Examination of Etching Agent and Etching Mechanism on Femtosecond Laser Microfabrication of Channels Inside Vitreous Silica Substrates†

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We examined the physical chemistry underlying a wet chemical etching-assisted femtosecond laser microfabrication technique. Close scrutiny of etching reagents and the etching process has led to further refinement of the method for practical use such as microchips for chemical total analysis systems (μ-TAS). Microchannels as long as a centimeter scale with less than 60 μm diameter (aspect ratio of ~200) were fabricated inside vitreous silica substrates. In this regard, we demonstrated that a concentrated aqueous solution of KOH is advantageous over commonly used aqueous HF because of least saturation behavior in elongating channel structures. Resultant nearly twice as large the etching selectivity of KOH as that of HF allowed substantial penetration depths within the laser-modified volume while leaving the unmodified regions practically intact. Furthermore, the mechanism of laser-modification that permits highly selective wet etching was investigated by photoluminescence and confocal Raman spectral measurements of the irradiated microvolumes. Based on the experimental results, we propose that the formation of a Si-rich structure is responsible for the remarkably enhanced etching rate of aqueous KOH, in addition to the densification of the silica structure previously advocated for the mechanism of waveguide formation.

Introduction

Photomodification by a controlled irradiation of focused femtosecond (fs) laser beams has been used to change material properties or to remove materials. While being useful for fabricating waveguides1,2 and related optical devices, the technique has found applicability, in particular, to the three-dimensional (3D) micromachining or microstructuring inside transparent solid materials.3,4 The structuring procedure normally involves succeeding chemical etching that ensures the fabrication of channels, void spaces, and optical/micromechanical elements.5 The fs laser method is much more versatile and controllable compared with the conventional laser ablation technique employing nanosecond UV lasers because the former can prepare a 3D object with various shapes as well as nontapered straight, bent, and even spiral channels with high aspect ratios. In contrast, the latter, the ablation technique, is only applicable to the formation of grooves on the material surface or straight and conically shaped one-dimensional channels inside the materials but only along the laser-beam direction.

An excellent nature of the fs laser relies on the fact that an intense laser beam tightly focused into a confined small area induces multiphoton absorption within a nonabsorbing material leading to material alteration due to an extremely high photon density. Because of physical and chemical modification associated with the multiphoton absorption, the irradiated areas acquire an increased solubility to acids such as aqueous hydrofluoric acid (HF). As a result, a fabrication of 3D microchannels has been realized for sapphire,6 crystalline quartz,7 vitreous silica,8,9 and borosilicate glasses10,11 in addition to photosensitive or photostructurable glasses.12,13 The structured transparent materials thus prepared can find useful applications such as micro total analysis systems (μ-TAS)14 and micro-optical elements15,16 because of high optical quality and high thermal, mechanical, and chemical durability.

In the method most implemented, a preparation of 3D structures consists of two steps: first, a photomodification was executed by irradiating a train of pulses of a focused fs laser beam into the transparent materials placed on a piezoelectric or motorized stage; second, the irradiated materials were immersed in etching solutions for a specified period of time. The method, however, suffers from a few drawbacks. For instance, the selectivity of etching rates by the commonly used aqueous HF for laser-modified region against unmodified material is practically not remarkable, given the fact that the unmodified area is soluble in HF solution as well. Besides this, unusual etching behavior was observed for sapphire: once the laser-irradiated part of the sapphire gave an excellent solubility to HF with a high selectivity of >10^4 but the etching selectivity decreased largely on additional irradiations.5 These findings suggest that it is a challenging task to fabricate, especially, long channels exceeding a millimeter scale, still maintaining high aspect (length vs diameter) ratios. Despite the enormous popularity of HF for etching glasses and removing oxides from the silicon surface in industry, exposure to the highly toxic and corrosive reagent is extremely harmful to human body. In this regard, a search for less harmful and environmentally benign etching reagents is a task of urgent need. Furthermore, the mechanism of enhanced solubility to the etching reagent still remains unexplored for silica and other glasses despite the fact that fs laser-induced amorphization is primarily responsible for etching susceptibility acquired by irradiated crystalline materials such as sapphire and quartz.6,7 With these points in mind, we initiated a study on further refinement of the method.

