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Sapphire Selective Laser Etching Dependence on Radiation Wavelength and Etchant

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Abstract: Transparent and high-hardness materials have become the object of wide interest. Most notably, it concerns technical glasses and crystals. A notable example is a sapphire – one of the most rigid materials having impressive mechanical stability and good optical properties. Nonetheless, using this material for 3D micro-fabrication is not straightforward due to its brittle nature. On the microscale, selective laser etching (SLE) technology is an appropriate approach for such media. Therefore, we present our research on c-cut crystalline sapphire microprocessing by using femtosecond radiation-induced SLE. Here we demonstrate a comparison between different wavelength radiation (1030 nm, 515 nm, 343 nm) usage for modification inscription and various etchants (Hydrofloridic acid, Sodium Hydroxide, Potassium Hydroxide and Sulphuric and Phosphoric acid mixture) comparison. We show that regular SLE etchants such as Hydrofluoric acid or Potassium Hydroxide are unsuitable materials for selective sapphire laser etching. Meanwhile, a 78% sulphuric and 22% phosphoric acid mixture at 270°C temperature is a good alternative for this process. We present the changes in the material after the separate processing steps. Finally, a protocol for advanced sapphire structure formation and a few exemplary structures are presented.

Keywords: Selective Laser Etching; 3D Laser Microfabrication; Crystals Microprocessing; Sapphire 3D structures; Femtosecond Laser Microprocessing;

1. Introduction

Sapphire is an attractive material in many applications. This material is highly desirable for various mechanical components due to its strength and chemical resistance. Moreover, because of its good optical properties, it is also a good alternative for optical components. However, the microprocessing of sapphire is highly complicated, because it tends to crack if it is affected by high stress during the processing. There have been already shown various laser machining techniques for sapphire microprocessing: for surface 2D structure formation dicing [1] or direct laser ablation could be used [2,3]. To improve the quality of laser-processed surfaces ablation could be mixed with additional processes such as laser-induced plasma-assisted ablation [4,5] or back side wet etching [6–8]. By using ablation in combination with additional thermal processing [9] or direct laser writing in combination with chemical post-processing, optical components such as lenses [10,11] or diffractive gratings [12,13] could be made. Nevertheless, these technologies have many limitations, and most cannot produce arbitrary shape 3D structures. Meanwhile, the SLE technique could be a good alternative for 3D structure formation out of sapphire.

Selective laser etching (SLE) is a unique technology that allows the production of 3D structures out of solid-state transparent materials [14]. SLE implementation consists of several steps. First of all, laser induced nanogratings are formed in the volume of the material by using ultrashort pulses of radiation. Then, laser-modified material is etched out using aggressive etchants such as Hydrofluoric acid (HF) or Potassium Hydroxide (KOH). The capabilities of this technology are widely investigated on amorphous silica glasses [15–18]. Critical parameters in SLE are etching rate and selectivity. The etching rate defines

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how fast material can be etched, and the selectivity is the ratio between the etching rate of modified and unmodified material. Selectivity describes the highest aspect ratio, which is obtained using a specific SLE processing protocol. Only by optimizing laser parameters selectivity above 1000 could be obtained for fused silica [15]. Optimizing the process with particular burst regimes [19] or adding organics to the etchant [20] selectivity above 2000 could be obtained. SLE is a perfect technology for high aspect ratio structure fabrication. The SLE-made structures could be applied in many areas such as micromechanics [21,22], microfluidics [23–25].

In some works, researchers have already applied SLE on various crystals, such as YAG [26–28] or crystalline quartz [29]. More than a decade ago, first ideas of SLE processed in sapphire were published [30]. This publication suggest inscribing nanogratings inside the sapphire volume and etching it with KOH. A similar procedure was demonstrated with HF acid [31]. The etching selectivity values of around 10000 [32] obtained. Compared with the value shown in fused silica, this is at least 4-5 times higher. Even though the selectivity in sapphire is impressive, no one has ever demonstrated SLE-made 2D or 3D objects out of sapphire. In this work we present a research on sapphire SLE and provide successful etching protocol. Finally, we demonstrate structures fabricated out of sapphire by using the SLE technique.

