

Studies on laser processing of glasses for micro-
and nanostructures

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General Introduction

Glass has been widely used as a key component in materials for consumer use to industrial applications such as for liquid containers, cooking utensils, windows, optical components including lenses and microfibers, electronic devices including cathode ray tubes, liquid crystal displays, and OLED displays and lightings [1]. The vast array of applications is due to the good characteristics of glass including gas barrier properties, chemical stability, transparency, and heat resistivity, where a high flexibility in the properties can be obtained by controlling the elemental composition. Important developments in glass processing technology will permit the fabrication of appropriate structures to further explore the applications of glasses. There are several methods for processing glasses such as machining, grinding, blasting, chemical etching, lithography, water jet, electron beam processing, and laser processing. Among these, laser processing has several advantages because it is a non-contact method, and the process is conducted in the presence of air, making it possible to apply this technique to large workpiece.

In 1960, a laser was developed, whose existence had been theoretically proven in 1958 [2]. The initial laser was a coherent optical oscillator adapted from the concept of a maser. Since then, various types of lasers have been invented. For industrial application, oscillating lasers with higher power, and various types of wavelengths and pulse widths have been successfully developed. By using lasers, various types of materials such as metals and polymers have been processed. Lasers have been used to process materials in many ways, such as cutting, scribing, drilling, welding, cladding [3], laser lift-off (LLO) [4], interference patterning [5], laser induced forward / backward transfer (LIFT / LIBT) [6], [7], and material growth [8]. On the other hand, relatively little research and development has been conducted on brittle materials, particularly glass, probably due to the difficulty in processing this material owing to possible cracking. Thus, there is much prospective for further developments.

Glass has a potential to be used as a functional material, particularly if it has fine structures. One-dimensional, micro- and nanostructures having simultaneously a small diameter and a large depth, that is a high-aspect-ratio, are interesting for use in semiconductor packaging [9], light

waveguide [10], and wound healing [11]. Although a laser is a suitable tool for processing on the micro and nanometer scale, it is difficult to concurrently obtain a small spot size and a deep processed structure because of the following reason: Here, let us consider the ray model, as shown in Fig. 1. Assuming a laser beam with a Gaussian profile, a diameter of D , a wavelength of λ , and focused using a lens with a focal length of f , the spot diameter of d_0 on the focusing location can be written as [12]

$$d_0 = 4f\lambda/\pi D \quad (1)$$

The spot diameter d on the surface with a distance of z from the focusing location, is described as

$$d = d_0 \sqrt{1 + (z/z_R)^2} \quad (2)$$

where z_R represents the Rayleigh length, the value of which can be described as [13]

$$z_R = \pi d_0^2 / 4\lambda \quad (3)$$

Here, the distance between the surface of the workpiece and the focusing location is set at Z_0 , where the value represents plus when the focal location is below the surface of the workpiece. As seen in Equation (2), the beam size increases as the location becomes farther away from the focusing location. Thus, it is necessary to overcome the above problems in order to achieve high-aspect-ratio structures. A basic understanding of the process is also very important for continuous, highly efficient, and controllable processing.

This thesis, as shown in Fig. 2, concerns the development of glass processing methods to explore new applications and to analyze phenomenon. The author particularly focuses on the following three types of processes using lasers with a continuous wave and with nanosecond order pulses:

(1) Microdrilling

High-aspect-ratio microdrilling has been reported for high density packaging for the semiconductor field. In this research, a laser was illuminated, then, glass is processed from the top-surface of the glass substrate. Here, it is expected that the smooth inner wall helps the

incident laser beam to propagate well deep inside the holes resulting in achieving small and deeper holes.

(2) Internal modification

Internal modification of glass was investigated to develop light waveguides using continuous-wave backside irradiation [14]. This process is initiated from the backside of the workpiece adjacent to the absorbent. It is expected that the once processed region is not prevented because of process from the backside. This idea is similar to the previous report on the laser induced backside wet etching process [15].

(3) Nanofiber spinning

Glass nanofibers are promising for medical use, optical materials, and catalysts. A laser is illuminated to the substrates, to the extent that the substrate is heated and melted. Here, it is expected that the viscosity of the molten glass induces spinability, leading to elongating molten glass into the fibrous structure. The nanofiber generation phenomenon, for example, was reported by Venkatakrishnan et al. using a high-repetition-rate ultra-short laser pulses from the top surface [16].

Summary of each chapter

Chapter 1:

By using a pulsed laser with a wavelength of 266 nm and pulse width of nanosecond order, holes with a diameter of $8.2 \pm 3.1 \mu\text{m}$ and the aspect ratio of 190 in glass were achieved [17]. Transition of the hole profiles depending on the shot number was investigated. By the experiment, it was found that the hole diameter in a certain depth became smaller resulting from the deposition of the ablated material from the bottom onto the hole wall. Also, the influence of the beam profile was elucidated. The laser fluence once became larger probably because of the multiple reflection inside the hole. Finally, the effect of heat accumulation was estimated by changing the pulse repetition rates.

Chapter 2:

By illuminating a visible, CW laser into the glass with an absorbent made from copper, modification with a speed of $\sim 200 \text{ mm/s}$ occurred. This phenomenon was successfully observed by high-speed monitoring. Then, the transmitted power of the incident laser was measured to estimate the absorbed power [18]. Moreover, during the experiment, it was found that a part of the metal absorbent was implanted into the glass as a spherical particle with a diameter of 3-50 μm with a speed of $\sim 10 \text{ mm/s}$ [19]. To clarify the phenomenon, the heat calculation around the absorbent was conducted. It was concluded that the property of melting point and thermal conductivity of the absorbent mostly influenced.

Chapter 3:

Nanofiber generation for medical use or optical materials was discussed. By illuminating the pulsed laser with a wavelength of 355 nm and a pulse width of nanosecond order, nanofiber generation was achieved from thin glass substrates [20]. The characteristics of the process are that the nanofibers were spanned from the back surface. The mean diameter of the generated nanofibers was $\sim 300 \text{ nm}$, then, the generation condition was clarified. By the in situ observation, viscous behavior of the molten glass was observed, and generation of the voids in the glass and molten glass around the back surface was pushed out into the air. Also, the melt ejection speed

was measured. By using the observed parameters, the pressure applied for the molten glass was estimated considering the balance of momentum [21].

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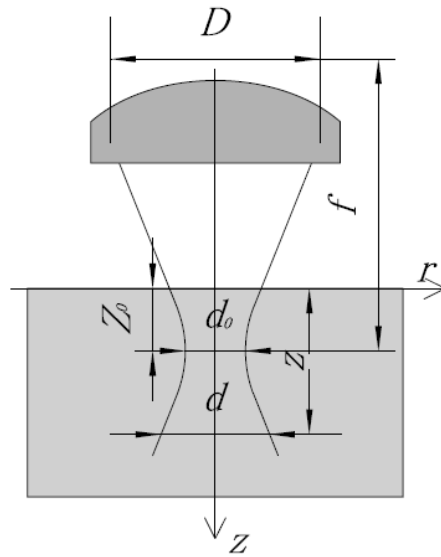


Fig. 1 Schematic of a ray model of the beam. The figure is deformed for illustration [12].

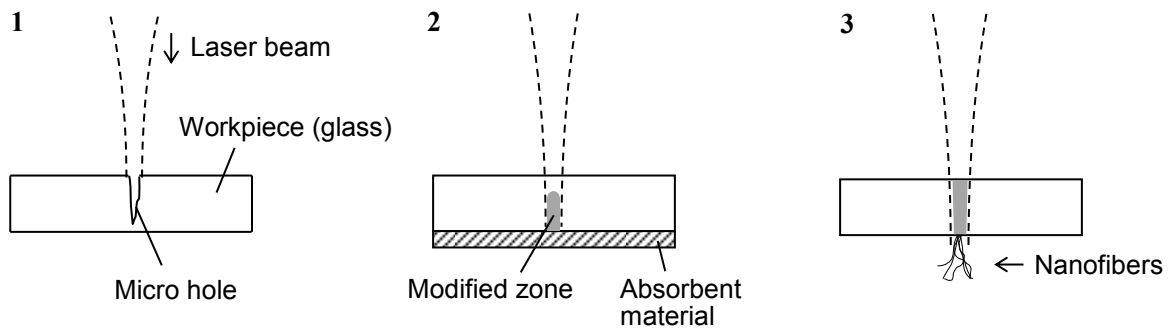


Fig. 2 Schematic image of the three types of processes: (1) microdrilling, (2) internal modification using the absorbent material, and (3) nanofiber spinning from the back surface.

Chapter 1

High-aspect-ratio microdrilling of glass using pulsed UV laser

1.1 Drilling holes with an aspect ratio of 190 in borosilicate glass

1.1.1 Introduction

High-aspect-ratio microdrilling has been in demand for fabricating through-silicon vias in semiconductors [1], microfluidic devices in dielectrics [2], and fuel injection nozzles in metals [3]. To achieve such microdrilling, several methods have been utilized such as laser irradiation [2], [3], mechanical drilling, electrical discharge machining (EDM) [4], and reactive ion etching (RIE) [1]. However, achieving ultrafine drilling and a high aspect ratio simultaneously is difficult. In particular, some processes using lasers utilize light sources with different wavelengths and pulse widths. To achieve microdrilling, UV lasers are widely used because of their small beam spot and high coefficient of absorption for various types of material. The UV lasers include Cu vapor lasers [5], excimer lasers [6–8], and Nd:YAG lasers with the third-harmonic [9] and fourth-harmonic waves [10].

Laser drilling includes various processes such as heating, melting, vaporizing, material ejection, shock wave generation, and plasma generation and expansion [10], [11]. Moreover, for high-aspect-ratio drilling, it is necessary to consider beam propagation, beam reflection in the hole, and molten debris ejection. Thus, these complicated processes make it difficult to clarify the factors of preventing high-aspect-ratio drilling.

Several studies have been conducted on high-aspect-ratio drilling including keyhole generation during high-power CO₂ laser irradiation [12], modeling of beam propagation during UV laser illumination [6], high-speed drilling by successive double-pulse irradiation [9], [13], [14], and the behavior of generated plasma [10], [15]. In particular, high-aspect-ratio drilling was achieved when an excimer laser was irradiated on resin, yielding hole diameters of several tens of μm and an aspect ratio of 600 by optimizing the beam divergence. Although an aspect

ratio of 600 was achieved in resin, high-aspect-ratio drilling has not yet been realized in other materials such as metals, dielectrics, and semiconductors.

As mentioned above, high-aspect-ratio microdrilling includes various processes, and the dominant process might differ depending on the irradiated material. Hence, the reasons for the difficulty of high-aspect-ratio drilling of materials other than resin have still not been clarified. Resin has a high light absorption coefficient in the range of UV light and low thermal conductivity, which result in a lower processing threshold than in the case of metals [16]. Moreover, the resulting debris is easily oxidized and removed. These characteristics of resin make high-aspect-ratio processing possible.

The factors preventing high-aspect-ratio processing using lasers are thought to be not only the ejection of removed molten materials but also the propagation of the laser beam to the bottom of the drilled holes. In particular, in the case of using a laser with a pulse width larger than picosecond scale, the generated plasma absorbs the beam, which reduces the energy of the beam as it approaches the bottom of the drilled hole. This effect will be particularly dominant in high-aspect-ratio deep holes because the generated plasma is not dispersed, but confined in the holes, increasing the density.

Several researchers have reported on the absorption of a laser beam by plasmas. In the UV region, the absorption of a laser beam by plasmas is in accordance with the Kramers–Unsold relation in the case of lower ionization levels, and the inverse bremsstrahlung effect in the case of higher ionization levels [17], which means that laser beams with shorter wavelengths are more difficult to be absorbed. Breitling et al. [18] found that the absorption by plasma is low when a shorter-wavelength beam was used, as determined by calculating beam absorption by plasmas and measuring the electron density in plasmas generated by irradiation of the fundamental (1064 nm), second-harmonic (532 nm), and third-harmonic (355 nm) waves of the Nd:YAG laser on SiN. Thus, a shorter-wavelength beam can easily propagate to the bottom of drilled holes without being absorbed by the generated plasmas.

During laser processing, a material is heated, melted, vaporized, ejected, and removed by the laser beam. If the material is heated before laser irradiation, the energy necessary for melting will decrease. As a result, the threshold of the fluence necessary for removal also decreases. Therefore, it is expected that material removal occurs even in a deep hole in which the beam hardly propagates. However, it is not desirable in industrial applications to heat an entire

material. Here, using a high-repetition-rate pulsed laser, the author heated only the area around the laser spot, which the author thought to be possible by irradiating the next pulse before the heat generated by the previous pulse diffuses.

Ancona et al. [19] evaluated the influence of the pulse repetition rate on the processing speed using a high-repetition-rate femtosecond laser; in particular, they founded that processing speed increases with the repetition rate. From this report, the author considered that the processing speed can be increased by choosing an appropriate repetition rate. Moreover, a low threshold is also expected at the same time. Thus, a high repetition rate is also effective for deep-hole drilling.

Thus, in this study, borosilicate glass, which makes it easy to evaluate the hole shape because of its transparency, was drilled using fourth harmonic waves of a nanosecond Nd:YVO₄ laser, with the aim of achieving high-aspect-ratio drilling using high-repetition-rate pulses. In this experiment, the transitions of drilled holes, hole shapes, and inner walls were observed.

1.1.2 Experimental setup

Figure 1 shows the experimental setup and Table 1 shows the irradiation conditions. The fourth-harmonic wave of a Nd:YVO₄ laser (DS20H-266, Photonics Industries International Inc., Bohemia, NY) as a light source was focused through a convex lens with a focal length of 30 mm. The focal depth was approximately 2 mm, which made it difficult to adjust the focal position precisely. Thus, drilled hole depths were measured, each of which was shifted by 0.5 mm in the irradiation direction. The drilled hole depths were nearly the same, approximately 1.5 mm, and further shifts decreased the drilled hole depth. Thus, the midrange was chosen as the focal position.

Borosilicate glass (Pyrex®, Corning Inc.), which is transparent in the range of visible light and has good heat resistance, was used as a sample for observing the inner holes. Although the glass is transparent in the range of visible light, the light of 266 nm wavelength was absorbed [20].

An optical microscope (VHX-200, Keyence) was used to observe the drilled holes from the transverse direction to the laser axis. The light source for observation was located on the opposite side of the camera across the sample. To observe the inner walls of the holes, the sample was cut along the central axis of the holes, and then polished and cleaned using piranha

solution (concentrated sulfuric acid: 30% hydrogen peroxide water = 3:1). An electrically conducting layer was deposited using an ion coater (IB-3, Eiko). Then, the holes were observed by scanning electron microscopy (SEM, S-2400, Hitachi).