During the course of our investigation along this line, we found that a concentrated aqueous solution of KOH is as good

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an etching reagent as aqueous HF for fs laser-modified vitreous quartz, borosilicate, and Pyrex glasses. Later, the KOH etching technique was applied to sapphire by Juodokazis and co-workers. Presently, we conducted experimental studies to access the capability of KOH as to whether it can fulfill the requirement of a desirable etchant with less toxic and better controllable nature. At the same time, we examined the physical chemistry underlying the fs laser-induced modification that facilitates the dissolution of silica materials because of the lack of such information. We made important progress in both understanding the mechanic aspect of laser-induced structural modification leading to increased solubilization and improving the technique to fabricate sufficiently long microchannels for practical applications.

Experimental Section

A regeneratively amplified output (Spectra Physics, Spitfire) from a Ti:sapphire mode-locked laser (Spectra Physics, Tsunami) was used for the irradiation (pulse width: 150 fs; central wavelength: 800 nm) of synthetic quartz glass substrates (Shin-Etsu Chemical, VIOSIL; density: 2.20 g/cm³), mounted on a computer-controlled piezoelectric transducer stage (Physik Instrumente, P-563–3CD) or motorized stage (Suruga Seiki, KS701–20LHD). The specimens were irradiated by a laser beam of various pulse energies tightly focused at 10−30 μm inside the substrate through a microscope objective (Olympus, UPlanApo, 100× Oil (NA: 1.35) or 40× (NA: 0.65)). The laser-modification was carried out by translating successively the specimen perpendicularly to the laser beam direction (transverse writing geometry). Here the spot-to-spot irradiation distance was set to 0.1 μm by adjusting the speed of the stage and the repetition rate of the laser shots (20−1 kHz). The threshold fluence for the photomodification estimated by the observation of optical microscopy images was 200 nJ/pulse for the 40× objective and 40−50 nJ for the 100× objective. For the wet etching, the substrate was submerged in a 2.0% aqueous HF solution at ambient temperature or 10 M aqueous KOH from a Ti:sapphire mode-locked laser (Spectra Physics, Tsunami) was employed for excitation based Raman spectroscopic measurements were performed on HF solution at ambient temperature or 10 M aqueous KOH. The wet etching, the substrate was submerged in a 2.0% aqueous HF solution, for 60 h in KOH at 80 °C, following the irradiation of femtosecond pulse trains (interval: 0.1 μm) through a 40 × objective lens (NA: 0.65), 10 μm below the surface at different laser powers, (a) 500, (b) 400, (c) 300, (d) 200, and (e) 100 nJ/pulse. The threshold fluence for the photomodification estimated by the observation of optical microscopy images was 200 nJ/pulse for the 40× objective. For the wet etching, the substrate was submerged in a 2.0% aqueous HF solution at ambient temperature or 10 M aqueous KOH solution (35.8%) at 80 °C. The structured specimen was inspected by an optical microscope (Olympus, IX 71) and a field emission scanning electron microscope, FE-SEM (Hitachi, S4700). In situ observation for the progress of etching was made by a CMOS camera (Trinity, IUC-200CN2) attached to a zoom lens (Chuo Precision, TV-Z-H, 1.8−14.4×). Confocal microscope-based Raman spectroscopic measurements were performed on a Nanofinder 30 spectrometer (Tokyo Instruments) in which a 488 nm light from a DPSS laser was employed for excitation through an objective (100×, NA=0.90). Raman signals were detected by a CCD (Andor, DV-420A) coupled with a 30 cm focal-length monochromator with a grating of 1800 grooves/mm through a pinhole of 50 μm diameter (an estimated diameter of airy disk: 0.6 μm). Photoluminescence spectra were acquired by a CCD spectrophotometer (a combination of Princeton, ITEA/CCD-576SBEM and Acton, SP 275) attached to a microscope (Olympus, IX 71) by exciting at 325 nm with a He–Cd laser (Kinmon, IK3551R-D).

