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Surface micro-fabrication of silica glass by excimer laser irradiation of organic solvent

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Abstract

Laser-induced backside wet etching (LIBWE) of silica glass plates was performed by the excitation of a pure toluene solution with an ns-pulsed KrF excimer laser at 248 nm. Well-defined grid micro-pattern was fabricated without debris and micro-crack around the etched area. The etch rate, which increased linearly with laser fluence, was 30% higher than that in the case of acetone solution of pyrene dye at a concentration of 0.4 mol dm^{-3}. To understand the etching mechanism, the formation and propagation of shock wave and bubble were monitored by time-resolved optical microscopy at the interface between the silica glass and the toluene solution during etching process. Transient high pressure as well as high temperature generated by UV laser irradiation plays a key role in the etching process.

Keywords: Silica glass; Ablation; ns-Pulsed UV laser; Toluene; Shock wave

1. Introduction

Surface micro-fabrication of silica glass is an important technique in application into optics and optoelectronics because silica glass shows outstanding properties, such as transparence in a wide wavelength range, strong damage resistance for laser irradiation, and high thermal and chemical stability. However, these properties make it difficult to fabricate micron-sized structures on the surface of silica glass. In the search for a simple and effective method on laser-induced material processing [1], there are several approaches to the use of pulsed lasers from the viewpoint of conventional laser ablation [2], vacuum UV laser processing [3,4], plasma-assisted UV ablation [5,6], and femtosecond laser micro-machining [2,7].

Recently, we have developed a one-step method to micro-fabricate a silica glass plate which we called *laser-induced backside wet etching* (LIBWE) upon irradiation with an ns-pulsed UV excimer laser [8–14]. Our idea of LIBWE is based on the deposition of laser energy on the surface of silica glass during the ablation of a dye solution. Fig. 1 shows the experimental setup for LIBWE method. As the UV absorption of silica glass was negligible, an incident laser beam penetrated through the glass plate, resulting in dye molecules in the solution were excited upon the laser irradiation. When the dye solution was ablated upon the laser irradiation with a sufficient fluence, the etching on a surface layer of the silica glass was achieved. The etch depth increased linearly with the number of laser shots. The etch rate of the material was typically 0.1–25 nm $pulse^{-1}$, which was dependent on irradiation conditions such as laser wavelength, laser fluence, and dye concentration. We have succeeded in the micro-fabrication of such transparent materials as silica glass [8–14], quartz [9], calcium fluoride [11], and fluorocarbon resin [10]. The advantages of our LIBWE method are as follows: (i) micro-fabrication without debris and cracks formation at an atmospheric pressure; (ii) simplification of pre-/post-treatment for a target substrate; (iii) large area irradiation with a conventional ns-excimer laser through a mask projection. In addition, we are able to select a dye solution from various liquids of pyrene/acetone [8,9,11,12], pyrene/THF [10], pyranine/water [13], naphthalenesulfonic acid/water [14] upon the irradiation with KrF and XeCl excimer lasers.

In this paper, we have investigated an extension of liquid media to include an organic solution without dye molecules. Commercialized high-purity toluene, which was simple and inexpensive, was used for this purpose. As toluene is a popular compound in both scientific research and practical use,

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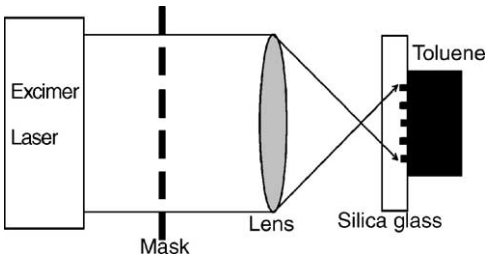

Fig. 1. Schematic diagram of the experimental setup for LIBWE method.

a large number of optical and thermal parameters have been reported. These fundamental data were so helpful that we could understand the etching mechanism of LIBWE method. In addition, we intended to analyze laser-induced transient phenomena at the interface between silica glass and toluene solution by time-resolved optical microscopy. The formation and propagation of shock waves and bubbles were monitored by this technique during a LIBWE process.

