface pits or cracks, which are expected to be excluded through further improvement of processing.

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1. Introduction

Despite recent progress in micro/nanotechnology, material processing with three-dimensional (3D) shape flexibility remains a challenging task in the micrometer domain. Sacrificial layer etching [1] is an established technique in the field of microelectromechanical systems (MEMSs) for fabricating suspended structures. Nevertheless, it requires large-scale semiconductor equipment. Femtosecond (fs) laser processing of photopolymers [2, 3] is a widely used technique for 3D submicrometer processing, but the target materials of that technique are limited to polymers. For that reason, the technique is inapplicable to solid materials.

Femtosecond laser-assisted etching offers the possibility of removal processing with 3D flexibility in the micrometer domain. The technique consists of two steps: irradiation of focused femtosecond pulses along a predesigned pattern and subsequent chemical etching. The modified region will be etched out selectively; a 3D empty space is fabricated if the irradiated region is more soluble to the etchant. In fact, 3D microstructuring by femtosecond laser-assisted etching was first reported in 1999 with a photosensitive glass [4]. Subsequently, similar 3D microstructuring was reported

with a nonphotosensitive material, silica glass [5], and other materials [6–9].

Sapphire (Al_2O_3 crystal) is a hard and inert material that plays important roles in optics and electronics. For example, it is used as a substrate material of a GaN light-emitting diode. Several techniques have been reported for micropatterning of sapphire and Ti:sapphire, such as a combination of ion implantation and wet chemical etching [10], reactive ion etching [11], and argon ion-beam etching [12]. Especially, a combination of ion implantation and wet chemical etching [10] enabled us to underetch the surface layer, but this technique requires very large and expensive equipment. Femtosecond laser-assisted etching is a promising technique for 3D microstructuring of sapphire; microchannels were fabricated by this technique [8, 13]. However, we have reported that complete removal of the volume region is difficult. Mesh-like residue remains after etching [14]. Volume etching is necessary for applications that require a complete hollow space, such as embedded optical components [15, 16], nanoaquariums for dynamic observation of living cells [17], and fluid mixing by optical rotators [18]. A new technique is necessary to achieve volume etching for sapphire. In all previous reports of femtosecond laser-assisted etching, wet etching was carried out at room

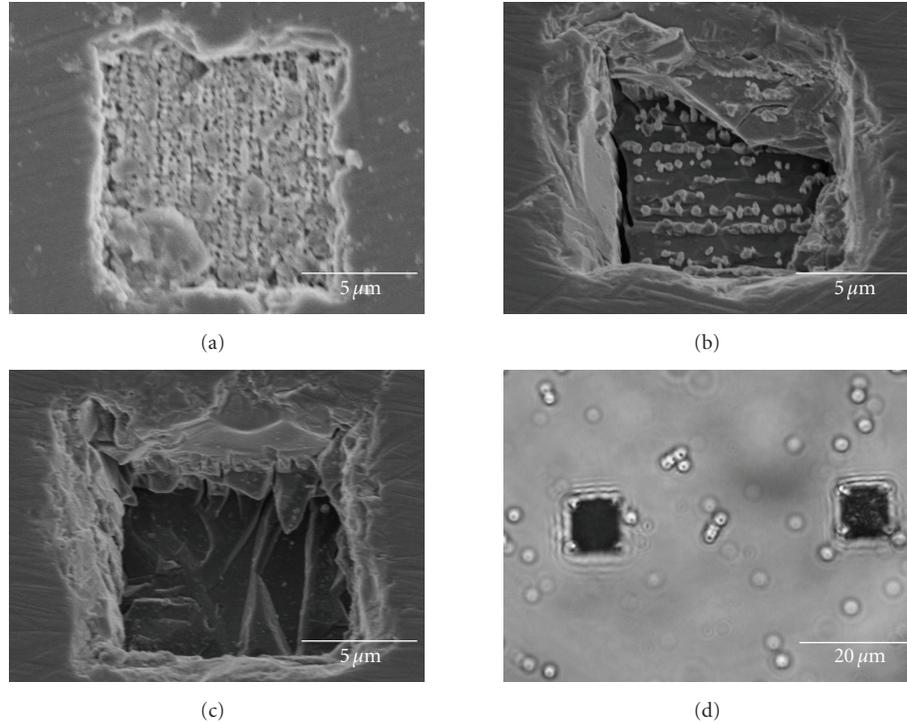


FIGURE 1: (a)–(c) SEM micrographs inside sapphire with a laser irradiation condition of $p_x = 0.2 \mu\text{m}$ and $p_z = 2.0 \mu\text{m}$, and after etching (a) at room temperature for 72 hours, (b) at 100°C for 24 hours, and (c) at 120°C for 24 hours. (d) Optical micrograph of sapphire after etching at 120°C for 48 hours. In this micrograph, both the surface and subsurface are visible.

temperature. In the present study, we carried out etching at high temperatures aiming at complete residue-free removal of the volume region inside sapphire.