Results and Discussion

1. Effect of Etching Agent: Aqueous HF vs Aqueous KOH. Figure 1 compares ex situ etching profiles in aqueous KOH with those in aqueous HF observed by optical microscope images of channels formed in vitreous silica substrates exposed to a fs laser irradiation. The most striking observation is a facile formation of nearly 1 cm-long channels (aspect ratio: ~200) penetrating completely through the substrate from one side to the other (Figure 1b,c). In contrast, attempts to fabricate such long channels through etching in aqueous HF fell short of our expectation (see Figure 1f–h). Fabrication of long channels is advantageous for microchip technology in which cm scale substrates structured extensively with microfluidic channels constitute an essential component. Such fabrication by the application of fs laser microfabrication technique has been difficult due mainly to the limitation of the etchant. For instance, at most a 1.8 mm long channel with an entrance diameter of 85 μm (aspect ratio: 21) has been realized inside a fused silica substrate in 20% aqueous HF placed in an ultrasonic bath. A difficulty in the channel fabrication by using the HF etching technique is exemplified by the fact that simply increasing etching periods provided no remedy. This situation was clearly
The selectivity is defined by the etching rate of photomodified material vs that of unmodified material. The photomodification estimated by the observation of optical microscopy exhibited by the time-dependent development of channel formation given in Figure 2 in which the progress of channel depth tends to saturate at longer etching periods. On the other hand, the channel width steadily increased even beyond the photomodified zone. This terminates with a formation of noticeably cone-shaped channels.

Previously, HF has been used as a standard reagent to remove SiO₂[20] but the alkali etching of silicon dioxide is also known. The rate of KOH etching has been reported to be considerably smaller than that of HF at ambient temperature but this increased appreciably with increasing temperature.[21] Presently, we measured the etching rates dependent on the polarization of the etching reagents as shown in Figure 4. Inspection of Figure 4 reveals that the progress of channel elongation is remarkable in KOH showing little sign of declining trend in curvature (panels a and b), which is consistent with the observation of long channel formation in Figure 1. Contrastingly, the saturation was observed for the etching in HF in the in situ measurement (Figure 4, panels c and d) as well as the ex situ measurement (Figure 2). This behavior was more pronounced by lowering the concentration of HF as depicted in Figure 4d. The lowering of the concentration of HF significantly suppressed unfavorable expansion of channel diameter: the aspect ratio of 50 in 0.5% HF was certainly improved compared with that of 30 in 2.0% HF at the expense of etching rate. The saturation of the etching rate in forming microchannels in laser-modified area seems to be a universal phenomenon in HF etching but so far rarely mentioned. Hnatovsky’s group described that the ability to react with the modified material is determined by the acid concentration and it may depend on the transport properties of the microchannel.[10] According to their explanation, the amount of fresh acid able to reach the channel end reduces and the etch rate gradually decreases as the channel length increases, leading to the production of microchannels with low aspect ratios. This was what was observed in the HF etching but not observed in the KOH etching.