1.1.3 Results and discussion

1.1.3.1 Hole shape

When more than 5000 laser pulses with an energy of 100 μJ and a repetition rate of 10 kHz were focused on borosilicate glass of 2 mm thickness, holes were drilled through the sample. Figure 2 shows a drilled hole observed from the transverse direction. Figure 2(a) shows an overview of the hole, where the laser pulses were irradiated from the top in this figure. Figure 2(b) shows the hole profile based on Fig. 2(a). Figures 2(c)–(f) show magnified images in the vicinity of the glass surface, 650 and 1200 μm from the surface, and in the vicinity of the back surface, respectively.

The hole diameter at the top surface was approximately 20 μm , which is slightly larger than the calculated spot diameter of 15 μm . This diameter remained the same up to a depth of 300 μm . Then, the hole diameter decreased to approximately 7.5 μm at a depth of 650 μm . The diameter remained the same at approximately 10 μm at depths of 850–1100 μm . At depths of 1100–1350 μm , the diameter gradually decreased and then remained nearly the same in the range of 1350–2040 μm .

The diameters were $\phi 8.2 \pm 3.1 \mu\text{m}$ and $\phi 6.3 \pm 1.0 \mu\text{m}$ at depths of 480–2040 μm and 1360–2040 μm , respectively. Therefore, if the hole around the glass surface was removed by grinding, or if the glass was drilled under the condition of lamination with a dummy layer of glass followed by removal of the dummy glass, diameters of $\phi 8.2 \pm 3.1 \mu\text{m}$ and $\phi 6.3 \mu\text{m} \pm 1.0 \mu\text{m}$ would be obtained resulting in aspect ratios higher than 190 and 100, respectively.

In the vicinity of the hole, modified layers were observed, as indicated by arrows in Figs. 2(c)–(e). Although the layers were transparent, they were found to be redeposited layers of debris, confirmed by the observation of drilling propagation as discussed later. While the thickness of the redeposited layer was 8 μm in the part shown in Fig. 2(d), it was approximately 5 μm in the other parts.

The streaks encircled in Fig. 2(d) and the white areas observed in the other parts were thought to be cracks generated in the glass. Cracks were particularly observed in the vicinity of the thick redeposited layers, as shown in Fig. 2(d).

Karnakis et al. [21] drilled borosilicate glass (D263, Schott) using a similar light source, that is, a UV copper vapor laser with a wavelength of 255 nm, a pulse width of 30 ns, and a repetition rate of 6 kHz. They obtained an aspect ratio of ~ 20 . On the other hand, in our experiment, the author obtained a 10-fold larger aspect ratio, which may be due to slight differences in the irradiation conditions. Clarifying these differences is part of our future research.

Figure 3 shows drilled holes on the top and back surfaces of the glass. The hole diameter on the top surface was $\sim 70 \mu\text{m}$. Cracks were observed at the edges of the drilled holes, and redeposited debris was found in the outer area. The hole diameter on the back surface was less than $10 \mu\text{m}$, and cracks and chipped edges were also observed. It has been reported that recoil pressure is generated during laser ablation [22]. Another report described that the back surface bulges immediately before penetration in the case of metals [5]. Thus, the cracks were thought to be formed by the recoil pressure generated during laser ablation.

1.1.3.2 Transition of the drilled hole

Transitional drilling propagation was observed when laser illumination was stopped every 500 pulses. Figure 4 shows the depth profiles of a hole. Although the depth of the drilled hole increased by $\sim 200 \mu\text{m}$ every 500 pulses, the ablation rate per pulse remained the same and was not affected by the hole depth. However, the drilled hole diameter decreased from the surface to a depth of $1600 \mu\text{m}$ with increasing number of laser pulses. The reason for this was thought to be the redeposition of the debris generated from the bottom of the hole. Therefore, the hole walls excluding the part from the bottom to a height of $\sim 400 \mu\text{m}$ above (i.e., at a depth of $1600 \mu\text{m}$ from the top surface) were considered to be covered with the redeposited layer. This layer coincides with that observed in Fig. 2, which was observed to be transparent under a microscope.

The dashed line in Fig. 4 shows the beam profile calculated from the specifications of the laser source and optical system. The focal location was set on the surface of the sample. This profile shows the location of 14% ($1/e^2$) power compared with the center of the Gaussian beam.

The radius of the profile at a depth of 2000 μm becomes $>24 \mu\text{m}$, which is not plotted in this graph. On the other hand, the hole radius is several of μm , which is smaller than the spot radius. Thus, the reason for achieving such a high-aspect-ratio hole cannot be explained by the beam profile. Other factors such as beam reflection at the inner hole wall are should be clarified.

Luft et al. [5] evaluated the redeposition of debris on the inner wall when drilling copper using a copper vapor laser and a Ti:sapphire laser. They observed redeposition at depths of several hundreds of μm from the bottom, and even when the part closer to the surface of the workpiece became thinner as a result of redeposition, the drilling still propagated. This mechanism is thought to be induced by multiple reflection on the hole walls, resulting in material removal by plasma or melting. Also in our experiment, drilling was thought to propagate by the same mechanism.

In the removed part, a pulse with an energy sufficiently high to ablate the material was irradiated. Therefore, if redeposition occurs at this part, the deposited material can be considered to be removed by the successive pulses. However, in fact, a redeposited layer of several of μm thickness was observed. This is considered to be because the incident angle of the beam to the surface of the hole wall (i.e., the angle of incident light to the normal direction of the hole wall) is sufficiently large. In the range indicated by the two sided arrow in Fig. 4, when 1000 pulses were irradiated, the laser was almost perpendicular to the bottom, forming a small illuminated area. In contrast, in the case of the more than 2500 pulses, the laser beam illuminated a wider area, which means that the pulse energy per area was smaller. Thus, the redeposited layer was not removed.

The redeposited layer in this experiment was transparent when observed under an optical microscope and did not include any voids. Moreover, when the redeposited layer was removed by methods such as chemical etching, the hole was still smaller with a higher aspect ratio than the previously reported holes.

1.1.3.3 Observation of the hole wall

To observe the hole wall, the workpiece was cut along the central axis of the hole and polished. After that, the workpiece was cleaned then observed by SEM after the deposition of an electrically conducting layer. Figure 5 shows images of a typical part. In the entrance of the hole (Fig. 5(a)), a smooth surface, which probably formed by melting, and a rough surface were

observed. In the depth range of 100–600 μm , small debris with a diameter of less than 500 nm were observed on the wall as shown in Fig. 5(b). In the vicinity of a depth of 650 μm , debris with diameters of 500 nm–1 μm were observed on the wall as shown in Fig. 5(c). This location with large debris corresponds to the neck of the hole (in the vicinity of 650 μm depth). Also, cracks were observed on the inner wall. When the edges of the hole and the polished surface were examined in more detail, the cracks were found to have a maximum depth of 1 μm and were generated only within the redeposited layer of molten debris. Hence, it is considered that the cracks were caused by the redeposited layer of molten debris, which can be shrunk by quenching.

No debris was observed and a flat wall was obtained at a depth of more than 700 μm , as shown in Fig. 5(d). Although the redeposited layer from the edge part was examined carefully, no voids or differences from the workpiece were observed.

At the interface between different materials, steps or delamination occurs after polishing. However, at the interface between the redeposited layer and the workpiece, no such difference was observed. Thus, the redeposited layer is thought to bind strongly to the workpiece.

In parts except for that approximately 400 μm from the bottom, cracks similar to those shown in Fig. 5(c) were observed at 50 μm intervals in the circumferential direction. In Fig. 2, no redeposited layer at a depth of 400 μm from the bottom was observed. The region where cracks were generated was almost in accordance with that with the redeposited layer. Thus, it was thought that the shrinkage of a molten material by quenching caused the cracks, as described above.

Although it has been reported that the surface roughness increases when drilling glass [23], the author obtained a smooth surface in our experiment. Karnakis et al. [21] obtained a smooth surface by grooving borosilicate glass using a UV laser. The smooth surface achieved in their experiment is thought to be due to both the short pulse peak and the weak shock wave of a nanosecond laser. Also, the high repetition rate keeps the temperature high around the irradiated spot, which results in a weak heat shock compared with that obtained using a lower-repetition laser.

1.1.4 Conclusions

In this experiment, during high-aspect-ratio microdrilling using a UV laser, laser beam propagation, the shape of the hole, and the inner hole wall were observed, which led to the following results: (1) Drilled holes with diameters of $\phi 8.2 \pm 3.1 \mu\text{m}$ and $\phi 6.3 \pm 1.0 \mu\text{m}$, resulting in aspect ratios higher than 190 and 100, respectively, were obtained, respectively. (2) A redeposited layer with a thickness of several of μm covered the inner hole. (3) The hole wall was smooth except for certain parts. The part in the vicinity of the redeposited layer included several cracks.

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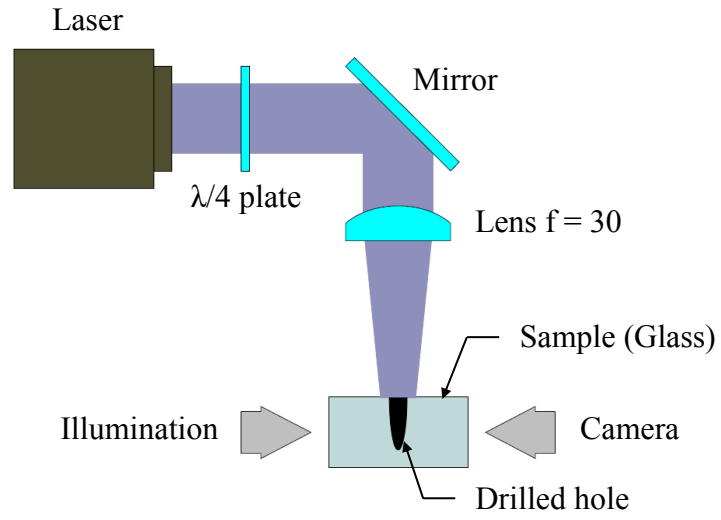


Fig. 1 Experimental setup.

Table 1 Irradiation conditions.

Laser	Nd:YVO ₄ laser (4th-harmonic wave)
Wavelength	266 nm
Power	100 μ J
Repetition rate	10 kHz
Pulse width	8 ns
Beam mode	TEM ₀₀
M ²	< 1.2
Focal length	30 mm
Workpiece	Borosilicate glass (Pyrex)
Thickness	2 mm

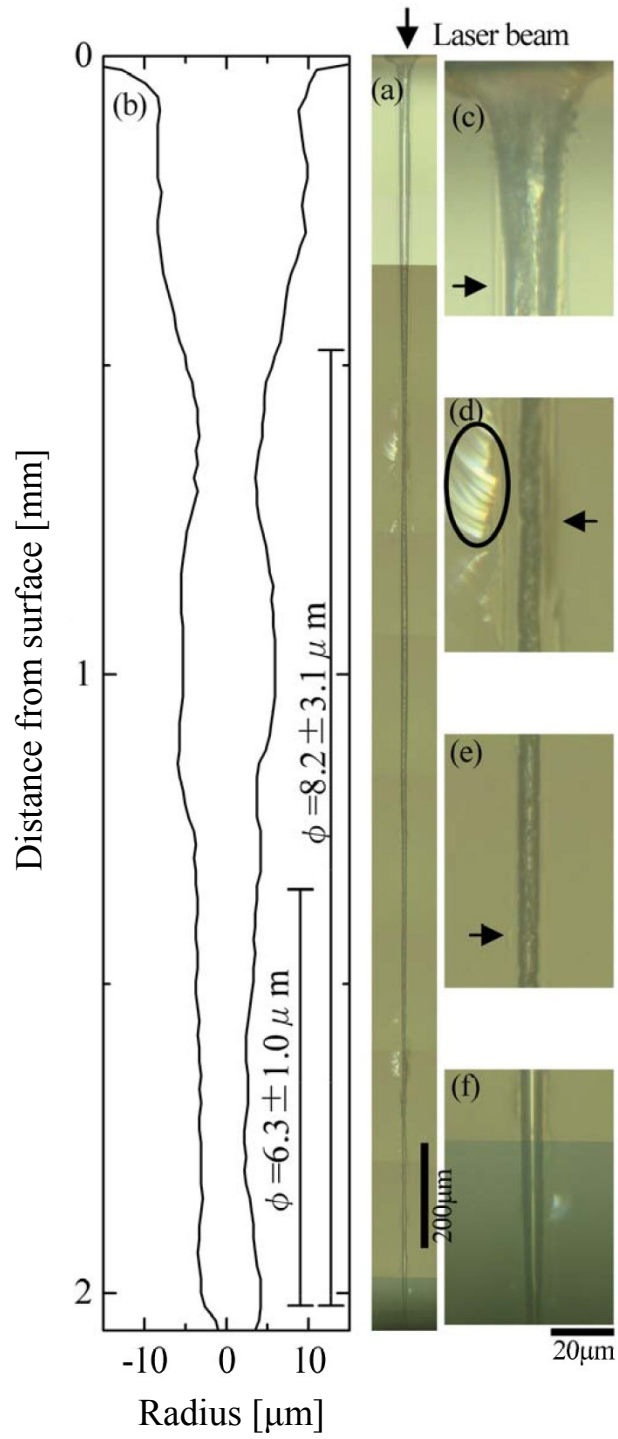


Fig. 2 Transverse section and profile of drilled hole. (a) Whole transverse section, (b) profile of hole, (c)–(f) magnified images of (a), at the surface (c), at 650 μm (d) and 1200 μm (e) from the surface and at the back surface (f). The pulse energy was 100 μJ and the number of pulses was 5000.

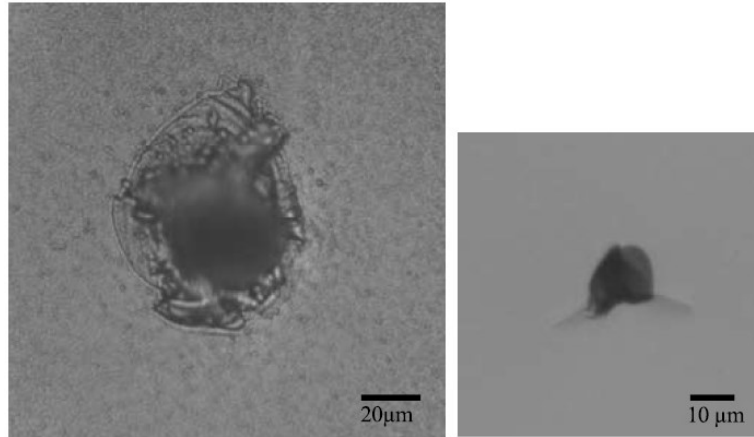


Fig. 3 Micrographs of laser-drilled holes observed from (a) front surface and (b) back surface. The pulse energy was 100 μJ and the number of pulses was 5000.