2. Experimental

A fused-silica glass plate (Tosoh SGM, ES grade) with a thickness of about 2 mm and a diameter of 20 mm was used as a sample. A KrF laser (Lambda Physik, EMG201MSC, $\lambda = 248$ nm, FWHM 30 ns) was used as a light source. The repetition rate of laser irradiation was set at 5 Hz. A square mask of 2.9 mm × 2.3 mm was used to investigate the etch rate. Depth profiles were recorded with a Stylus instrument (Talystep, Taylor-Hobson). A copper grid with an array of 46 μm × 46 μm holes was used to etch a grid pattern.

An organic solvent, toluene (Wako Pure Chemical Industries, S grade), was used without further purification. The penetration depth (d) of pure toluene at the wavelength of 248 nm was estimated to be $d = 8.9$ μm on the basis of single photon absorption ($d = M_w/\varepsilon\rho$; $M_w = 92\,\mathrm{g\,mol^{-1}}$, $\rho = 0.86\,\mathrm{kg\,dm^{-3}}$, $\varepsilon = 120\,\mathrm{mol^{-1}\,dm^3\,cm^{-1}}$ (hexane solution) [15]). When the laser beam was incident into the solution at 0.19 and 1.6 J cm^{-2}, the ratio between the number of incident photons (I) and the number of toluene molecules (N) in the unit volume for the penetration depth was calculated to be $I/N = 0.05$ and 0.4, respectively.

The transient optical images of toluene ablation were monitored by time-resolved back-illumination technique [16]. The solution in a quartz cubic cell was irradiated with a KrF laser through a pinhole and the irradiated diameter was 170 μm. A dye solution (Rhodamine B in ethanol) pumped with a XeCl laser provided a peak emission at 560 nm with the duration of 25 ns, which was used for back illumination. The delay time between the KrF laser and the XeCl laser was regulated with a digital delay and pulse generator (Stanford Research Systems, DG535). By changing the delay time, the time-resolved images of the ablation process were taken with a conventional CCD camera (Nikon, Coolpix 990) and a microscope (Olympus, SZ6045TR).

3. Results and discussion

3.1. Micro-fabrication of silica glass

Fig. 2 shows that well-defined patterns free of debris and micro-cracks were fabricated by 300 pulses of KrF laser irradiation at 0.72 J cm^{-2}. Under this condition, the etch rate is around 15 nm pulse^{-1}. The relationship between the etch depth and the number of laser pulses indicates a linear function within the investigated range, as shown in Fig. 3. The slopes of the straight lines in Fig. 3 correspond to etch rates at each of the given laser fluences. As the etch rate increased linearly with laser fluence, the threshold fluence for toluene was extrapolated to be 0.19 J cm^{-2} (Fig. 4). This excellent linearity affords the potential to be used for fine etch depth control in applications, such as the fabrication of three-dimensional structures, currently done using a contour or gray scale mask [17,18].

The etch rate in the case of toluene solution was about 30% higher than that obtained in acetone solution of pyrene dye at concentration of 0.4 M, while the absorption coefficient of pure toluene ($\alpha = d^{-1} = 0.11\,\mu\mathrm{m^{-1}}$) is about