2. Experimental

The sample used was sapphire (0001) substrate (Shinkosha Co., Ltd., Yokohama, Japan) grown using the Kyropoulos method. The typical FWHM of its X-ray rocking curve is 4 seconds. The sample was set on an inverted microscope (IX-70; Olympus Corp., Tokyo, Japan), and femtosecond laser pulses (800 nm, 130 femtoseconds) were focused by an objective lens (UPlanApo100; Olympus Corp.) and irradiated to the sample. Irradiation of a single femtosecond pulse with a typical pulse energy of about 40 nJ produced a micrometer-scale modified spot (amorphous region surrounded by a strain field [8]) inside the sapphire without cracking. Hereinafter, this spot is referred to as voxel.

The whole modified region is a square cuboid $10 \mu\text{m}$ below the surface, with four paths which connect the square cuboid and the surface. The size of the square cuboid was $x \times y \times z = 10 \times 10 \times 10 \mu\text{m}^3$, where the z -axis is the direction perpendicular to the substrate surface. In the square cuboid region, voxels are arranged in a simple tetragonal lattice. The period on the x -axis and y -axis, p_x , was typically $0.2 \mu\text{m}$. The period on the z -axis, p_z , was $1\text{--}4 \mu\text{m}$; here the results with $p_z = 1 \mu\text{m}$ and $2 \mu\text{m}$ are reported. After irradiation, the sample was observed using optical microscopy.

The etchant was a 10% aqueous solution of hydrofluoric acid. Etching was carried out in a teflon-coated high-pressure cell. The cell, containing etchant and sample, was put in an electric oven at $80\text{--}150^\circ\text{C}$. After etching, the sample was inspected using optical microscopy and scanning electron microscopy (SEM). SEM observation was carried out on the surface and the subsurface irradiated region. For SEM observation of the subsurface irradiated region, the sample was mechanically polished so that the region was observable directly. The direct SEM observation of the irradiated region is important because nondestructive optical observation alone might be insufficient to reveal the residue [14].

3. Results and Discussion

Through these experiments, we discovered that both irradiation and etching conditions can improve removal capability, although each has its own disadvantages.

First, the results with $p_z = 2 \mu\text{m}$ are described. Figure 1(a) depicts an SEM micrograph inside after etching at room temperature for 72 hours. Volume etching only slightly advanced; a mesh-like residue was observed. Figure 1(b) presents an SEM micrograph of the interior after etching at an elevated temperature of 100°C for 24 hours. Volume etching was somewhat improved. A single layer was removed, but further advances in depth (in the z direction) did not take place. When etching temperatures were further elevated to 120°C , much advance took place in volume etching; residue was lost and complete removal was achieved, as

shown in Figure 1(c). However, another problem appeared. Figure 1(d) shows an optical micrograph of sapphire after etching. In addition to the subsurface etched regions (dark squares), surface pits (small bright spots) can be seen. The pits were absent before etching but they appeared after etching for a long period. Reportedly, pits are generated on the surface of sapphire during high-temperature etching; the origin of the pits is related to dislocations [19]. The pits observed here have a hexagonal shape and are aligned to the same direction, which suggests that the shape is related to the crystalline nature of sapphire. In the present experiments, the generation of surface pits became a problem when the etching temperature was elevated. The pits on the surface scatter light to unintended directions. For that reason, they are undesirable for optical applications. We have performed examination with several etching temperatures and etching periods, but we were unable to find a temperature-period window in which complete volume etching can be achieved without surface pits. The surface pits can probably be removed by polishing subsequent to the etching, but it is a time-consuming process. A complete etching method that leaves no surface pits is desired. It is noteworthy that the roughness of the surface in the pit-free region did not deteriorate by etching ($R_a \lesssim 1 \text{ nm}$; R_a is the average of the roughness profile, as evaluated using atomic force microscopy).

For $p_z = 1.0 \mu\text{m}$, etching advanced better than in the case of $p_z = 2.0 \mu\text{m}$. Figure 2(a) depicts an SEM micrograph inside after etching at 100°C for 24 hours. From comparison with Figure 1(b), volume etching appears to be much more advanced with $p_z = 1.0 \mu\text{m}$. However, another problem, cracking, appeared with $p_z = 1.0 \mu\text{m}$. Figure 2(b) portrays optical micrographs inside sapphire after laser irradiation with $p_x = 0.2 \mu\text{m}$ and $p_z = 1.0 \mu\text{m}$ before and after etching. As shown there, cracks are visible from the corner of the square cuboid to the outside before etching (b1). After etching (b2), the laser-irradiated region darkened; the cracks are still observable. Cracks reduce the precision of fabrication and enable fluid to penetrate to unexpected regions. For that reason, generation of cracks should be avoided.