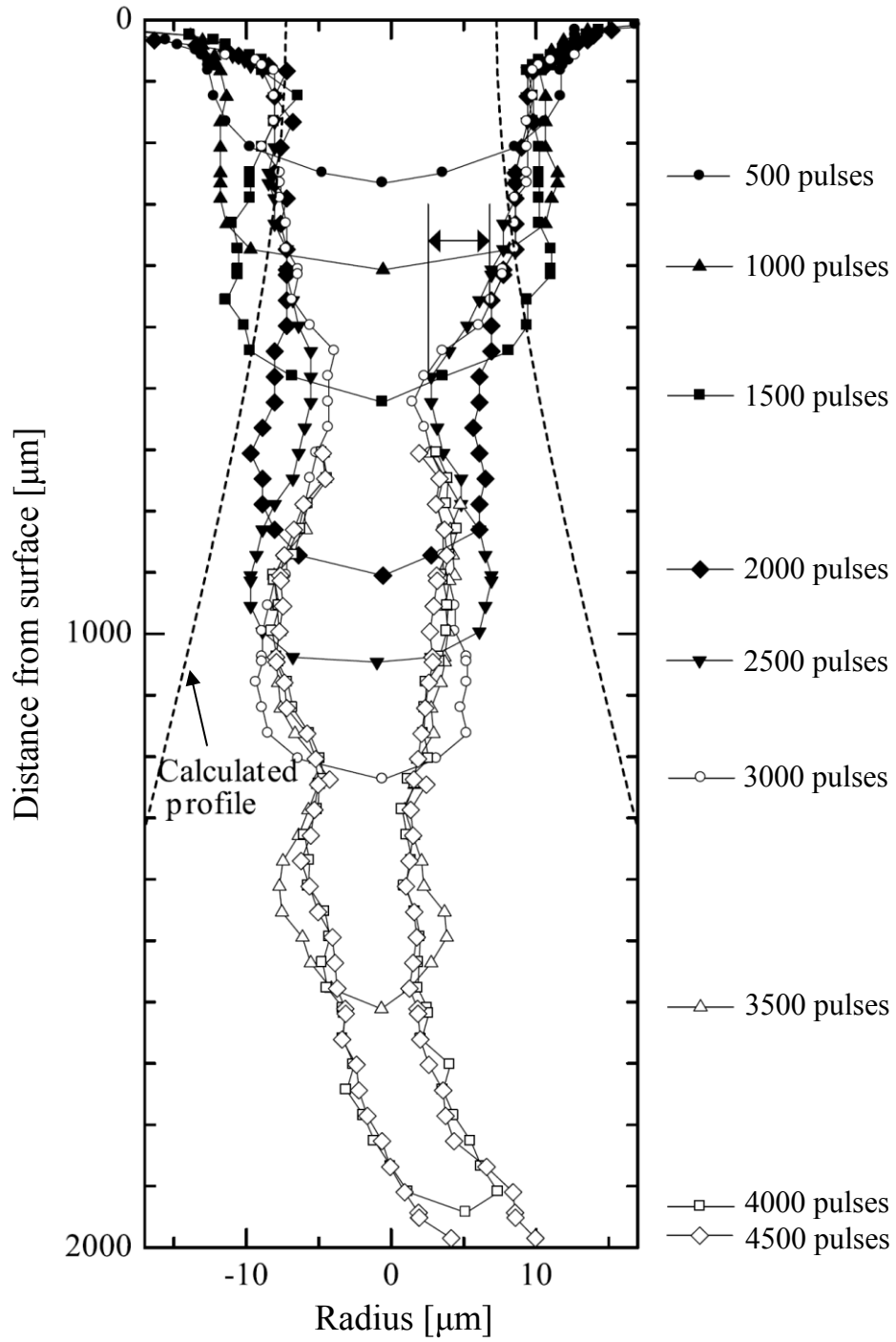


Fig. 4 Reconstructed depth profiles of a hole drilled in borosilicate glass with different numbers of pulses. The dashed line is the calculated beam profile. The focal length was 30 mm. The pulse energy was set at 100 μJ .

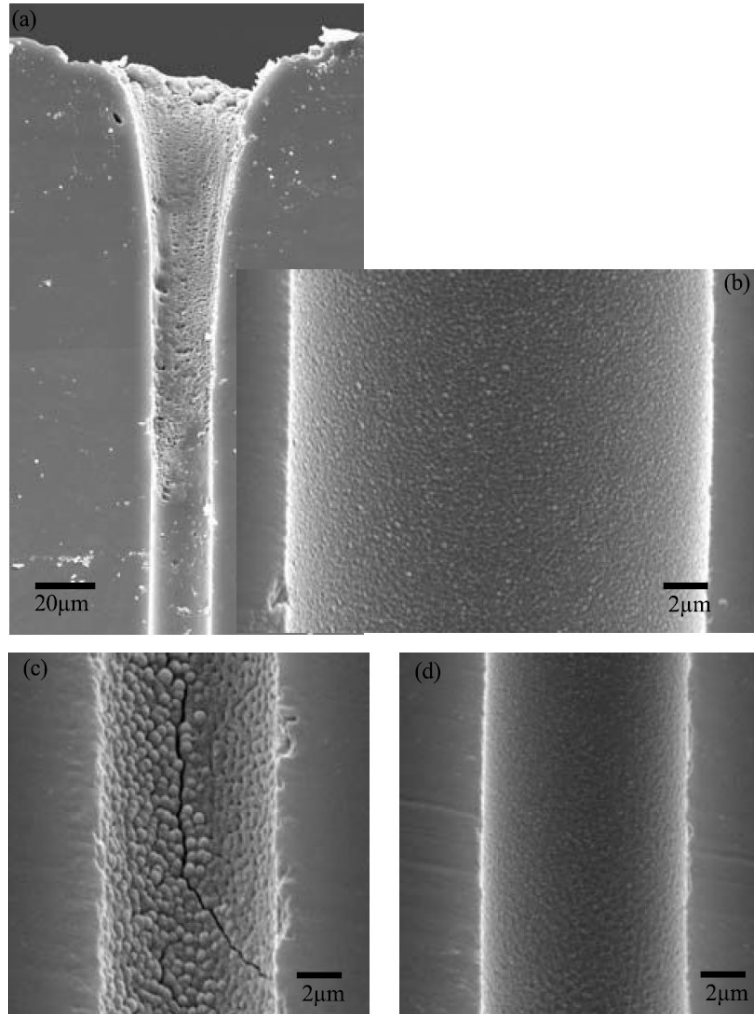


Fig. 5 Cross-sectional SEM images of a hole at (a) the entrance of the hole, (b) $\sim 300\ \mu\text{m}$, (c) $\sim 650\ \mu\text{m}$, and (d) $\sim 750\ \mu\text{m}$ from the surface. The focal length was 30 mm. The pulse energy was set at 100 μJ . The number of pulses was 5000.

1.2 Influence of beam parameters on hole profile

1.2.1 Introduction

In the previous section, the author demonstrated microdrilling using a high-repetition-rate pulsed laser, by which a high processing speed and low ablation threshold were expected owing to the low plasma absorption in the range of UV light and heat accumulation. As a result, holes with a diameter of $8.2 \pm 3.1 \mu\text{m}$ with an aspect ratio of 190 and a diameter of $6.3 \pm 1.0 \mu\text{m}$ with an aspect ratio of more than 100 were obtained [1].

To determine the mechanism leading to such high-aspect-ratio drilling, it is necessary to clarify the phenomenon of beam propagation inside the holes. Various models have been proposed for beam propagation during the processing of deep holes. Tokarev et al. [2] reported the modeling of hole shapes, and a comparison with experimental results was performed to evaluate its validity, focusing on the beam propagation and incident angle when drilling polymers using a KrF excimer laser. An aspect ratio of 600 was yielded by optimizing the beam parameters. In their model, beam reflection on hole walls was not considered owing to the high light absorption of polymers (approximately 95%). Matsumura et al. [3] reported a model of beam propagation in inner holes when processing silicon using a femtosecond laser, assuming that light was attenuated in accordance with the lambert–beer law, which is similar to that in light waveguides. Brajdic et al. [4] considered the influence of beam reflection on the bottoms of holes and on inside walls near the hole bottoms for the irradiation of stainless steel using a Nd:YAG laser. Li et al. [5] reported the high-aspect-ratio drilling of quartz by using polymer cover layers attached on substrates and illuminating the fourth harmonic of a Nd:YAG laser. They utilized beam reflection on tapered hole walls generated in the polymer cover layers, which behaves similarly to that in waveguides. Compared with the case of irradiation without polymer cover layers, a higher fluence was demonstrated. Modest [6] discussed drilling propagation, proposing a beam-tracing method that considered reflection on hole walls, when illuminating aluminum with the third harmonic of a Nd:YAG laser. Kuwata et al. [7] considered the processing mechanism by combining ray tracing considering reflection on hole walls and thermal analysis for the case of drilling ceramics using a YAG laser. Moreover, the influence of beam polarization on the hole shape was also considered while discussing the change in the hole profile [8], [9] and the curving phenomenon [10].

In this section, the influence of focusing conditions, particularly the focal length of the lens

and the focusing location, was investigated. Then, the mechanism of high-aspect-ratio drilling is discussed along with clarification of the conditions that enable high-aspect-ratio drilling.

1.2.2 Experimental setup

1.2.2.1 Experimental apparatus and method

The experimental apparatus was the same as that in the previous section. The fourth harmonic of a Nd:YVO₄ laser was used as a light source, which was focused using a lens with a focal length of 100 mm, 50 mm, 30 mm, 20 mm, or 10 mm. For easier observation of the inner holes, borosilicate glass (Pyrex®, Corning Inc.) was used because of its transparency in the range of visible light and good heat resistance. The thickness of the sample was 10 mm. Although the glass is transparent in the range of visible light, this glass absorbed the light of the processing laser used, which had a wavelength of 266 nm [11].

The focusing location was adjusted by measuring each hole depth by drilling holes with a shift of the focusing location because of the difficulty of precise adjustment. Details will be given in 1.2.3.2. Drilled holes were observed using a microscope (VHX-200, Keyence), then their profiles were plotted.

1.2.2.2 Transverse mode of the laser beam

In laser processing, the transverse mode of the laser beam greatly affects the shape of the drilled hole. Here, the beam profile was measured. After the focusing lens was removed, a beam profiler (SP503U, Ophir Optronics Ltd.) was set at the location of the sample. Figure 1 shows the measurement result. The vertical and horizontal spot diameters that is, the range of diameters where the intensity becomes 13.5% ($1/e^2$) of that of the beam center, were 690 μm and 620 μm , respectively, and the correlation coefficient with the Gaussian distribution was 0.94.

1.2.2.3 Calculation of the beam diameter

As the M^2 factor of the laser used in this study was <1.2 , the transverse mode is close to the Gaussian distribution. Thus, the analysis of beam propagation was conducted on the basis of a Gaussian beam (i.e., $M^2 = 1$). The analysis was conducted using the model shown in Fig. 1 in *General Introduction*.

1.2.3 Results and discussion

1.2.3.1 Influence of polarization

It is well known that transverse hole profiles change [8], [9] and become curved [10] in accordance with the polarization of a laser beam. Here, by using a that was linearly or circularly polarized by rotating a $\lambda/4$ plate, drilled hole profiles were compared. It was difficult to evaluate holes on the top and back surfaces of the sample because of chipping. Thus, by polishing the workpiece to a depth of 0.1 mm from each surface, hole cross sections at this depth were evaluated. Figure 2 shows the holes on polished surfaces. As shown in the images, cracks generated during polishing were observed. No influence of the polarization direction was recognized. Also, no difference in the shapes of holes formed by linearly and circularly polarized beams was recognized. Then, the hole curving (straightness) was evaluated from the transverse direction. Although some holes were curved, no differences originating from the polarization were recognized. Thus, the author can conclude that there is no influence of polarization on the drilled holes for the processing conditions in this study. The reason for the lack of influence of polarization is attributed to the fact that heat, which is not dependent on the polarization, is more dominant than for other types of lasers. This is because a high-repetition-rate nanosecond laser was used in this study, which is different from the case of a femtosecond or picosecond laser [8–10] or a low-repetition-rate nanosecond laser [10].

1.2.3.2 Influence of the focal length and focusing location on the hole depth

Hole depths were measured by illuminating the laser while varying the focal length and focusing location. The Rayleigh length of the lens used in this study was large, approximately 1.7 mm in the case of a 50 mm focal length. Thus, it was difficult to determine the focusing location precisely. Here, hole depths were measured while varying the focusing location by smaller increments than the Rayleigh length. The measured depths were $<400\text{ }\mu\text{m}$ and $<700\text{ }\mu\text{m}$ in the case of 10 mm and 100 mm focal lengths, respectively. In contrast, the measured depths were $>2000\text{ }\mu\text{m}$ in case of 20 mm, 30 mm, and 50 mm focal lengths. Figure 3 shows the relationship between the focusing location and the depth. In this graph, average hole depths were plotted after drilling three times under the same conditions, where the results for the deepest and shallowest holes were plotted as error bars. Also, the ranges of the Rayleigh length

were plotted as broken lines. Among the plots in Fig. 3, the focusing location ($Z_0 = 0$) was defined as the location for which the graph became the most symmetrical horizontally.

For the focal lengths of 50 mm, 30 mm, and 20 mm, the hole depths were >2 mm within the range of approximately 70% of the Rayleigh length with the center at $z = 0$. By further shifting the focal location, the depths decreased. No difference caused by the direction of the shift (the sign of Z_0) was recognized.

1.2.3.3 Influence of focusing location on the hole shape

Figure 4 shows the hole profiles drilled when using the lens with a focal length of 30 mm and setting the focusing location to $Z_0 = 0 \mu\text{m}$ and $\pm 1000 \mu\text{m}$. No difference between $Z_0 = 0 \mu\text{m}$ and $+1000 \mu\text{m}$ was recognized. In the case of $Z_0 = -1000 \mu\text{m}$, the depth was smaller. The diameters of $\sim 500 \mu\text{m}$ along the z axis in the vicinity of the hole tip were similar for $Z_0 = 0 \mu\text{m}$ and $+1000 \mu\text{m}$. Then, in the figure, the calculated spot diameter at each depth was plotted. Although in the case of $Z_0 = +1000 \mu\text{m}$, the hole diameter is similar to the spot diameter in the vicinity of the depth of $z = 1000 \mu\text{m}$, at greater depths, the hole diameter is smaller than the calculated spot diameter. In contrast, in the case of $Z_0 = 0 \mu\text{m}$, from the surface to $z = 200 \mu\text{m}$, the beam spot was smaller than the hole diameter, and at greater depths, the beam spot was larger. At the depth of $2400 \mu\text{m}$ (not shown in the graph), the spot radius was $29 \mu\text{m}$. This is approximately 10 times larger than the hole radius of $3 \mu\text{m}$. As the hole diameter and spot diameter differed greatly, the reason why such a small hole was obtained cannot be explained only by the calculated spot diameter.