2. Materials and Methods

SLE experiments were performed with C-cut crystalline sapphire. In these tests, 0.5 mm thickness sapphire substrates were exploited. During the tests, many different laser parameters, as well as, various etching protocols were tested. In these experiments, different wavelengths - 1st (1030 nm), 2nd (515 nm), and 3rd (343 nm) harmonic of Yb: KGV femtosecond laser (Pharos, Light Conversion Ltd., Lithuania) - were tested. Various focusing optics were chosen to maintain the same focusing conditions for all tested wavelengths. To focus 1030 nm radiation 0.4 NA aspherical lens was used. To focus 515 nm radiation 0.2 NA aspherical lens was used, and to focus 343 nm radiation 0.1 NA objective was used. All tested wavelengths were focused to approximately 1.5 μm beam spot. Radiation wavelength itself could change the size and periodicity of nanaogratings [33] which later affects the etching properties of inscribed modifications. Sample positioning was done by using XYZ linear positioning stages (Aerotech, USA). In described experiments, circular and linear polarised light was used. It was shown that in fused silica, the light polarization determines the orientation of the nanaogratings, which affects the etching rate significantly [34]. A similar tendency of nanogratings orientation depending on light polarization has been demonstrated in crystalline sapphire samples, as well [35]. Thus, in single-line experiments, linear polarization perpendicular to the scanning direction was used to maintain a high etching rate. Meanwhile, circularly polarised radiation was used in the experiment where scanning in all XY directions was needed. In this work, inscribed nanogratings were etched with various chemicals such as 35% Potasium Hydroxide (KOH) mixture with water, 25% Sodium Hydroxiode (NaOH) mixture with water, 48% Hydrofluoridic acid (HF) and 78% Sulphuric and 22% Phosphoric acid mixture (H_2SO_4 and H_3PO_4). Utilization of all of these etchants differs: KOH and NaOH are used at 90°C, HF is used at ambient temperature (20°C) and H_2SO_4 and H_3PO_4 is used at 270°C. Thus, 4 separate etching protocols were examined.

First of all, principal 1D experiments (single lines in XY plane) were performed to test how pulse energy, radiation wavelength (1030 nm, 515 nm, 343 nm), and the used etchants (NaOH, KOH, HF, H_2SO_4 and H_3PO_4) affects etching rate. In this experiment, pulse duration (200 fs) and pulse repetition rate (610 kHz) remain constant. The light was linearly polarised perpendicularly to the scanning direction to obtain etching rates as high as possible. This experiment gives us data about the etching rate of the modified material. The idea of this test is shown in Fig. 1 part (a). Also, during the same experiment, etching rates of unmodified material were evaluated by measuring substrate thickness before and after etching. The etching rate of unaffected material allows us to estimate selectivity in

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each case. Selectivity is defined as a ratio of modified and unmodified material etching rates. However, since the unmodified material etching rate is negligible in NaOH, KOH, and HF, it cannot be accurately evaluated. For these etching rates, the material was etched for 24 hour, and the etching material thickness was around 1 μm, which is on a scale of fidelity of the used device. Thus, we only can think about possible boundaries of selectivity of each etching protocol.

Subsequently, etching experiments of 2D structures were executed. During this experiment, cylindrical 2D structures were inscribed into a plate of sapphire. The scheme of this experiment is depicted in Fig. 1 part (b). This experiment tested etching dependency on radiation wavelengths, pulse duration (200 fs - 1 ps), and different etchants to find a protocol for 2D structure fabrication. Finally, when optimal parameters for the etching were found, modification morphology was investigated after and before the etching process. For that, 10 μm width surface modifications were inscribed and etched in various previously mentioned etchants. The scheme of this experiment is shown in Fig. 1 part (c). These morphologies give some insights into why some etchants are not suitable for sapphire 3D structures fabrication. After all, a few 2D structures out of sapphire were fabricated using the same setup and employing found fabrication protocol.