As described above, cracks did not appear by irradiation of a single femtosecond pulse with the present irradiation condition. After irradiation of the cuboid region with a small p_z of $1.0 \mu\text{m}$, cracks appeared at the outside of the corner of the cuboid region. These results suggest that cracks are generated by superposition of stress of multiple voxels. Consequently, the decrease in the period of voxels enhanced the generation of cracks.

Figure 3 schematically summarizes the results. The horizontal axis indicates the laser irradiation condition: the right side corresponds to the higher density (smaller period of voxels) and higher pulse energy. The vertical axis indicates etching conditions: "up" corresponds to the higher temperature and longer period. Three thick lines mark the borders of the issues to be overcome. Corresponding double arrows mark the desirable side. The three double arrows point to the different directions. Therefore, the overlapping region of the three is small even if it exists. We have not yet found such an overlapping region. Three borderlines cross at a point in

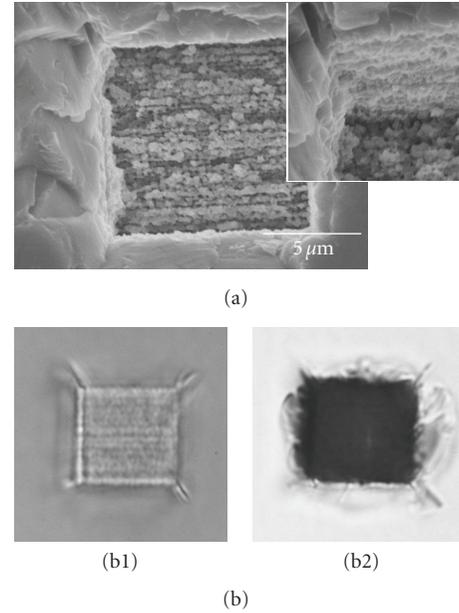


FIGURE 2: (a) SEM micrographs inside sapphire with a laser irradiation condition of $p_x = 0.2 \mu\text{m}$ and $p_z = 1.0 \mu\text{m}$ after etching at 100°C for 24 hours. The inset presents a close-up oblique view tilted at 20° . (b) Optical micrographs of the same sample as (a), (b1) before etching, and (b2) after.

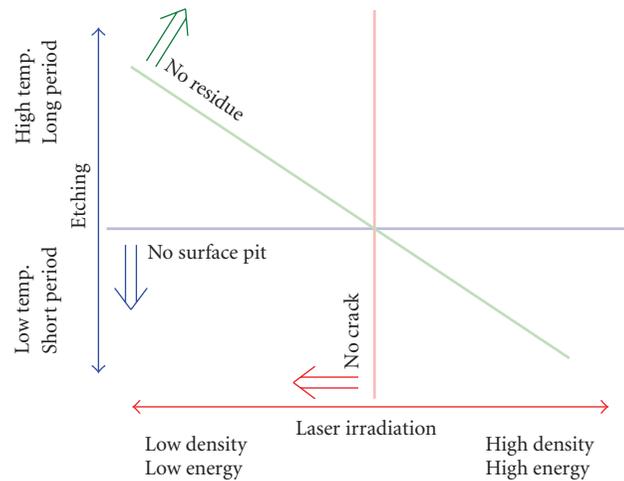


FIGURE 3: Schematic diagram of removal property of sapphire by femtosecond laser-assisted etching. Thick broken lines are borderlines of three issues; corresponding double arrows show the desirable region.

Figure 3, but the relative position of the lines has not been clarified yet. The existence of the overlapping region remains as an open question.

Another remaining problem is the roughness at the interface between etched and unetched regions. As shown in Figure 1(c), where complete volume etching was achieved with a generation of surface pits, the bottom of the etched cuboid is rough. At present, this roughness cannot be controlled during processing. A new processing strategy is

necessary for applications in which roughness hinders its use, as in optical applications.

4. Conclusion

Complete removal of the volume region by femtosecond laser-assisted etching inside sapphire was achieved. The increased etching temperature and increased density of laser irradiation points aided the progress of etching. Changes in the experimental parameters, however, caused undesirable phenomena of surface pits and cracks. The compatible region of experimental parameters, where complete etching is achieved without such problems, is expected to be small. For that reason, refinement of the experimental parameters or establishment of a new processing strategy is required.

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