Figure 5 shows the calculated fluence and hole radius (broken lines) at the focal location $Z_0 = 0 \mu\text{m}$ in order to more precisely consider the relationship between the fluence and the hole diameter at different depths. The hole radii were $6.0 \mu\text{m}$, $6.1 \mu\text{m}$, and $2.6 \mu\text{m}$ at the locations of $z = 200 \mu\text{m}$, $1000 \mu\text{m}$, and $2000 \mu\text{m}$, respectively. As reported in the previous section, debris from the bottom of the hole was deposited in the vicinity of the hole entrance, which formed a redeposited layer, resulting in thinner holes after drilling. Then, the outer radius of the redeposited layer (i.e., the radius of the hole before redeposition) was also measured. The radii including the redeposited layer were $12.7 \mu\text{m}$ and $9.2 \mu\text{m}$ at the depths of $z = 200 \mu\text{m}$ and $1000 \mu\text{m}$, respectively (shown by the chain lines in Fig. 5). No redeposited layer was observed at a depth of $z = 2000 \mu\text{m}$. From the figure, holes were obtained when the fluences were

approximately $>35 \text{ J/cm}^2$ and $>28 \text{ J/cm}^2$ at the depths of $z = 200 \text{ }\mu\text{m}$ and $1000 \text{ }\mu\text{m}$, respectively. However, compared with the radii of the ablated holes before redeposition (i.e., the outer radius of the redeposited layer), holes were obtained when the fluence was $>0.4 \text{ J/cm}^2$, $>14 \text{ J/cm}^2$, and $>10 \text{ J/cm}^2$ at the depths of $z = 200 \text{ }\mu\text{m}$, $1000 \text{ }\mu\text{m}$, and $2000 \text{ }\mu\text{m}$, respectively, which means that the fluence necessary for ablation depended on the depth.

Therefore, the deep-drilling mechanism cannot be explained by the model in which the beam reached the drilled holes without considering the beam reflection on the hole wall, and the part where the fluence threshold was exceeded was ablated.

1.2.3.4 Laser power transmitted through the drilled hole

Then, the fluence at each depth was evaluated by measuring the laser power transmitted through the drilled holes using thin substrates. The laser beam was illuminated on substrates with thicknesses of 0.5 mm , 0.7 mm , 1.0 mm , and 2.0 mm , and a power meter was set below the substrates. The beam was focused on the surface of the sample ($Z_0 = 0$) using a lens with a focal length of 30 mm . The transmitted laser power was measured while continuing the irradiation after holes were drilled. Then, the hole sizes on the back surface were measured, then the fluence was calculated by dividing the laser power by the hole area. Figure 6 shows the calculated results. Five drilled holes were measured under each condition and the error bars show the standard deviation. In the figure, the average fluence at each depth was also plotted assuming that the same laser beam propagated in the atmosphere without the samples. From the figure, the average fluence of the actually transmitted laser beam was in accordance with the calculated value until $z = 1000 \text{ }\mu\text{m}$. In contrast, the measured fluence was 33 J/cm^2 at the depth of $z = 2000 \text{ }\mu\text{m}$, which was three times larger than the calculated fluence of 11 J/cm^2 .

These results were in accordance with the fact that drilling was achieved up to a depth of $2000 \text{ }\mu\text{m}$. The fact that the actually transmitted laser fluence was larger than the calculated value cannot be explained without taking account of the beam reflection on the hole wall. As hole walls with smooth surfaces, particularly at the tips of the holes, were obtained according to the previous observation [1], this is consistent with the fact that beam reflection occurred. Also, the slight curvature of the drilled holes while maintaining almost the same diameter cannot be explained without the beam reflection on the wall.

1.2.3.5 Influence of the focal length on the hole profile

The influence of the focal length was also evaluated. The beam was focused on the surface of the sample. Figure 7 shows the obtained profiles of the drilled holes along with the calculated spot radius at each location. As described before, the depths of the holes were $<400\text{ }\mu\text{m}$ and $<700\text{ }\mu\text{m}$ when using focusing lenses with focal lengths of 10 mm and 100 mm, respectively. In contrast, the drilled hole depths were $>2200\text{ }\mu\text{m}$ when using lenses with focal lengths of 50 mm, 30 mm, and 20 mm. In particular, the profiles were almost the same at depths of $>500\text{ }\mu\text{m}$. Thus, there was little influence of the spot radius at depths of $>500\text{ }\mu\text{m}$.

The obtained diameters were $10\text{--}15\text{ }\mu\text{m}$, $12\text{--}15\text{ }\mu\text{m}$, and $4.5\text{--}5.7\text{ }\mu\text{m}$ at the depths of $z = 500\text{ }\mu\text{m}$, $1000\text{ }\mu\text{m}$, and $2000\text{ }\mu\text{m}$, respectively. Thus, a diameter of $<15\text{ }\mu\text{m}$ and an aspect ratio of >110 were obtained in a depth range of $1700\text{ }\mu\text{m}$, i.e. from $z = 500\text{ }\mu\text{m}$ to $2200\text{ }\mu\text{m}$. In each case, the hole was not completely straight and curved in various directions by an amount on the order of μm until $z = 1700\text{ }\mu\text{m}$. However, at depths of $>1700\text{ }\mu\text{m}$, the hole curved in one direction. The part where the curving was observed was in accordance with the part where the redeposited layer was observed as described in the previous section.

Regarding the hole entrance, the diameter for the focal length of 20 mm was smaller than that for the focal lengths of 30 mm and 50 mm. This is thought to be due to the difference in the beam diameters as the obtained hole diameter for the focal length of 20 mm was in accordance with the beam spot size.

Here, the reason for not obtaining a deep hole when the lens with the focal length of 10 mm was used is considered. When using this lens, the beam divergence was larger than that using the other lenses. Thus, the incident angle of the laser to the hole wall (i.e., the angle of the incident light to the normal direction of the hole wall) was small. Generally, the reflectance of the glass increases with the incident angle and becomes 100% at an incident angle of 90° [12]. Thus, in the case of a small incident angle, the reflectance was small, leading to easier absorption on the wall. Therefore, the laser power delivered to the bottom of the hole was smaller, causing a shallower hole. The laser was absorbed gradually when reflection occurred on the hole wall. Thus, the absorbed power per area was smaller, causing the hole size to be maintained. To confirm this assumption, the fluence at the bottom of the hole was calculated, assuming that the beam was transmitted in air, without taking into consideration the reflection on the hole wall, similarly to in Fig. 5. The calculated value was approximately 30 J/cm^2 at the

center of the bottom of the hole. This value was in good accordance with that of the transmitted fluence, 28–40 J/cm² obtained from Fig. 6, and the fluence at this depth was lower than the processing threshold in the case of no reflection. Thus, a deep hole was not achieved because there was no reflection on the hole wall.

The reason for not achieving a deep hole in the case of a 100 mm focal length is considered to be the lower fluence at the point of irradiation due to the larger spot radius. Thus, the conditions were compared for the same fluence and different focal lengths. As the spot radius is in proportional to the focal length, the spot radius in the case of a 100 mm focal length is twice that for a 50 mm focal length. Thus, to obtain the same fluence, it is necessary to utilize a four times larger power. To compare the case of a 100 mm focal length with that of a 50 mm focal length in Fig. 7, a 400 μ J pulse is necessary. However, as such a large power could not be obtained owing to the specifications of the laser oscillator, 200 μ J pulses with a 100 mm focal length were compared with 50 μ J pulses with a 50 mm focal length. Although in the case of a 100 mm focal length, the depth was <1000 μ m, the same as in Fig. 7, which means that deep drilling was not achieved, in the case of a 50 mm focal length, the hole depth was >1700 μ m. Thus, the reason for the failure to achieve a deeper hole for a 100 mm focal length cannot be explained by the laser fluence.

When using a lens with a longer focal length, the beam divergence will become smaller, which results in effective transmission of the laser beam to the bottom of the hole due to the lower beam absorption on the hole wall. Thus, it also cannot be explained by beam propagation. In the case of using lenses with other focal lengths, i.e., 50 mm, 30 mm, and 20 mm, the beam spot radii were different but no difference in the hole radii was observed. Instead of the focusing condition, other causes such as beam reflection on the hole wall and the ejection of the debris are possible.

In the analysis in the previous studies [2], [6], [7], a ray-tracing method based on geometrical optics was utilized, and larger holes than those in this study were considered. In contrast, in this study, because smaller holes with a radius comparable with the spot radius were discussed, it is necessary for the influence of diffraction to be considered. Also, plasma was generated in the holes. A detailed investigation is planned as part of the author's future research.

1.2.4 Conclusions

In this study, the effect of the laser focusing conditions on high-aspect-ratio microdrilling using a UV laser was investigated. In particular, the influences of the focusing location and focal length on the hole shape were discussed and the following results were obtained. (1) The obtained hole depths were $>2200\text{ }\mu\text{m}$ when using focusing lenses with focal lengths of 50 mm, 30 mm, and 20 mm. In contrast, the obtained depths were $<800\text{ }\mu\text{m}$ in the case of 100 mm and 10 mm focal lengths. (2) Regarding the focusing location, depths of $>2000\text{ }\mu\text{m}$ were obtained using a beam that deviated from the focus by 70% of the Rayleigh length. (3) In the part with a depth of $>2000\text{ }\mu\text{m}$, the transmitted laser fluence was larger than that calculated from the beam profile. As a result, the laser light is thought to be reflected on the hole wall. (4) No difference in the hole shape was observed for focal lengths of 50 mm, 30 mm, and 20 mm.

1.2.5 References

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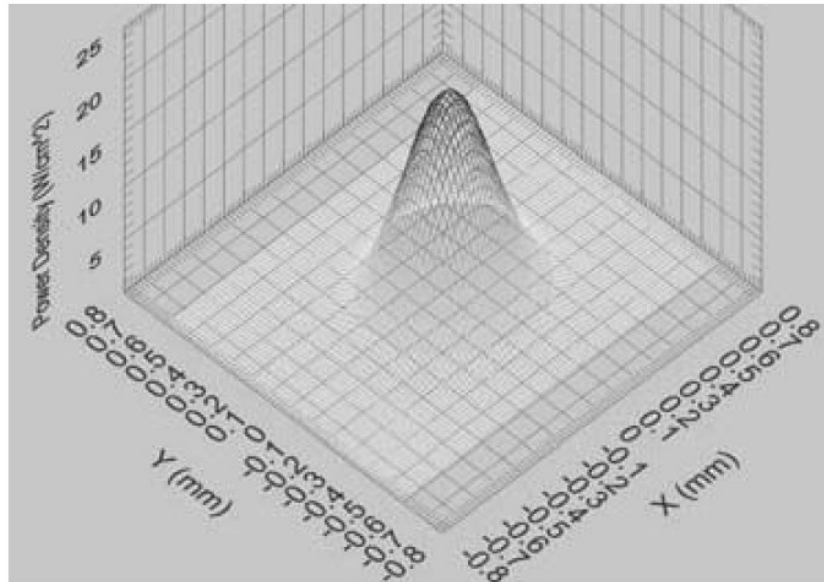


Fig. 1 Beam profile of the laser.

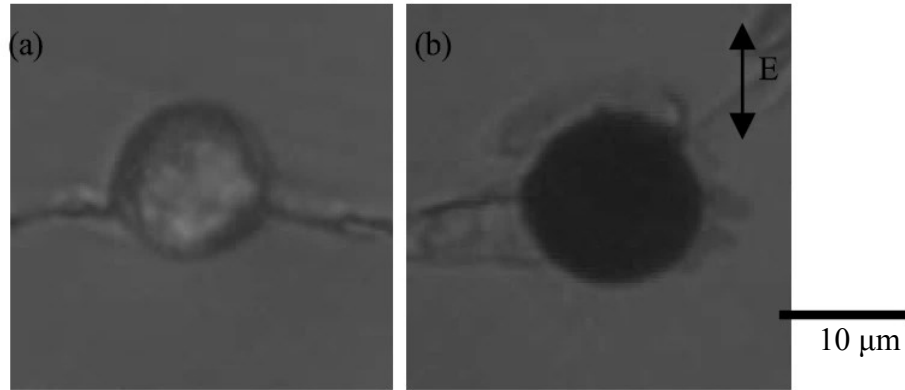


Fig. 2 Micrographs of the holes at a depth of 0.1 mm from the surface drilled with circularly (a) and linearly (b) polarized light. The focal length was 30 mm, the pulse energy was set at 100 μJ , and the number of pulses was 2000.

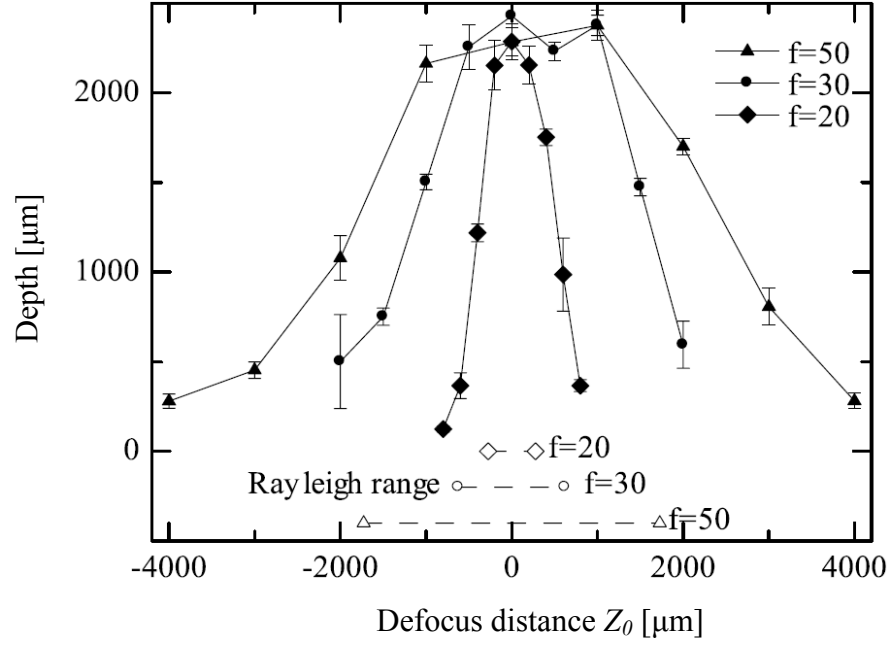


Fig. 3 Depths and Rayleigh ranges of holes drilled in borosilicate glass focused with focal lengths of $f = 50$ (▲), $f = 30$ (●), and $f = 20$ (◆). The pulse energy was set at $100 \mu\text{J}$, and the number of pulses was 5000.