In order to investigate in further detail the etching behavior, we measured the etching rates dependent on the polarization of the incident laser beam. A previous study by Hnatovsky’s group revealed that the etching rate of a fs laser-exposed silica glass by HF is strongly dependent on the polarization of the laser light, especially at the low laser fluence region.[10] For instance, an exposure to a linearly polarized light with its electric vector perpendicular to the scanning direction of irradiating laser (transverse writing) gives etching rates greater than those of.
the area exposed to a light polarized in the scanning direction (longitudinal writing). This result was correlated with the observation of nanograting (low laser power) or nanocracks (at extremely high laser power) appearing in the direction perpendicular to the polarization of the incident laser light when the irradiated parts were inspected after etching by HF. They concluded that well-interconnected nanogratings/nanocracks running in the direction of a laser trace are more favorable for the channel formation. Figure 4 also gives the polarization dependence of the channel propagation for the etching by both KOH and HF. The close scrutiny of the polarization dependence in Figure 4 reveals that the etching rate by KOH was indeed affected by the polarization of the irradiating laser at laser powers of both 70 and 100 nJ/pulse. A larger difference in the polarization-dependent etching rates was observed at the lower fluence, which is still above the modification threshold of 40–50 nJ/pulse. By contrast, the polarization dependent difference in etching rate was only observed at 70 nJ/pulse but not at 100 nJ/pulse for etching by HF. Our result of HF etching is in line with the results by Hnatovsky’s group because they observed that the difference in the polarization-dependent etching rate is greater at low laser powers but makes little difference at high laser powers. This concept is better fitted to a mild etchant, KOH, than a strong etchant, HF, and therefore, we observed differing etching rates dependent on the polarization in KOH even at high laser powers.

The present achievement of centimeter-long microchannels by the application of KOH etching technique relies upon two key factors. In the first place, we employed a sufficiently high concentration that retards the depletion of the number of OH− ions due to the consumption by the chemical reaction at the etching front. Second, etching at high temperature facilitated the diffusion of solutes, both etchant, OH−, and the product, Si(OH)4, despite the fact that the precipitates were formed at a considerably high laser power because of highly efficient etching of severely photomodified regions. In this regards, application of an optimum laser power is preferred for preparing long channels without suffering from the precipitate formation. Additionally, during the etching at 80 °C, we noted the generation of bubbles, presumably hydrogen gas (see below for reasoning) from the very end of the channels, moving through the channels and then going out of the channel entrance as typically shown in Figure 5. Such movement of the bubbles

Figure 4. In situ observation of channel formation inside a vitreous silica substrate irradiated through a 100× objective lens (NA: 1.35), (a) channel length vs time; laser power: 70 nJ/pulse; etching: 10 M aqueous KOH (20 mL) at 80 °C; (b) channel length vs time; laser power: 100 nJ/pulse; etching: 10 M aqueous KOH (20 mL) at 80 °C; (c) channel length vs time; laser power: 70 nJ/pulse; etching: 2.0% aqueous HF (20 mL) at ambient temperature; (d) channel length vs time; laser power: 100 nJ/pulse; etching: aqueous HF (20 mL) at ambient temperature. Keys (i) to (iii) represent the polarization of laser beam with respect to the scanning direction; (i) perpendicular, (ii) circular, and (iii) parallel and keys (p) and (q) represents the concentration of HF: (p) 2.0% and (q) 0.5%. Each data point represents an average value for the measurement of three channels. Note that no difference was discernible for the polarization direction of laser beam for etching by HF at a laser power of 100 nJ/pulse.
the laser irradiation in our experimental condition actually brings about increased population of 3-membered ring structures in the irradiated parts resulting in more dense and unstable structures. However, our Raman spectroscopic measurement failed to detect the different extent of modification dependent on the polarization of writing laser (see the Supporting Information, Figure S1b). Note also that Bellouard and co-workers observed the opposite correlation of the D2 intensity vs the modification expected from the polarization-dependency; the longitudinal writing gave a bigger intensity than that of transverse writing. These results suggest that the D2 intensity still comes short of our need for a qualitative measure of the laser modification.