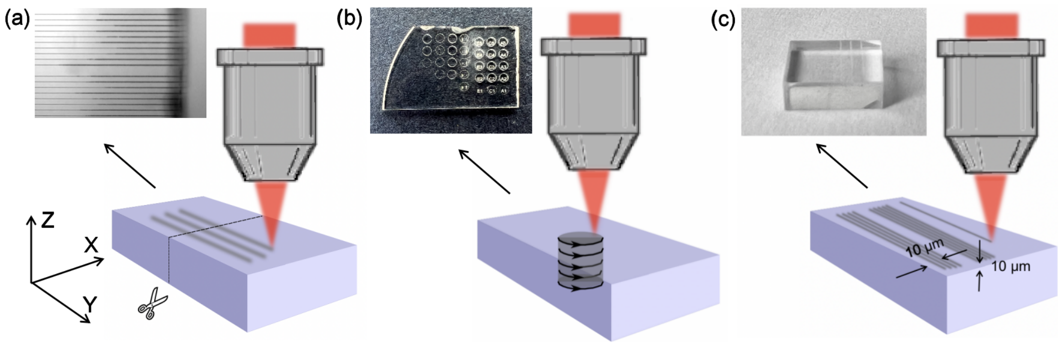

Figure 1. The schemes and the result pictures after the etching of performed experiments. (a) 1D or single lines experiment when lines by a single scanning are inscribed in the volume of material to test the etching rate of modified material. (b) Scheme of 2D experiments when cylindrical structures are written through the whole plate thickness. (c) Surface structure inscription for modification morphology observation after the etching procedure.

3. Results

The results of single line tests are discussed first. The results of this experiment are shown in Fig. 2 part (a). After a 1D investigation, we have found that the highest etching rate (200 μm/h) is obtained with H_2SO_4 and H_3PO_4 mixture when modification is inscribed with 1st harmonic radiation and the highest tested pulse energy - 500 nJ which corresponds to 28.2 J/cm^2 energy density. Meanwhile, lower etching rates up to 100 μm/h were obtained with NaOH and KOH enchant. The lowest etching rates up to 50 μm/h were demonstrated by modifications etched with HF. In all the cases, 1st harmonic radiation allowed us to obtain the highest etching rates. Only slightly lower etching rates were achieved by using 2nd harmonic radiation. Meanwhile, 3rd harmonic laser radiation inscribed modifications showed only a few μm/h etching rates. To fabricate 3D structures, the etching rate of modified versus unmodified regions also matter. To obtain a high aspect ratio of fabricated structure features high ratio between modified and unmodified material etching rate is required. Thus, the unmodified material etching rate was evaluated and subsequently, the selectivity value can be calculated. For some tested etchants, the unmodified material etching rate value was in the range of the accuracy of the used device. Therefore, only approximate selectivity values are provided. The results of unmodified material etching rate and evaluation of selectivity are shown in Fig. 2 part (b). Only H_2SO_4 and H_3PO_4 mixture showed a significant unmodified material etching rate which is around 3 μm/h.

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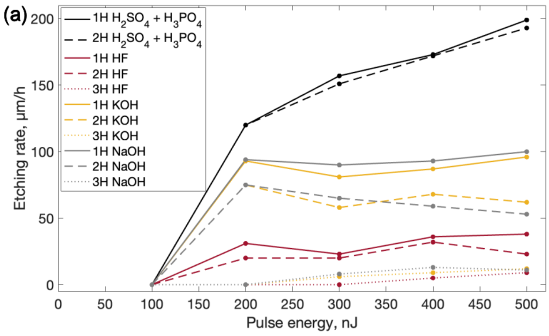
Meanwhile, unmodified material could be barely etched by using NaOH, KOH, or HF. When we try to evaluate selectivity with such a low unmodified material etching rate for NaOH, KOH, and HF, it leads to high selectivity values starting from 1000. The high etching rate of unmodified material with sulfuric and phosphoric acid leads to a low selectivity value of 66, although this etchant shows the highest etching rate of modified material.



(b)

ETCHANT	ETCHING RATE OF UNMODIFIED MATERIAL	SELECTIVITY
25% NaOH	< 0.1 μm/h	from ~1000
35% KOH	< 0.1 μm/h	from ~1000
48% HF	< 0.1 μm/h	from ~200
78% H_2SO_4 + 22% H_3PO_4	3 μm/h	max. ~66

Figure 2. (a) Graphs of etchings rates of single lines inscribed and etch by diffident processing protocols. (b) Table of the etching rate of unmodified material etch by different enchant and selectivity evaluation according to modified and unmodified material etching rate results.