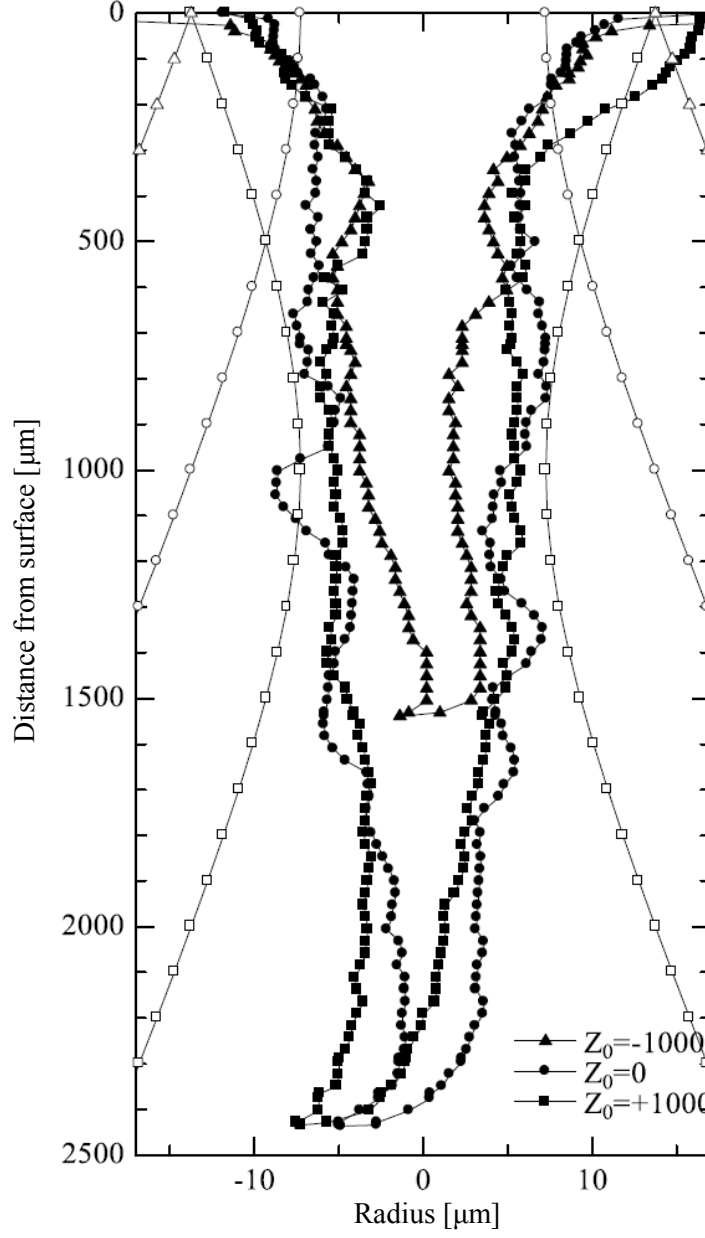


Fig. 4 Reconstructed depth profiles of holes drilled in borosilicate glass with focal positions at $Z_0 = -1000 \mu\text{m}$ ($\blacktriangle$), $Z_0 = 0 \mu\text{m}$ ($\bullet$), and $Z_0 = +1000 \mu\text{m}$ ($\blacksquare$). Calculated beam profiles with focal positions at $Z_0 = -1000 \mu\text{m}$ ($\triangle$), $Z_0 = 0 \mu\text{m}$ ($\circ$), and $Z_0 = +1000 \mu\text{m}$ ($\square$) are also shown. The focal length was 30 mm, the pulse energy was set at 100 μJ , and the number of pulses was 5000.

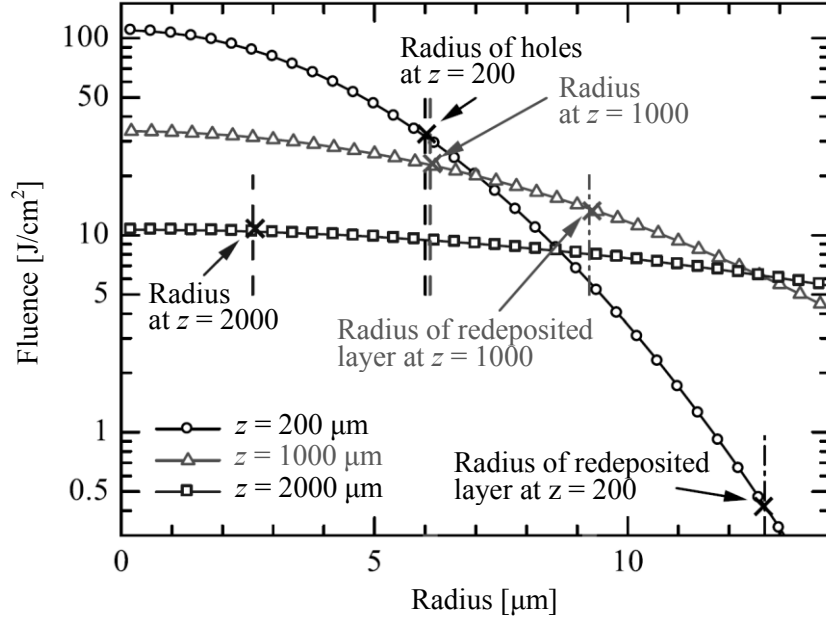


Fig. 5 Fluence profiles of the laser beam at $z = 200 \mu\text{m}$ ($\circ$), $z = 1000 \mu\text{m}$ (Δ), and $z = 2000 \mu\text{m}$ ($\square$). Broken lines represent hole radii. Chain lines represent the radii of the redeposited layers. The pulse energy was set at $100 \mu\text{J}$, the number of pulses was 5000, and the focal length was 30 mm.

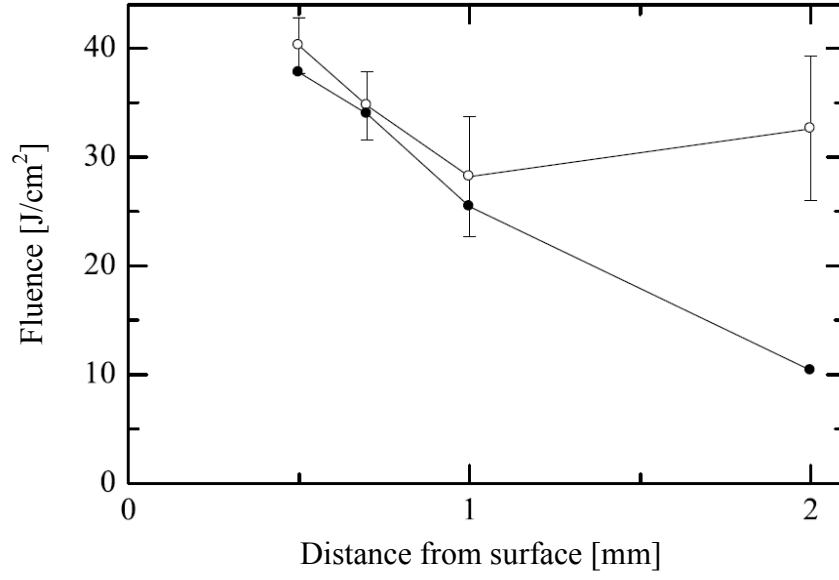


Fig. 6 Laser fluences (○) transmitted through glass plates with thicknesses of 0.5 mm, 0.7 mm, 1.0 mm, and 2.0 mm. Error bars show the standard deviation. Calculated laser fluences (●) in the same area assuming that the beam propagated in air without the samples. The pulse energy was set at 100 μJ and the focal length was 30 mm.

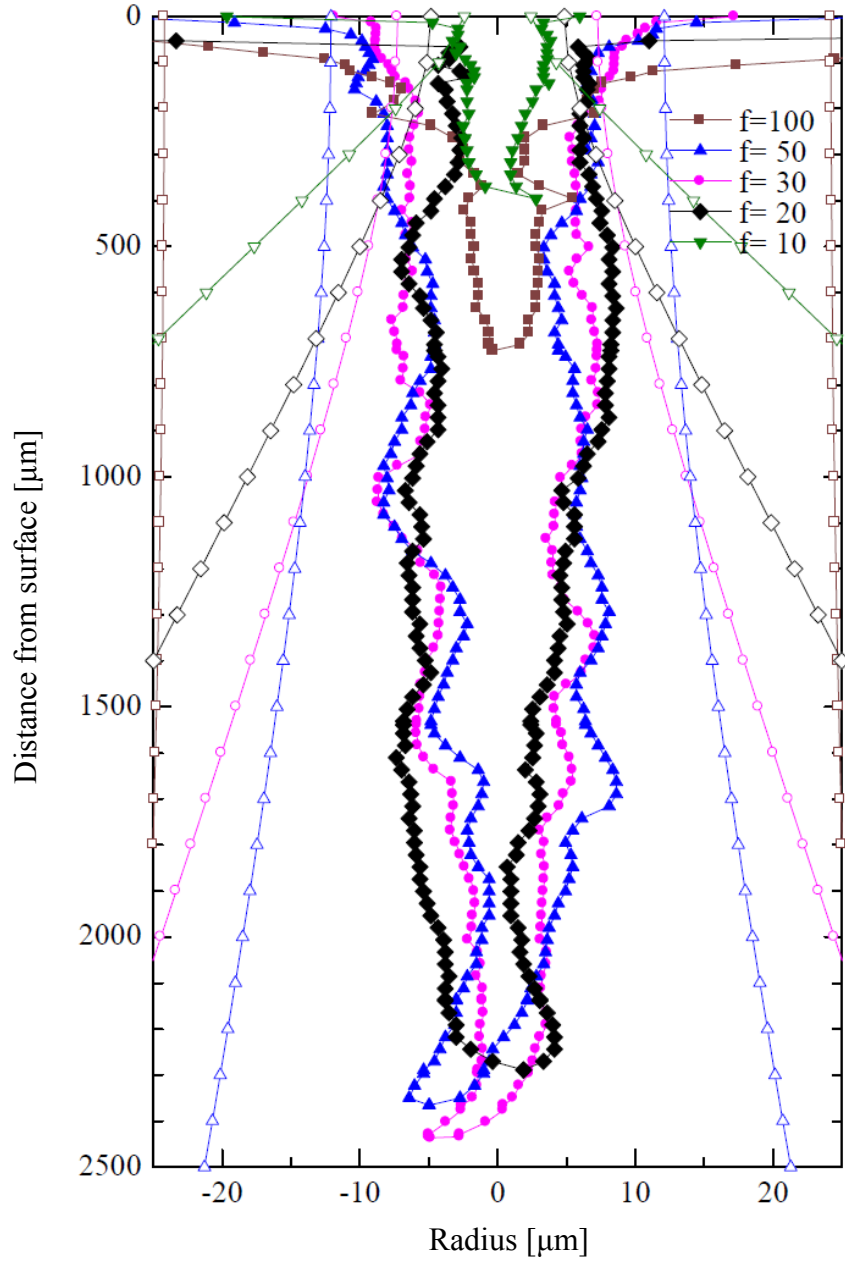


Fig. 7 Reconstructed depth profiles of holes drilled in borosilicate glass focused with focal lengths of $f = 100$ ($\blacksquare$), $f = 50$ ($\blacktriangle$), $f = 30$ ($\bullet$), $f = 20$ ($\blacklozenge$), and $f = 10$ ($\blacktriangledown$). Calculated beam profiles with focal lengths of $f = 100$ ($\square$), $f = 50$ ($\triangle$), $f = 30$ ($\circ$), $f = 20$ ($\diamond$), and $f = 10$ ($\triangledown$) are also shown. The focal position was set at $Z_0 = 0$, the pulse energy was set at $100 \mu\text{J}$, and the number of pulses was 5000.

1.3 Effect of heat accumulation

1.3.1 Introduction

With regard to laser drilling, in most cases, material was ablated by melting and vaporizing by using a pulse laser, and several researches have been conducted on the mechanism [1–5]. Among these, in the case of using a high-repetition-rate laser source, it was reported that the successive pulse was illuminated before the heat generated by the previous pulse was cooled, resulting in lowering energy for melting and vaporizing. As a result, improving the processing rate, and the lower threshold (i.e., a pulse energy necessary for the ablation) can be achieved.

Several studies have been reported on heat accumulation in the laser illuminated area. Ancona et al. [2–3] reported that stainless and copper were drilled using a femtosecond laser, then drilling rate increased with the repetition rate (50–975 kHz). However, drilled hole shapes were not discussed, instead of drilled hole depths. Brygo et al. [4] reported that ablation threshold decreased when processing polymer along with modeling the temperature rise of the workpiece by laser irradiation using one-dimensional heat equation. Hiramoto et al. [5] reported the repetition rate necessary for heat accumulation and its influence on the hole shape when SiN and acrylic polymer were drilled using a CO₂ laser. In this report, heat accumulation prevented achieving the high-aspect-ratio drilling.

Among these, the author tried high-aspect-ratio drilling using a laser having a high repetition rate by which higher processing rate and lower ablation threshold caused by heat accumulation were expected, and having a wavelength of UV region by which lower plasma absorption was expected. In the section 1.1, holes with a diameter of $8.2 \pm 3.1 \mu\text{m}$ and aspect ratio of more than 190 were obtained in borosilicate glass [6]. In the section 1.2, it was reported that more energy was propagated into the bottom of the hole by the reflection on the hole wall, by evaluating the influence of the beam profile [7]. Also, in the last report, the influence of the pulse width was investigated, reporting that deeper holes were achieved when the smaller pulse width was utilized [8].

In this study, by varying the repetition rate, the condition of ultra-fine and high-aspect-ratio drilling was clarified, and the influences of heat accumulation, hole shapes and shielding effect by molten debris were investigated.

1.3.2 Experimental setup

Figure 1 shows the experimental setup. The fourth harmonic of a Nd:YVO₄ laser was used as a light source, the same as in the previous sections. The beam was focused onto the surface of the workpiece using the lens with a focal length of 50 mm. Transmission images were captured by using a high-speed camera from the transverse direction to the laser beam for in situ observation. The delay generator (DG645, Stanford Research Systems) was used for controlling the camera shutter. Circularly polarized beam was used by using a $\lambda/4$ plate. As a laser specification, the pulse width of the laser became larger with the repetition rate of more than 20 kHz. Borosilicate glass (Pyrex®, Corning Inc.) for easier observation, the same as the previous sections, and sapphire substrates ((0001), Shinkosha) which were also transparent, and have different property on heat, were used as workpiece. Table 1 shows the properties.