Previous Raman spectral investigations of fs laser irradiated areas were not linked to the etching study. Regarding the HF etching rate of silica glass, Tomozawa and co-workers revealed that a greater rate is associated with the increased fictive temperature, Tf, of the glass, and hence, with the greater density. Therefore, it is reasonable to assume that the densification of silica acquired by fs laser irradiation is mainly responsible for a greater susceptibility to the HF etching. However, the exact mechanism at the molecular level and, in particular, the rate determining step is not completely understood. The dissolution of silica takes place through a chemical process in which water molecule interacts with the surface to cleave the Si–O–Si linkages, resulting in hydrolyzed products. This reaction is pH dependent and, especially, OH− is known to attack Si–O–Si⇔ groups, cleaving this bond to give Si–OH and Si–O−. Silica is also known to be severely attacked by aqueous HF according the reaction scheme

\[
\text{Si–O–Si} + H^+ F^- \rightarrow \text{Si–OH} + \text{SiF}^\cdot
\]

Here, the occurrence of the nucleophilic attack by F− on the silicon atom simultaneously with the electrophilic attack by proton on oxygen atom is assumed to cause highly effective disruption of O–Si bond. Thus, the enhanced dissolution of photomodified area is ascribed to the formation of strained Si–O–Si bond represented by the planar three-membered ring structures which can be more vulnerable to the attack by HF than the stable six-membered ring structure. However, molecular orbital and/or molecular dynamics calculations are absolutely necessary to fully account for this ring structure-dependent reactivity of Si–O–Si linkages. Such aspect is beyond the scope of the present experimental study and will be conducted as a subsequent project. Additionally, Bellouard and co-workers pointed out that mere consideration of the densification of silica structure cannot explain the increased etching rate dependent on the polarization state of the laser beam.

We observed a markedly increased reactivity of the photomodified area toward aqueous KOH as well as HF. The question is whether the etching mechanism is essentially the same as that of the unmodified area and only the etching rate differs or a completely different mechanism operates to the etching of laser exposed area for KOH. Obviously, the important step in intact silica is the cleavage of the Si–O–Si bond by the attack of OH− or F−. Therefore, one possibility is that the densified area acquires a greater reactivity equal to both etchants leading to a facile Si–O–Si cleavage because of the severely modified ring structures. The other possibility we should point out is the fs laser-induced material modification of SiO2, namely the formation of SiOx (x < 2), which may increase the reactivity of the irradiated area, in particular, toward OH−. Previous studies by Murakami and co-workers, along with Miura and co-workers pointed out that Si-rich structures or Si–Si bonds are
formed in fs laser irradiated silica and silicate glasses. Miura and co-workers suggested that localized high temperature, high pressure, and the generation of shock waves, which are processes generally taking place in the fs laser irradiated materials, are important in forming Si-rich structures. It was revealed that the laser irradiation of vitreous silica allows the generation of a positively charged defect known as the E’ center (≡Si’') which decays with time to give the oxygen-deficiency center (ODC: O2≡Si−Si≡O1 or O2≡Si’) by capturing electrons. This means that the transformation of SiO2 to a Si-rich structure can also be the origin of increased refractive index of the irradiated area in addition to the densification stated above. The implication of Si−Si bond formation is significant because this bond is quite easily attacked by OH− given that KOH is a popular etching agent for silicon. Such possibility of the laser-induced material modification is likely in our present system based upon two observations.

First, we observed a photoluminescence spectrum with peaks at 550 nm (2.2 eV) and at 650 nm (1.9 eV) from the fs laser exposed area when excited at 325 nm (Supporting Information, Figure S2). Previously, a similar spectrum has been reported for γ ray35 and 355 nm nanosecond pulsed laser-irradiated amorphous silica36 as well as the fs laser-irradiated material.37 Most importantly, the assignment of the 550 nm band has been made to small Si clusters formed in the amorphous silica while that of 650 nm band was made to the nonbridging oxygen hole center (NBOHC: ≡Si−O−) because of their peak positions.35,36