In the literature many groups have shown results on sapphire etching, however, most of them struggled which at least 2D structure demonstration. Thus, after 1D tests, 2D tests were performed to find out the protocol which could allow us to get 2D structures. Identical parameters set for the 1D test were investigated, additional to that various pulse durations were tested. Cylindrical structures were inscribed into a 500 μm thickness sapphire plate by changing parameters for each cylinder. The results of this experiment can be seen in Fig. 3. The 2D experiment has shown that the best parameters which allow the most efficient etch of the structures are 1st harmonic radiation with 200 fs duration pulses and 300-500 nJ pulse energies which correspond to 16.9-28.2 J/cm^2 energy densities of one pulse. The only etchant which etched out the structures out of the plate was a H_2SO_4 and H_3PO_4 mixture. By using other tested etchants KOH, NaOH and HF cylindrical structures could not be etched out of the plate even after 48 hours of etching. This result brought the question of what is the reason why other tested etchants cannot etch out 2D structures.

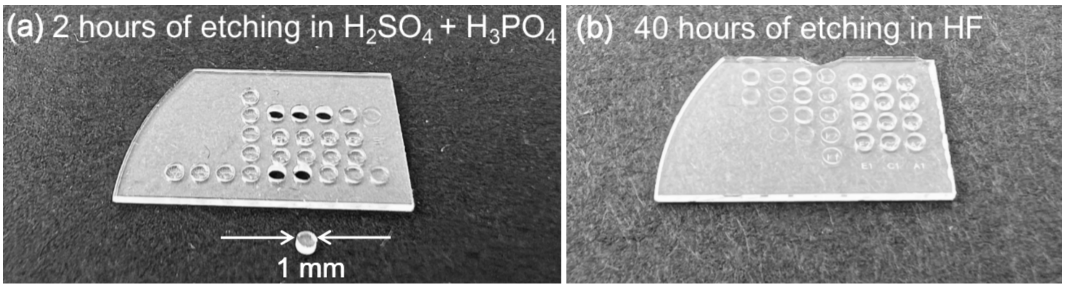


Figure 3. 2D cylindrical structures inscribed with different wavelength and pulse duration radiation. (a) Structure etched in H_2SO_4 and H_3PO_4 mixture, (b) structure etched in HF acid.

To test this phenomenon, it was decided to investigate etched and unetched surface modification and indicate its behavior before and after the etching. Surface modifications were inscribed within the previous experiment parameters determined the most efficient laser parameters (1030 nm wavelength radiation, 600 kHz pulse repetition rate, 200 fs pulse duration and 500 nJ pulse energy). Inscribed 10 μm depth and 10 μm width modification were etched in different etchants. SEM pictures of variously etched and unetched modifications are presented in Fig. 4. Moreover, the depth of the etched modifications were measured in each case. In Fig. 4 part (a) can be seen unetched modification right

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after the inscription. Before the etching, material modifications are covered by residue remaining after the modification inscription. Unetched modification already has a depth of approximately 0.5 μm. After 1 hour of etching in 35% of KOH and 25% of NaOH at 90°C and at 48% of HF all the residue are etched and nanogratings are uncovered. Pictures of nanogratings after the etching are depicted in Fig. 4 parts (b - d). Modification depth of modifications etched in KOH, NaOH and HF are 3 μm, 3 μm and 7 μm, respectively. Meanwhile, after etching modification only for 20 min in H_2SO_4 and H_3PO_4 mixture not only residue of reaction, but the nanogratings themselves are etched which can be seen in Fig. 4 part (e). The depth on etched groove is 9 μm. All these etchants react to material differently. Visually, HF etches out impurities from the surface the most efficiently, after etching in NaOH the highest amount of residue remain. In comparison with 1D results, HF tends to etch everything from the surface, NaOH and KOH tends to penetrate inside nanogratings. Nevertheless, none of these etchants does etch nanogratings itself. Thus, this is the reason why these etchants cannot etch out 2D structures. On the other hand, H_2SO_4 and H_3PO_4 could etch all crystalline material and nanogratings themselves.