1.3.3 Results and discussion

1.3.3.1 Influence of the repetition rate on the drilled depth

Figure 2 shows the relationship between pulse repetition rates and hole depths. Figures 2(a)–(c) represent drilled holes in borosilicate glass with pulse energies of 100 μJ , 20 μJ , and 5 μJ . Figure 2(d) shows drilled holes in sapphire with a pulse energy of 20 μJ . There was no data in the range of the higher repetition rate, which was due to power limitation of the oscillator. In each case, more than 10000 pulses did not induce drilling.

As shown in Figs. 2(a)–(c), in the case of borosilicate glass, the deepest holes were obtained by the pulses with energies of 100 μJ at 10 kHz, 20 μJ at 15 kHz, and 5 μJ at 25 kHz. The reason for the influence of the repetition rate will be discussed in the next section. In the case of pulse energies of 5 μJ at <10 kHz, and 20 μJ at >1 kHz, the depth was <150 μm even after 10000 pulses were illuminated. In the cases that the maximum depth was not reached, the difference on the repetition rate was not observed. For example, when 1000 pulses were illuminated, the depth was approximately 500 μm in all pulse energies, and approximately 1 mm when 2000 pulses.

Figure 2(d) shows the results on sapphire. The maximum hole depth depended on the pulse repetition rate, the same as borosilicate glass, and the maximum reached at 15 kHz. In contrast, the holes were deepened in the case of fewer pulse numbers, which is different from the case of borosilicate glass. This result was in accordance with that reported by Ancona et al [2–3].

1.3.3.2 Influence of repetition rate on hole shape

Figure 3 shows hole shapes when 1000 pulses were illuminated, plotted from the optical microscopic images. Figures 3(a)–(d) show the drilled holes corresponding to those plotted as ▲ in Figs. 2(a)–(d), respectively. The broken lines show calculated beam profiles. Although the hole tip was sometimes curving, the shape was plotted assuming that the diameter maintained without curving.

By varying the pulse energy and repetition rate, the diameter and depth changed. For example, in the case of 100 $\mu\text{J}/\text{pulse}$, the diameter increased with the repetition rates from 1 kHz to 10 kHz, as shown in Fig. 3(a). The diameter reached the maximum value at 10 kHz, and the diameter decreased at 15 and 20 kHz. In the previous report, redeposition of the ablated glass occurred in inner hole. Also in this study, the hole became thinner by the redeposition when the pulse number increased. However, in the case of changing the repetition rate, the diameter at the same depth was not changed. That is to say, at the same pulse number, the diameter increased with the repetition rate from 1 kHz, reached the maximum at 10 kHz, and decreased at 15 and 20 kHz.

Here, in Figs. 3(a)–(c), the diameter at the depth of approximately 300 μm , where almost no tapered shape was observed, was discussed. The maximum diameter was reached at 100 $\mu\text{J}/\text{pulse}$ at 10 kHz, 20 $\mu\text{J}/\text{pulse}$ at 15 kHz, and 5 $\mu\text{J}/\text{pulse}$ at 25 kHz. Compared between this result and that in Fig. 2, the repetition rate at which the depth reached its maximum, was in accordance with that at which the diameter reached the maximum when 1000 pulses were illuminated. In the section of 1.2, it was clarified that high value of fluence was maintained in the bottom of the hole which deviates from the focal point, because of the beam reflection on the hole wall. From the result, the possibility of more energy was delivered into the bottom of the hole due to the large diameter of hole entrance, was also considered. The reason will be discussed in the next section.

Li et al. [1] reported that by irradiating workpiece with laminated polymer layer, holes in the polymer became tapered shapes, then light reflected on the hole wall, resulting in higher fluence on the workpiece.

On sapphire, as shown in Fig. 3(d), the diameter reached the maximum at 15 and 20 kHz. The variation of the hole diameter caused by the repetition rate was smaller than the case of borosilicate glass, while hole depths increased with the repetition rate.

1.3.3.3 Estimation of temperature rise by heat analysis

From Fig. 2, as deep holes were obtained by higher repetition rate than 1 kHz, by irradiating the pulses with short intervals, successive pulses were illuminated before the heat by the previous pulses were cooled. Thus, heat was accumulated resulting in lower processing threshold, enabling to obtain deep holes. In this section, heat accumulation was investigated. In the inner holes, it is difficult to compare the phenomenon because of the influence of the beam waveguiding in the hole. However, from Fig. 2, in the case of 100 $\mu\text{J}/\text{pulse}$ at 1 kHz, 20 $\mu\text{J}/\text{pulse}$ at 5 kHz, and 5 $\mu\text{J}/\text{pulse}$ at more than 15 kHz, hole depths of more than 200 μm were obtained. Also on the surface, deep holes were obtained in the case of high repetition rate, which probably results in the lower threshold. Here, the influence of the heat accumulation on the surface of the workpiece was investigated. The influence was investigated by calculating the temperature rise by heat analysis. In fact, various types of phenomenon was included such as phase transition, interaction of laser beam with generated plasma, change in the hole shapes and fluences, and ejection of heated debris. As the laser wavelength was 266 nm, which means photo chemical reaction was assumed, precise analysis is difficult. Then, in this study, explanation of the reasons why deep holes were obtained by the higher repetition rate, was attempted by calculating the temperature rise on the surface of the workpiece when illuminating a laser, and comparing the processing results and calculated temperature rise in the different conditions.

Figure 4 shows the analysis model. The situation that a laser pulse having Gaussian profile was illuminated onto the surface of the workpiece, was considered. The analysis object was set as borosilicate glass. The heat diffusion length ($= \sqrt{D\tau_i}$) [11] until the successive pulse was illuminated at 1 kHz, was calculated as approximately 25 μm . Here, $D = k/\rho C$, where D represents heat diffusion coefficient, τ_i pulse cycle, k heat conductivity, ρ density, and C specific heat capacity. The workpiece size was assumed to be infinite because the workpiece was sufficient large compared with the heat diffusion length. The heat diffusion from the surface to the air was neglected, and initial temperature was assumed to be steady. It was also assumed that all of the laser power was absorbed on the surface of the material because of high absorption of

the laser beam. If the beam power transition was rectangular, the temperature rise at the center of the beam can be expressed analytically [12]:

$$\Delta T(0, 0, t^*) = \frac{2}{\pi} \theta_c \arctan(2t^{*1/2}) \quad (t < \tau_l, \text{ i. e., during irradiation}) \quad (1)$$

$$\Delta T(0, 0, t^*) = \frac{2}{\pi} \theta_c \left\{ \arctan\left(2t^{*\frac{1}{2}}\right) - \arctan\left[2(t^* - \tau_l^*)^{\frac{1}{2}}\right] \right\} \quad (t > \tau_l, \text{ i. e., during pulse intervals}) \quad (2)$$

Here, the relative change was discussed, instead of the absolute value of temperature. In the equations, $t^* = Dt/w_0^2$ and $\theta_c = \sqrt{\pi} I_0 w_0 / 2k$. T represents time, τ_l pulse width, w_0 beam radius, I_0 maximum fluence. The properties were set using the values in the table 1. The pulse energy was set at 20 μJ , pulse width 8 ns, beam radius 11.85 μm which is calculated value from the equation in the section of 1.2 [7]. If the irradiating energy per second was P , the maximum fluence is $2.8 \times 10^8 \text{ W/cm}^2$ estimated from $I = 2P/\pi w_0^2$. The temperature dependency of the property was neglected.

Figure 5 shows the analysis result in the case that 5 $\mu\text{J/pulse}$ was illuminated to the borosilicate glass. This figure shows temperature transition at the center of the beam on the surface after one pulse was illuminated. The temperature increased by the laser beam, then the temperature decreased by the heat conduction. Here, the temperature just before the successive pulse was illuminated, was discussed. The successive pulse was illuminated after 0.1 ms at 10 kHz and 1 ms at 1 kHz. The temperature rises were calculated as 730 K and 34 K, respectively. Therefore, the temperature at 10 kHz increased more than 20 times higher than that at 1 kHz.

Table 2 shows the values of temperature rise when the second pulse was illuminated on the surface at each repetition rate. The results were compared with Fig. 2. Colored conditions in the table represent that more than 200 μm was achieved by 1000 pulses in Fig. 2. In the case of 5 $\mu\text{J/pulse}$, if the temperature rise was less than 730 K (less than 10 kHz repetition rate), processing was not occurred, while if more than 1130 K (15 kHz), the depths of more than 200 μm were observed. Likewise, in the case of 20 $\mu\text{J/pulse}$, processing not occurred when the temperature rise was lower than 140 K (1 kHz), while deep holes were obtained from more than 1250 K (5 kHz). The temperature rises in both conditions were in good accordance. Thus, the ablation threshold is thought to be lowered by heat accumulation. In the case of 100 $\mu\text{J/pulse}$,

glass was drilled from 1 kHz, while the temperature rise was estimated to be 680 K at 1 kHz. It is considered that ablation occurred even the temperature rise was small because the pulse energy of 100 $\mu\text{J}/\text{pulse}$ was large enough than 20 $\mu\text{J}/\text{pulse}$ and 5 $\mu\text{J}/\text{pulse}$.

This experimental result, as described before, neglected many causes such as phase transition, more precise consideration is necessary on the absolute temperature. However, because the hole shapes in the vicinity of surface of the workpiece have not big difference, it is considered that temperature rise was calculated by each irradiation condition, thus, relative comparison was valid.

Then, the reason why the ablated amount was steady at more than a certain repetition rate, was considered that the temperature was risen enough, and influence of the difference became smaller. On the other hand, on sapphire having high heat conductivity, the influence of the heat accumulation occurred at a higher repetition rate. Thus, it was considered that processing speed increased with the repetition rate.

From these results, it was confirmed that glass was drilled by lower pulse energy due to the influence of the heat accumulation by increasing the repetition rate. Although this calculation was based on smooth surfaces, if holes became deep, the processing threshold was lowered by a high repetition rate. That is to say, the transferred energy was lowered in the deep hole where the beam deviated from the laser focus. For example, considering the depth where the fluence was equal to 5 μJ , ablation stopped at less than 10 kHz, and still propagated at 15 kHz. Thus, deeper holes were obtained. Therefore, the fact that the hole depth increased with the repetition rate in the section of 1.3.3.1, was explained by the lowered ablation threshold caused by heat accumulation on the surface.

1.3.3.4 Influence of heat accumulation and hole shapes

From the results in 1.3.3.2 and 1.3.3.3, the reasons why the hole depths were depending on the repetition rate was implied to the influences of diameter of the hole entrance and heat accumulation. Here, the following two cases were compared to elucidate the influence: (1) preparing pre-drilled holes with same diameters of the hole entrance, pulses with various repetition rates were illuminated, (2) preparing pre-drilled holes with the different diameters of the hole entrance, pulses with the same repetition rates were illuminated.

1.3.3.4.1 Heat accumulation effect

After preparing pre-drilled holes with the depth of approximately 600 μm by irradiating 1000 pulses with the energy of 20 μJ at 10 kHz, processing speed was investigated by irradiating different repetition rates.

Figure 6 shows a transmitted image when 0, 100 and 200 pulses were illuminated at each repetition rate. The ablated depths were measured from the bottom of the holes in the case of 0 pulse as shown in the broken line in the figure. The modified layer which is considered as heat affected layer, was observed. As the range of the modified layer was largest at 10 kHz, the higher temperature was expected. Figure 7 shows the relationship between the ablated depth and number of pulses. Just after irradiation start, processing speed was the highest at 10 kHz, and lowest at 1 kHz. Processing was stopped at the depth of 100 μm at 1 kHz, 300 μm at 5 kHz, and 600 μm at 10 kHz.

From the result, as the higher repetition rate enables high processing rate and deep drilling independent of the influence of the size of the hole diameters, deep holes were obtained by the influence of the heat accumulation.

1.3.3.4.2 Influence of hole shapes

Then, the hole depth change was investigated by illuminating pulses with the same repetition rate after preparing pre-drilled hole with the different diameters of hole entrance. The depth of pre-drilled holes were 500 μm , the diameters were 10 μm , 15 μm and 25 μm (measured at the depth of 200 μm). After that, by changing repetition rates with a pulse energy of 20 μJ , the reached depths were measured after enough pulses (10000 pulses) were illuminated.

Figure 8 shows the relationship between the maximum hole depth and diameter of the pre-drilled hole. Except for the case of 1 kHz repetition rate, the drilled depth was increased with the hole diameter. From the result, there is a possibility that the dependence of repetition rate on the maximum hole depth was owing to the influence of the diameter of the hole entrance. Only in the case of 1 kHz, the tendency was different. The drilled depth was smaller when the diameter became larger. This reason has not been clarified yet.

Then, the hole depth increased with the repetition rate, which is thought to be caused by the heat accumulation. However, the tendency was different only at 20 kHz. The depth was smaller than that at 15 kHz. Although the depth of pre-drilling hole was 500 μm , more than 1600 μm hole was obtained depending on the irradiation conditions, thus the influence of the diameter of the newly drilled hole, was also considered. Here, the maximum depth was investigating by

changing the depth of the pre-drilled hole from 400 to 1800 μm . The diameter of the pre-drilled hole was set at approximately 25 μm . Figure 9 shows the relationship between the maximum hole depth and the depth of pre-drilled holes, in the condition of 15 kHz and 20 kHz. As a result, the drilled depth was larger at 15 kHz, even if the pre-drilled hole depth was larger. Thus, the reason why the deeper holes were achieved in case of 15 kHz than 20 kHz, cannot be explained by the difference of the hole diameter. Then, by taking account of heat accumulation, deep holes should be obtained in the case of 20 kHz. For this reason, the reason for the maximum depth in the case of 15 kHz, is thought to be different causes from heat accumulation and the difference in the diameter of hole entrance.

1.3.3.5 Reason for shallow hole when high repetition rate

The reason for obtaining deeper holes by increasing the repetition rate has been considered. In contrast, the drilled depth decreased from more than 25 kHz. This reason was thought to be the influence of the pulse width and ejection of the molten debris.