Second, we observed the generation of bubbles at the etching front during the in situ etching experiment (Figure 5). Although it is difficult to identify the exact nature of the bubbles because of too small quantity to assay, we tentatively identify this as a hydrogen gas (H2) based upon circumstantial evidence. Dissolution of silicon in aqueous KOH is known to proceed through the following reaction scheme:

\[
\text{Si} + 4\text{OH}^- \rightarrow \text{Si(OH)}_4 + 4e^- \\
4e^- + 4\text{H}_2\text{O} \rightarrow \text{OH}^- + 2\text{H}_2
\]

giving rise to hydrogen. Although our in situ etching experiment was carried out at 80 °C, we are quite sure that the bubbles produced at the etching front cannot be a water vapor or air dissolved in water. We removed the air from etching solutions by heating a sufficient period of time before starting the experiment. Evolution of air dissolved in the silica glass as bubbles is unlikely because we saw no bubbles when the etching was carried out in HF. The formation of oxygen (O2) is theoretically possible as a counterpart of SiO2; however, the observation of gaseous oxygen is least-likely because of its high solubility in water. Under the circumstances, the material modification of SiO2 to Si-rich structures can constitute a good reason for hydrogen evolution on etching by KOH and the type of modification must be responsible for the enhanced etching rate. Nevertheless, our result is still qualitative and further experimental study is necessary to substantiate the presence of Si-rich structures or Si clusters in laser-irradiated area. Besides, unambiguous identification of the bubbles generated during the etching is needed. Such experiments are now underway and will be reported soon.

In contrast to the picture based upon the structural and material modification due to the laser irradiation, the etching mechanism proposed by Hnatovsky and co-workers was based on the mechanical damage:10 dissolution of modified silica takes place due to the formation of laser-induced nanocapillaries which allow the etchant to penetrate into the glass to form microchannels. The etching mechanism based upon laser-induced mechanical damage is straightforward but Bellouard and co-workers argued against this view. They pointed out that the increased etching rates are observable at the lowest fluence where cracks are not found and that nanocracks by themselves do not explain the increase of refractive index. According to the traditional view, a large structural modification of materials is essential to achieve high etching susceptibility as well as large refractive index change. For instance, crystalline materials such as sapphire and quartz undergo amorphization upon exposure to the fs laser light and this phase transformation is largely responsible for the markedly increased etching rate observed for the irradiated material.6,7 Besides this, crystallization of medium surrounding Ag nanoparticles due to heat treatments after exposure to the light has been known to allow 20–50 times enhanced solubility in HF observed for photosensitive glasses.38 We should emphasize that the large chemical modification represented by the Si cluster formation and related phenomena is important especially for the mild etchant, KOH to attain facile etching. At the same time, we need to assess the changes taking place in the modified area properly and quantitatively. At this moment, spectroscopic parameters obtained by applying Raman and photoluminescence measurements are promising but we need to further sophisticate these parameters to make more convincing explanations for the extent of photomodification.

**Summary**

We made a significant improvement in implementing femtosecond laser microfabrication techniques to a transparent inorganic material, vitreous silica. Close scrutiny of etching reagents and the etching process was an important step toward further refinement of the method. We demonstrated that concentrated aqueous solution of KOH is advantageous over commonly used aqueous HF because of its low saturation behavior in elongating channel structures. As a result, we fabricated microchannels as long as nearly 1 cm with less than 60 μm diameter (aspect ratio of ~200) inside the silica substrates. Such a technique should be extremely useful for practical applications such as microchips for chemical total analysis systems (μ-TAS).

At the same time, we investigated the mechanism of laser-modification that permits the highly selective wet chemical etching, in particular, by KOH. We proposed that the formation of Si-rich structure is responsible for the remarkably enhanced etching rate of aqueous KOH, in addition to the densification of silica structure previously advocated for the mechanism of waveguide formation.

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**Supporting Information Available:** Femtosecond laser-induced evolution of Raman spectra in vitreous silica and photoluminescence spectra of fs laser-irradiated and pristine regions in vitreous silica. This material is available free of charge via the Internet at http://pubs.acs.org.

**References and Notes**