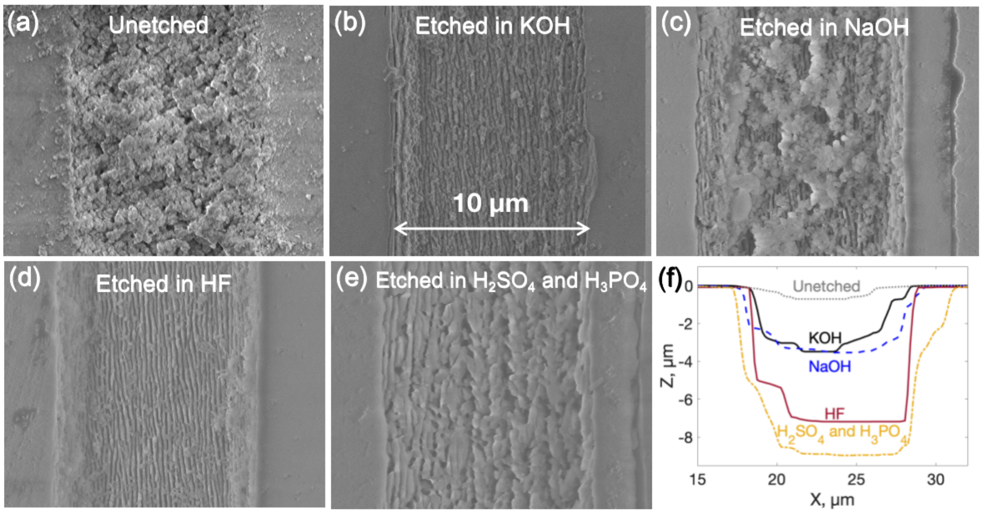

Figure 4. SEM pictures of laser inscribed surface morphologies and measured profiles of the processed material. (a) Unetched surface modification, (b) surface modification etched in 35% KOH solution for 1 hour, (c) surface modification etched in 25% NaOH solution for 1 hour, (d) surface modification etched in 48% HF for 1 hour, and (e) surface modification etched in H_2SO_4 and H_3PO_4 for 20 min. (f) Optical profilometer measured processed profiles of all presented modifications.

After all the previous insights were made, the best protocol was used for structure fabrication out of crystalline sapphire. A few basic 2D structures were fabricated for demonstration. These structures were fabricated out of 0.5 mm C-cut sapphire plate using H_2SO_4 and H_2PO_3 mixtures as an enchant. The first demonstrational structure is a hole array. In one case, wide channels of 100 μm diameter through the hole height of the plate with the pitch of 1 mm have been produced Fig. 5 part (a) and (b). Also, a narrow single Z scanning line channels fabrication with a pitch of 10 μm were demonstrated in Fig. 5 part (c) and (d). In Fig. 5 can be seen that after the etching, the etched walls are not perfectly sharp. The edges of the structure have non-inscribed planes cut and it forms after the etching due to the sapphire crystalline lattice. This is caused by the high etching rate of unmodified crystalline material. Subsequently, the honeycomb structure out of sapphire was produced. Structure with 400 μm wall of hexagon and 200 μm wall thickness between hexagons is shown in Fig. 5 parts (e-g). The surface roughness of etched walls is approximately 300 nm RMS. This value is comparable with ones shown in fused silica SLE-made surfaces [36]. The lowest demonstrated etched fused silica surface roughness is approximately 300 nm RMS. Surface roughness is mostly determined by the morphology of induced nanaogratings and how effectively material between nanograting could be

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etched. Since fused silica is less chemical inertial material than sapphire, the expected etched sapphire structure roughness should be higher than for the same surfaces made in fused silica. To show the versatility of this technology, similar honeycomb designs with 100 μm and 50 μm wall thickness were also made (Fig. 5 part (h) and (i)). Thinner walls than 50 μm were very fragile and did not survive the etching procedure. The same tendency of repeating sapphire crystalline structure can be seen in honeycomb structures. The edges of etched structures are not very sharp and are rather inclined according to a sapphire crystalline lattice. Nonetheless, these structures show the possibility of producing 3D structures out of crystalline sapphire.