Because of the specification of the laser oscillator, the laser pulse width depended on the repetition rate, i.e., 8 ns at less than 15 kHz, 9 ns at 20 kHz, and 11 ns at 30 kHz. In the previous report [8], the pulse width was artificially widened by splitting the beam and propagating through the different length (5 ns) and combining, then the influence of the pulse width on the hole depth was investigated. As a result, 10000 pulses with 100 μJ at 10 kHz were illuminated, the reached depth was 90% compared with the case that pulse width was not widened. On the other hand, in this study, in the case of 10000 pulses with 100 μJ , the depths were 3000 and 2000 μm at 10 and 20 kHz, respectively, that is the difference was more than 70%. The repetition rate, by which the deepest hole was obtained, was also dependent on the energy. The deepest holes were obtained at 100 μJ /pulse at 10 kHz, 20 μJ /pulse at 15 kHz, and 5 μJ /pulse at 25 kHz. Regarding these results, as it is difficult to be explained only by the influence of the pulse width, the other influence is thought to be larger.

Here, the influence of the shielding effect of the laser beam caused by the ablated molten debris is considered. When a high energy laser beam was illuminated to the workpiece, the surface was rapidly heated, leading to the ejection of molten debris. This vaporized workpiece also absorbs the laser beam, causing the plasma generation. The speed was several 1000 m/s in

the vicinity of the workpiece. Although the speed decreases with the distance from the surface, the debris might be moved in the range of more than several of mm.

In the case of a high repetition rate, the successive pulse was illuminated in shorter period after the previous pulse was illuminated. Compared with shallow hole, it takes a longer time for debris to be ejected in the deep hole. Thus, the influence of the repetition rate will appear at a lower repetition rate. Assuming that the molten debris moved by a steady speed v from the bottom of the hole, and that the processing stopped at the depth where the molten debris cannot reach the hole entrance, the relationship between the hole depth L and pulse interval t (reciprocal of the repetition rate) was expressed as $L = vt$, which is in proportional relation.

Figure 10 shows the relationship between the depth and pulse interval in the case of higher repetition rate compared with the case that the deepest holes were obtained in Figs. 2(a)–(c). From the figure, the relationship between the depth and pulse interval was in proportional. From the result, in the case of a higher repetition rate, the beam cannot reach the bottom of the hole caused by the shielding effect resulting from the molten debris, then the process was stopped. The straight lines in the figure show the approximate line at each pulse energy, and by the slope of the lines, averaged speeds were measured as 28–36 m/s. This value was smaller than that of several 100–1000 m/s in the case of irradiation to titanium alloy reported by Man [13]. This difference is thought to be owing to the difference in the fluence. They utilized the fluence of 3.5×10^9 W/cm², which is 10 times larger than the value in this study, which is close to the ablation threshold.

Although, in the case of the sapphire, the hole was shallower than the case of glass, the repetition rate by which the maximum depth was obtained, was same as glass. Evaluation of the repetition rate in the case of different material, and in situ observation of the molten debris are a part of the author's future work.

1.3.4 Conclusions

In this study, the influence of the heat accumulation with regard to high-aspect-ratio drilling was investigated, the following results were obtained. (1) Regarding borosilicate glass and sapphire, the obtained hole depths were dependent on the repetition rate, and peaked in a certain repetition rate. (2) Although the depth was not dependent on the repetition rate in the case of low number of pulses irradiating to borosilicate glass, the deep holes were obtained by increasing the higher

repetition rate using sapphire. (3) The reason why the hole depths were differed by the repetition rate, is that heat was accumulated by the increased repetition rate, and the diameter of the hole entrance was different. (4) When the repetition rate was increased further, the drilled hole depths decreased because the diameter of the hole entrance was decreased, and because the shielding effect occurred by the molten debris.

1.3.5 References

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Table 1 Thermal properties of the materials at room temperature [9–10].

	ρ g/cm ³	C J/g · K	K W/cm · K
Borosilicate glass	2.23	0.71	0.01
Sapphire	3.98	0.75	0.42

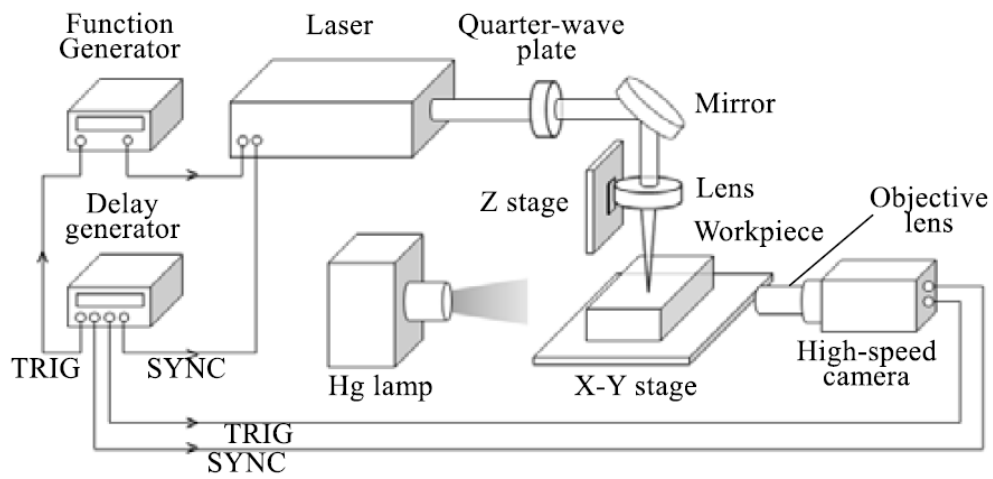
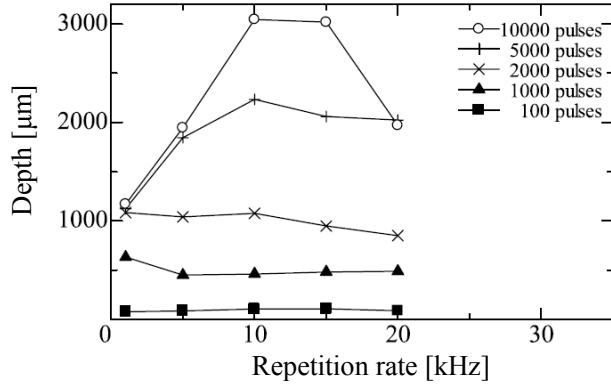
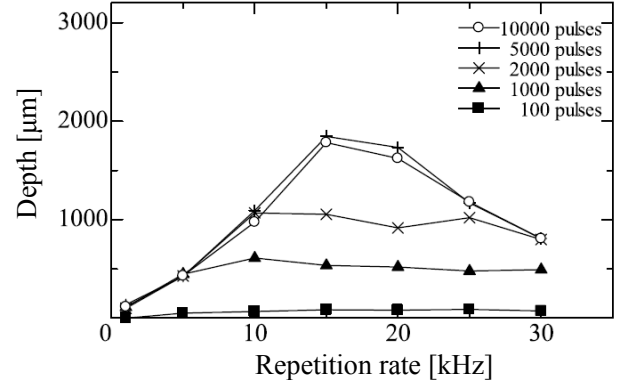


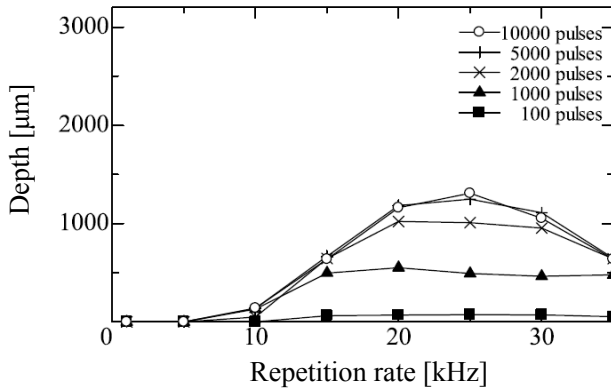
Fig. 1 Schematic drawing of experimental setup.



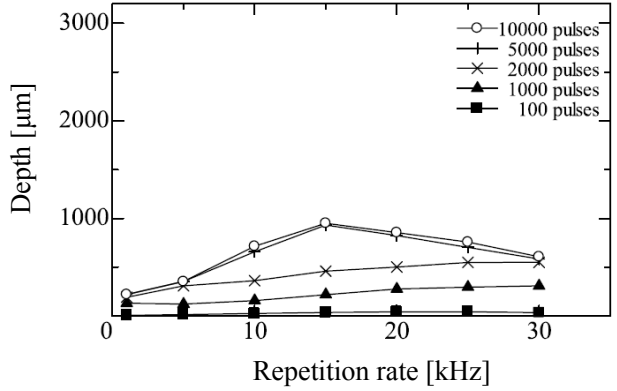
(a) Borosilicate glass, 100 $\mu\text{J/pulse}$



(b) Borosilicate glass, 20 $\mu\text{J/pulse}$

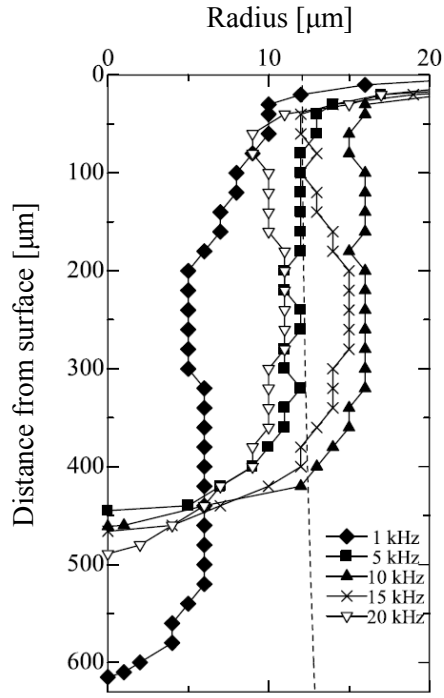


(c) Borosilicate glass, 5 $\mu\text{J/pulse}$

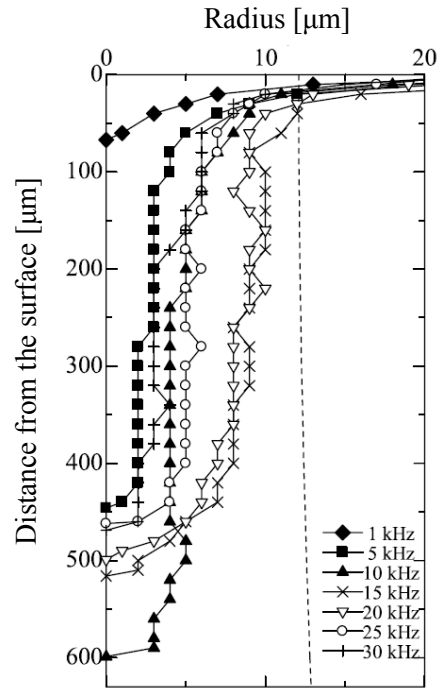


(d) Sapphire, 20 $\mu\text{J/pulse}$

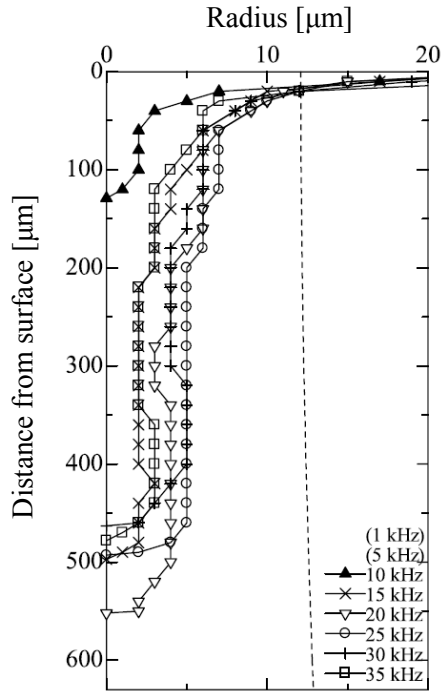
Fig. 2 Influence of repetition rates and shot numbers on depth of the holes on (a)–(c) borosilicate glass, (d) sapphire drilled with each repetition rates and pulse energies.



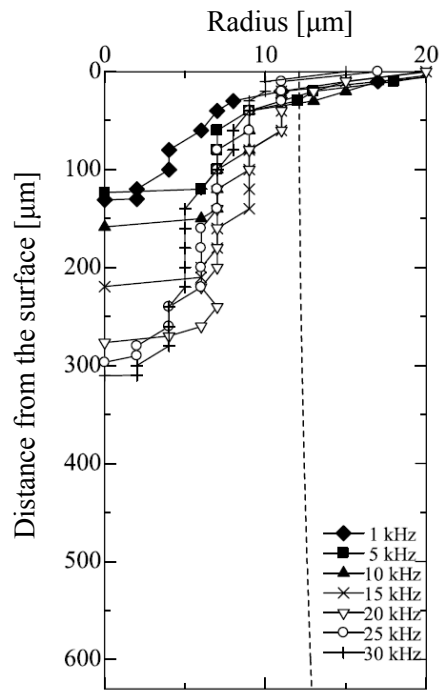
(a) Borosilicate glass, 100 $\mu\text{J}/\text{pulse}$



(b) Borosilicate glass, 20 $\mu\text{J}/\text{pulse}$



(c) Borosilicate glass, 5 $\mu\text{J}/\text{pulse}$



(d) Sapphire, 20 $\mu\text{J}/\text{pulse}$

Fig. 3 Transverse sectional shapes of the holes on (a)–(c) borosilicate glass, (d) sapphire, drilled with 1000 pulses at each repetition rate and pulse energy. Broken line shows the beam profile.

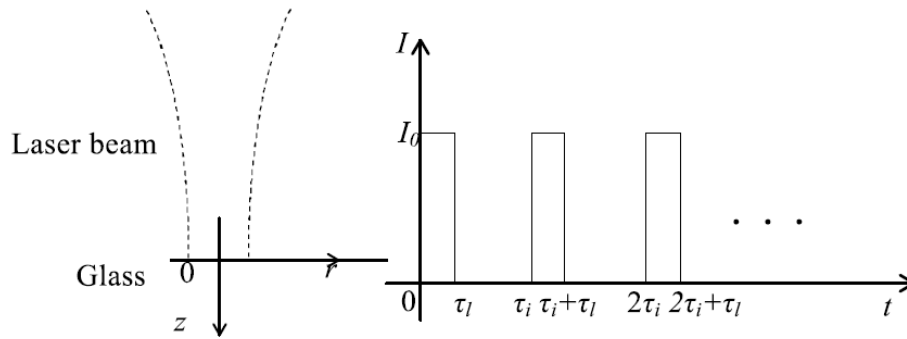


Fig. 4 Schematic drawing of the analytical model.