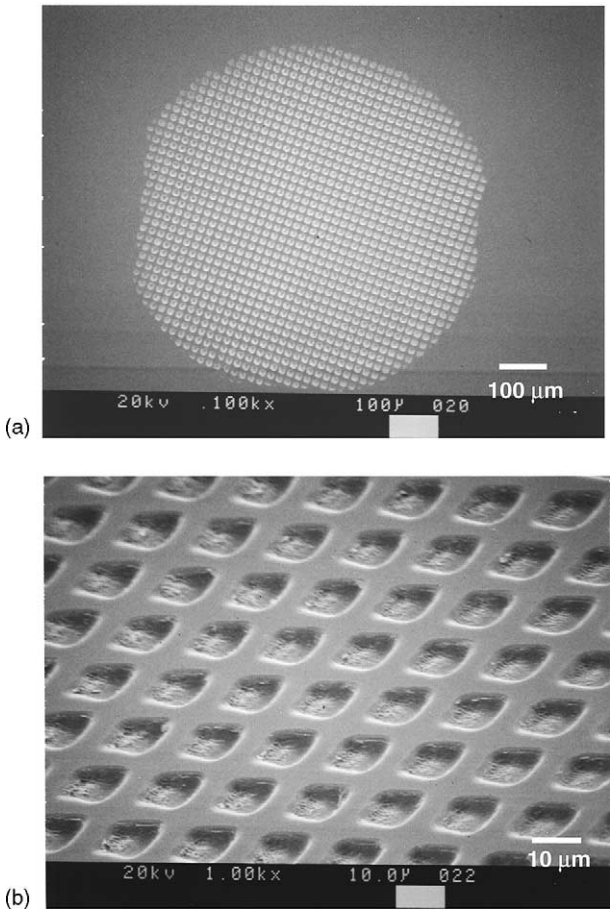

Fig. 2. Scanning electron micrographs of a grid pattern on silica glass surface. The sample was fabricated by 300 pulses of irradiation from a KrF laser at a fluence of 0.72 J cm^{-2} and the etching medium was a pure toluene liquid.

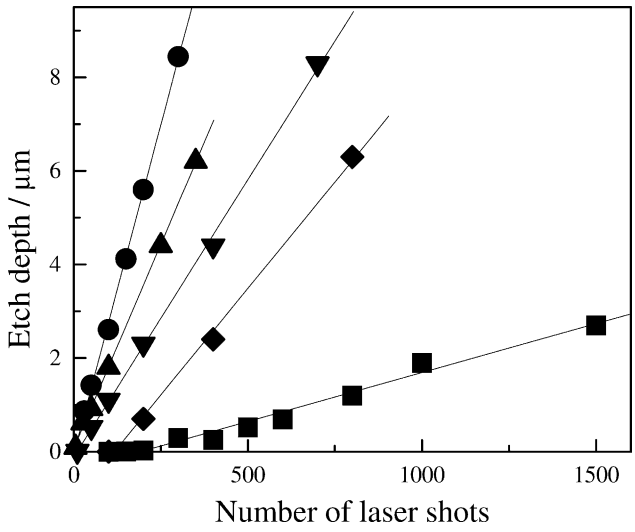

Fig. 3. Etch depth on silica glass surface vs. number of KrF laser pulses at various fluences: (●) 1.14 J cm^{-2}; (▲) 0.88 J cm^{-2}; (▼) 0.60 J cm^{-2}; (◆) 0.40 J cm^{-2}; (■) 0.35 J cm^{-2}.

one-seventh of that of the pyrene solution (0.78 μm^{-1} [8]). Our previous investigation indicated that etch rate depended on the concentration of dye molecules in a solution [8]. A higher etch rate was obtained by a higher absorption coefficient of the solution. However, although toluene showed a smaller absorption coefficient in comparison with the pyrene solution, the toluene system accelerated the etch rate. These results suggested that etching mechanism was different between toluene and pyrene solution. It is noted that, during LIBWE process with hundreds of laser shots, black-colored fine particles were gradually formed and suspended in the toluene solution, while the particles were not observed in such dye solutions as pyrene derivatives. Raman spectrum of the particles showed two broad peaks at 1354 and 1603 cm^{-1}, suggesting that carbon soot

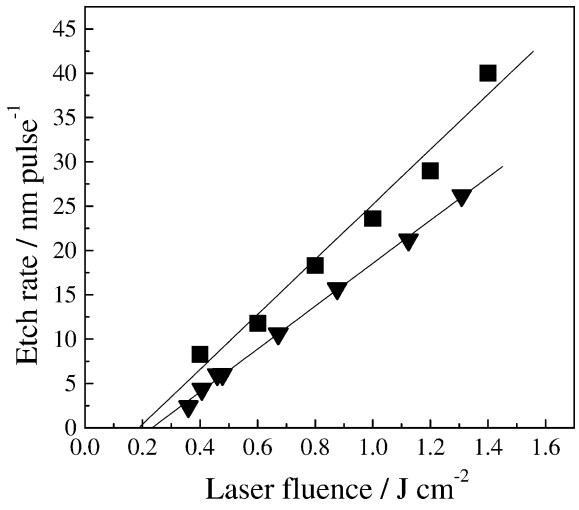

Fig. 4. Etch rate vs. laser fluence of a KrF laser: (■) pure toluene liquid; (▼) pyrene in acetone solution (concentration: 0.4 mol dm^{-3}).

was produced from toluene photolyzed by UV laser irradiation. This observation will be discussed at the next section.