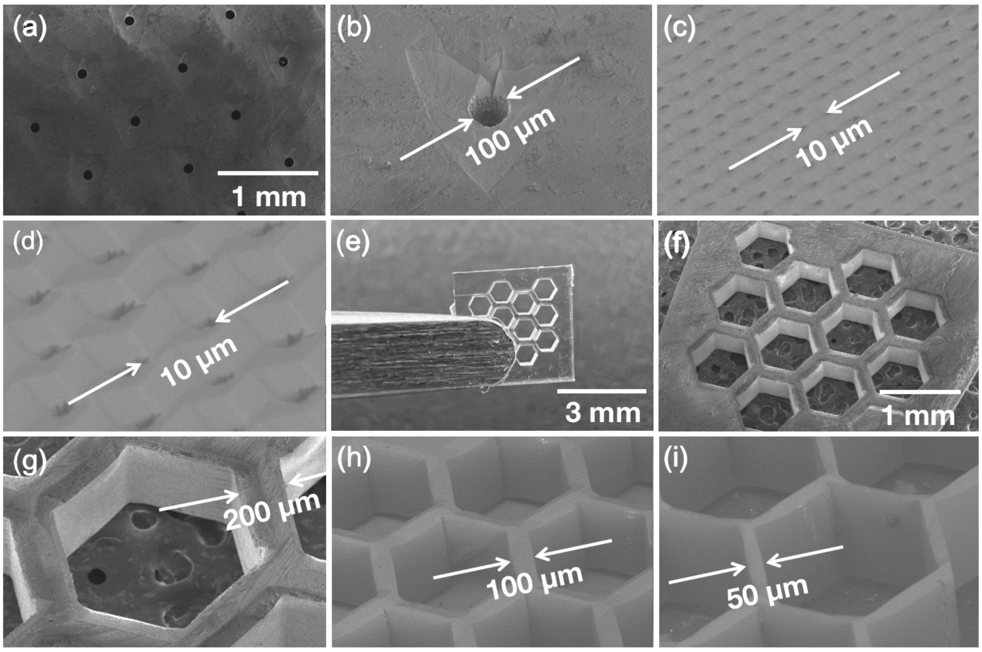

Figure 5. Structures fabricated out of crystalline c-cut sapphire. (a-b) 100μm diameter hole matrix, (c-d) single line 10 μm pitch hole matrix, (e-g) honeycomb structure where the side of the hexagon is 400 μm, and the walls between hexagon are 200 μm, (h-i) similar hexagon structure with diminished walls between hexagon respectively 100 μm and 50 μm.

4. Discussion

In SLE, we always desire to have high selectivity and a high etching rate. High selectivity values are needed to maintain good accuracy and a high aspect ratio of etched features. On the other hand, a high etching rate is required for fast processes. The main problem is that usually, these two are achieved with different etching protocols. It means that at the same time, we cannot get both, but in one structure, it is possible to combine both etching protocols. For fused silica, this was already demonstrated [37] when structures parts that do not require precision are tech with HF and precise features are etched with KOH solutions which give the highest selectivity. The same could be done with the etching of sapphire by combining KOH, NaOH, or HF etching with a sulphuric and phosphoric acid mixture. In that way, etching time with H_2SO_4 and H_2PO_3 can be minimized, and, as a result, higher accuracy could be obtained.

5. Conclusions

In this work, we have presented the comparison between different sapphire SLE processing algorithms. During previously shown tests, various laser parameters for modification inscription were tested. The best results were obtained with 1030 nm wavelength 200 fs pulse duration radiation. Moreover, four different etchants: HF, NaOH, KOH, and

H_2SO_4 with H_3PO_4, were tested. The only etchant which allows the total removal of laser-modified sapphire is a H_2SO_4 with H_3PO_4 mixture. While other tested etchants only etch material in between laser-formed nanogratings. After a moderate protocol was found a few structures: hole matrix and honeycomb structure, were fabricated out of c-cut crystalline sapphire. After fabricating these structures, we noticed that sapphire repeats its crystalline lattice during the etching. This property leads to less accurate features of the fabricated object and self-organized patterns on the structure surface. However, this effect could be diminished by combining two different etching steps for the same structure. Thus, in this work, we have demonstrated a protocol that allows 3D structure formation out of crystalline sapphire. However, additional improvements to the protocol could be made to refine the quality of produced structures. These results will contribute to the rapid SLE fabrication of future devices.

Author Contributions: A. Butkute planned and led the research, fabricated demonstration structures, did part of the measurements, and prepared publication and figures. R. Sirutkaitis performed etching procedures. R. Sirutkaitis, D. Gailevičius, D. Paipulas and V. Sirutkaitis consulted and contributed in publication preparation.

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