3.2. In situ observation of liquid ablation

To elucidate the etching mechanism, the laser-induced ablation of a toluene solution was monitored by a back-illumination technique. Fig. 5 shows side view images of toluene ablation at the delay time between 100 ns and 100 μs after KrF laser irradiation at fluence of 1.6 J cm^{-2}. The formation of shock wave and vapor bubble was observed around the interface between silica glass and toluene liquid (Fig. 5(a)–(c)). Initial velocities of hemispheric expansion for shock wave and vapor bubble were ca. 1.4 km s^{-1} and 200 m s^{-1}, respectively. At the delay time of 50 μs, hemispheric vapor expansion reached the maximum size of 600 μm on the glass (Fig. 5(e)), and the vapor dome shrunk gradually up to 150 μs. Similar formation and propagation of shock wave and vapor bubble were also observed upon the laser irradiation at the fluence of 600 mJ cm^{-2}.

The impact pressure of the liquid jet can be estimated roughly from the following formula [19]:

$$P = \rho C V_{\text{jet}},$$

where ρ and C are the density of toluene and the acoustic velocity in toluene, respectively ($\rho = 0.86$ g cm^{-3} and $C = 1300$ m s^{-1} at 300 K). A velocity V_{jet} of 200 m s^{-1} corresponds to a pressure of 220 MPa. When we assume another simple model where incident photon energy was totally converted to thermal energy for vaporizing toluene without decomposition of the molecular structure, the initial pressure and temperature of toluene bubble upon the laser irradiation at fluence of 1.6 J cm^{-2} was estimated to be ∼100 MPa and ∼1000 K from the calculation based on the state equation using thermal properties of toluene molecule such as heat capacity and heat of evaporation. These two types of estimates suggest that the laser irradiation of toluene solution provided a unique environment under a transient high pressure and temperature.

Masuhara and coworkers [20] reported that threshold fluence for nanosecond-pulsed KrF excimer laser ablation of a pure toluene solution was 35 mJ cm^{-2} in ambient air. On the other hand, the etching of silica glass by LIBWE method occurs above the fluence of 190 mJ cm^{-2}, while we have observed the bubble formation of toluene at 100 mJ cm^{-2} by the in situ optical microscopy. On these observations upon the laser irradiation at 100 mJ cm^{-2}, we have found several specific phenomena. First, a tiny small size of bubble was formed. The maximum size of the bubble at 100 mJ cm^{-2} was ca. 30 μm at the delay time of 5 μs (V_{jet} = ca. 40 m s^{-1}). Secondly, the shock wave was hardly discernible by the microscopy. Thirdly, the soot in the solution was observed negligibly. Toluene solution was still colorless and transparent upon 10,000 shots irradiation. These three findings are

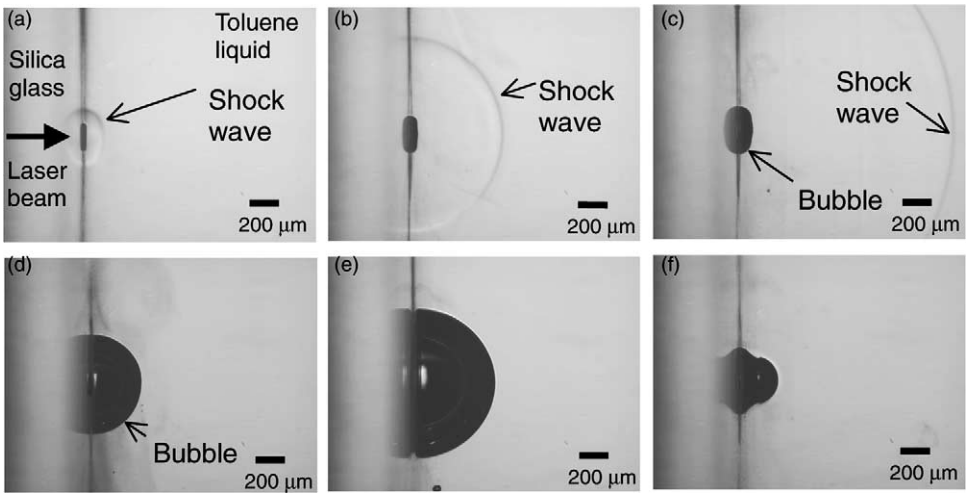

Fig. 5. Time-resolved optical micrographs for KrF excimer laser ablation of toluene liquid at the delay time of (a) 100 ns, (b) 500 ns, (c) 1.2 μs, (d) 10 μs, (e) 50 μs, (f) 100 μs (KrF laser: fluence 1.6 J cm^{-2} pulse^{-1}).

clearly distinct from those upon the laser irradiation above 190 mJ cm^{-2}.

On the study of toluene ablation with a photoacoustic measurement, two break points in the intensity of photoacoustic signals were detected as a function of laser fluence [20]. The first break point at 35 mJ cm^{-2} corresponded to the threshold fluence for ablation. The origin of second point located at 200 mJ cm^{-2} was not clear. According to the above-mentioned basic model, at the fluence of 200 mJ cm^{-2}, toluene solution reaches the boiling point (383 K at 1 atm) and starts to vaporize. Interestingly, the threshold fluence of LIBWE method overlaps with that of the second break point. These results indicated that transient high pressure, as well as high temperature, where shock wave and carbon soot would be produced by UV laser irradiation, played a key role in the etching process.

4. Conclusion

We demonstrated a new technique for silica glass etching by use of ns-pulsed laser ablation of toluene solution. Our LIBWE method has several advantages compared to previous methods for micro-machining of transparent materials: a lower laser fluence and higher etch rate, a constant etch rate, sharp edges for micro-pattern, free from cracks and debris, etc. This is a one step simple process at ambient pressure, which seems to be profitable for mass production.

References

[1] D. Bäuerle, Laser Processing and Chemistry, 3rd ed., Springer, Berlin, 2000.
[2] J. Ihlemann, B. Wolff, P. Simon, Appl. Phys. A 54 (1992) 363.
[3] P.R. Herman, R.S. Marjoribanks, A. Oettl, K. Chen, I. Konovalov, S. Ness, Appl. Surf. Sci. 577 (2000) 154–155.
[4] K. Sugioka, S. Wada, H. Tashiro, K. Toyoda, A. Nakamura, Appl. Phys. Lett. 65 (1994) 1510.
[5] J. Zhang, K. Sugioka, K. Midorikawa, Opt. Lett. 23 (1998) 1486.
[6] J. Zhang, K. Sugioka, K. Midorikawa, Appl. Phys. A 67 (1998) 499.
[7] H. Varel, D. Ashkenasi, A. Rosenfeld, M. Wähmer, E.E.B. Campbell, Appl. Phys. A 65 (1997) 367.
[8] J. Wang, H. Niino, A. Yabe, Appl. Phys. A 68 (1999) 111.
[9] J. Wang, H. Niino, A. Yabe, Appl. Phys. A 69 (1999) S271.
[10] J. Wang, H. Niino, A. Yabe, Jpn. J. Appl. Phys. 38 (1999) L761.
[11] J. Wang, H. Niino, A. Yabe, Appl. Surf. Sci. 154–155 (2000) 571.
[12] Y. Yasui, H. Niino, Y. Kawaguchi, A. Yabe, Appl. Surf. Sci. 186 (2002) 552.
[13] X. Ding, Y. Yasui, H. Niino, Y. Kawaguchi, A. Yabe, Appl. Phys. A 75 (2002) 437.
[14] X. Ding, Y. Kawaguchi, H. Niino, A. Yabe, Appl. Phys. A 75 (2002) 641.
[15] H.-H. Perkampus, UV-Vis Atlas of Organic Compounds, 2nd ed., VCH, Weinheim, 1992, p. 338.
[16] Y. Tsuboi, H. Fukumura, H. Masuhara, Appl. Phys. Lett. 64 (1994) 2745.
[17] R. Böhme, A. Braun, K. Zimmer, Appl. Surf. Sci. 186 (2002) 276.
[18] K. Zimmer, R. Böhme, A. Braun, B. Rauschenbach, F. Bigl, Appl. Phys. A 74 (2002) 453.
[19] J.C. Isselin, A.P. Alloncle, A. Autric, J. Appl. Phys. 84 (1998) 5766.
[20] Y. Tsuboi, K. Hatanaka, H. Fukumura, H. Masuhara, J. Phys. Chem. 98 (1994) 11237.