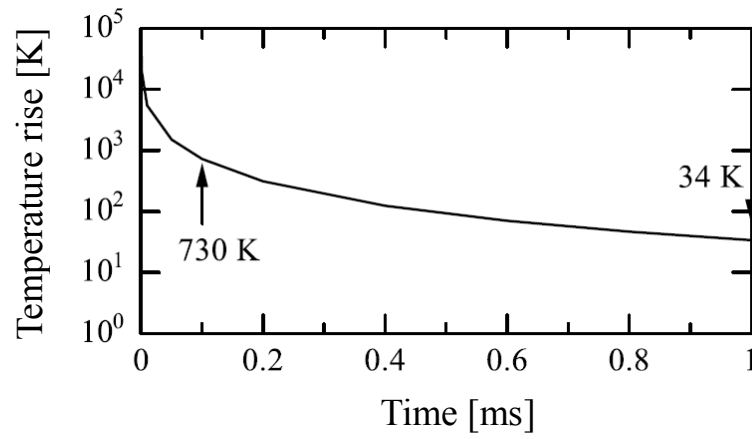


Fig. 5 Result of heat analysis of temperature rise on borosilicate glass drilled with 5 μ J pulses at 10 kHz and 1 kHz.

Table 2 Temperature rise at the center of the beam drilled with different repetition rates and powers when the second shot arrives at the surface.

	15 kHz (67 μ s)	10 kHz (100 μ s)	5 kHz (200 μ s)	1 kHz (1 ms)
100 μ J	22640 K	14530	6250	680
20 μ J	4530	2910	1250	140
5 μ J	1130	730	310	30

Note: values in parentheses are pulse duration.

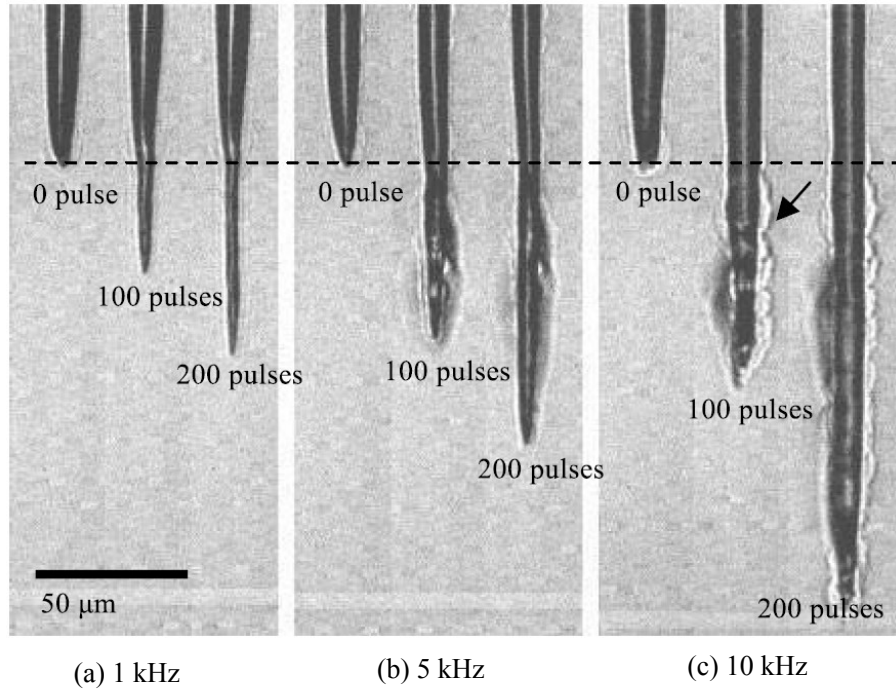


Fig. 6 Shadowgraphs of the holes drilled with (a) 1 kHz, (b) 5 kHz, (c) 10 kHz pulses. The pulse energy was at 20 μ J. Broken line shows measurement start.

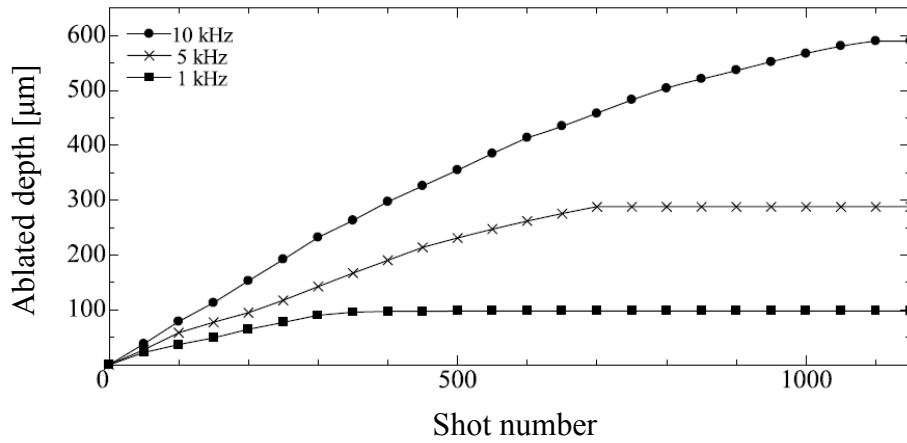


Fig. 7 Ablated depth vs shot number with pulses at 1, 5, 10 kHz. The pulse energy was set at 20 μ J.

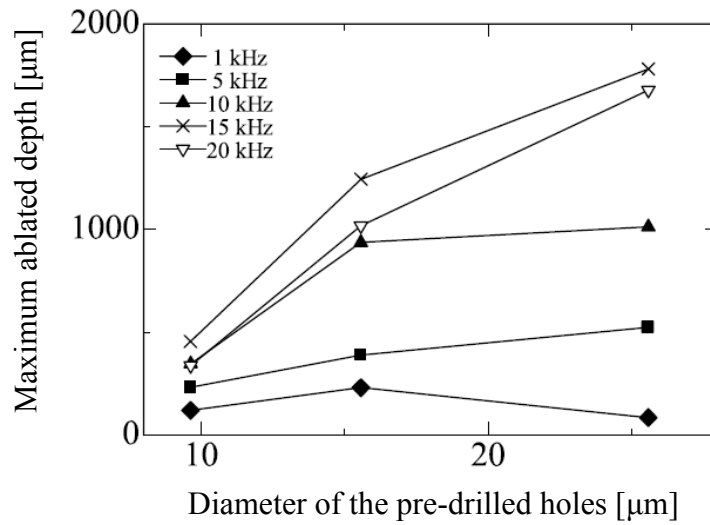


Fig. 8 Relationship between maximum ablated depth of the holes vs. diameter of the pre-drilled holes. Depth of the pre-drilled holes was approximately 500 μm.

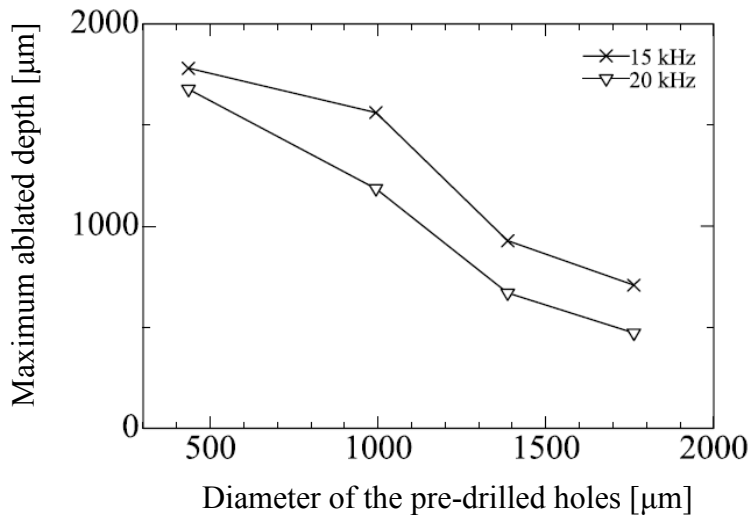


Fig. 9 Relationship between maximum ablated depth of the holes vs. depth of the pre-drilled holes. Diameter of the pre-drilled hole was approximately 25 μm.

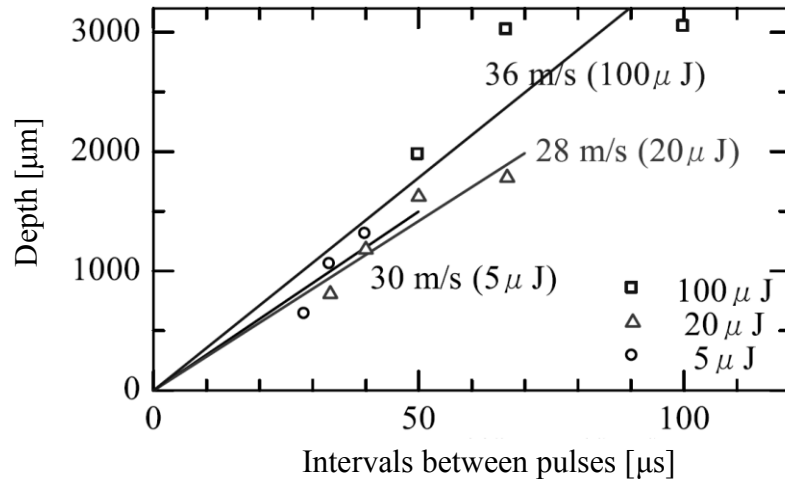


Fig. 10 Relationship between maximum ablated depths of the holes vs intervals between pulses. 10000 pulses were illuminated.

Chapter 2

Internal modification of glasses by continuous-wave laser backside irradiation (CW-LBI)

2.1 Study on the mechanism of glass modification process

2.1.1 Introduction

Three-dimensional processing of the interior of transparent materials, particularly glass, using a femtosecond laser has been studied. The modified zone in the glass resulting from this method can be used for optics such as waveguides [1], diffraction gratings [2], and optical memories [3] because of the change in the refractive index. However, this technique has not been utilized in industry because of its low processing efficiency; for example, the processing speed when using a femtosecond laser is $\sim 50 \mu\text{m/s}$.

A new method of modifying glass using a continuous-wave laser, named continuous-wave laser backside irradiation (CW-LBI) [4–6], in which CW laser illumination induces a change in the refractive index without cracking the glass, was previously proposed. The process of glass modification by the CW-LBI method involves the following steps. (1) An absorbent material placed on the backside of the glass is heated by a laser beam through the glass. (2) The part of the glass in contact with the heated absorbent material is also heated by thermal conduction from the absorbent material and then starts to absorb the laser beam because of its enhanced absorption due to the increased temperature. (3) The heated glass also heats the surrounding zone, which also starts to absorb the laser beam. By repeating this process, the heated spot moves backward (toward the light source) until it reaches the point where the fluence is insufficient to heat the glass because of defocusing. The modified zone is formed by heating and quenching.

The modification speed exceeds 100 mm/s , which is much faster than that using a femtosecond laser. The modified zone has a cylindrical, two-layered concentric structure, as shown in Fig. 1. A cross section of the modified zone is shown in Ref. [5]. In the inner zone, the

fictive temperature and density become higher than those in the non-modified zone, as revealed by Raman spectroscopy. In the outer zone, the fictive temperature remains unchanged; however, the outer zone is subjected to tensile stress due to the decrease in volume of the inner zone [5]. The change in the fictive temperature depends on the heating and quenching history. Therefore, to apply this method to microprocessing such as drilling assisted by etching and to control the size of the modified zone, the change in fictive temperature must be investigated in detail and the mechanism of its modification needs to be clarified.

As a similar phenomenon to CW-LBI, the fiber fuse effect has been reported [7]. This phenomenon involves melting and void formation in the core of optical fibers, which is triggered by a defect or bent point when a high-power laser is illuminated. Several studies have been carried out on this phenomenon. In particular, the dependence of the fiber temperature on the absorption coefficient, which is related to defects generated by the heating of the fiber, was reported by Hand and Russell [8]. Shuto considered that SiO₂ was generated from a defect and that the absorption coefficient increases as a result of plasma formation [9]. Dianov et al. estimated the temperature of the fiber during fusion from its radiation spectrum [10]. Golyatina et al. [11] and Yakovlenko [12] formulated the dependence of the fiber temperature on the absorption coefficient and estimated the temperature distribution in the core by solving the heat equation, and also considered the reason for void formation. However, a comparison of the modified zone and temperature history with the aim of applying the modified zone to microprocessing has not been performed to the best of our knowledge.

In this study, the process of glass modification by the CW-LBI method was investigated. The heated spot in the glass during its modification was observed with a high-speed camera. The time-lapsed behavior of the transmitted laser power was measured to evaluate the absorbed laser energy. Moreover, the time-lapsed temperature distribution was calculated and the results of the calculation were compared with experimental results.

2.1.2 Experimental procedure

The apparatus used for observation was installed in the apparatus used for modification, which was identical to that used in previous research [4–6]. Figure 2 shows the experimental setup for (a) in situ observation and (b) measurement of the transmitted laser power. An Ar-ion laser (TSM-20, Coherent, Inc.) with a wavelength from 454.5 to 514.5 nm and a TEM₀₀ beam mode

was used as the processing laser because of the high-power emission in a continuous wave in the range of wavelengths of transmission through the glass. The laser light was focused onto an absorbent material through a workpiece with a lens, the focal length of which was ~ 170 mm, and the focused spot diameter was calculated to be ~ 36 μm . Quartz glass with a thickness of 10 mm was used as the workpiece. Copper foil with a thickness of 10 μm was used as the absorbent material and was attached to the glass on the opposite side to the processing laser because the reflectivity of copper is low at the wave length of Ar-ion laser light. A He–Ne laser (GLT2331, NEC) provided illumination for the observation. The movement of the heated spot was observed perpendicularly to the Ar-ion laser beam using a high-speed camera. Light with a wavelength outside the range of 600 to 800 nm was filtered using optical filters to reduce the intensity of the scattered Ar-ion laser beam and thermal radiation from the heated zone.

To measure the power of the transmitted laser beam, the absorbent material has to be eliminated. Thus, a technique to induce a branched modified zone was utilized. As shown in Fig. 2(b) the beam was split using a polarization beam splitter. The absorbent material was illuminated vertically with one beam (beam A) and the other beam (beam B) irradiated the glass perpendicularly to beam A. The two beams were adjusted to intersect in the glass. The output laser power of beam B exiting the glass was measured using a photodiode (S2281, Hamamatsu Photonics K.K.) after passing through a neutral density filter for attenuation.

2.1.3 Numerical simulation model

To control the size of the modified zone and fictive temperature, it is helpful to clarify the temperature distribution around the heated spot. However, it is difficult to monitor the temporal temperature distribution in glass because the modification speed is higher than 100 mm/s. Therefore, the time-lapsed temperature distribution in this process was calculated numerically.

Figure 3 shows a schematic image of the simulation model. Two-dimensional axisymmetric cylindrical coordinates were used because both the laser beam and the modified zone were symmetrical to the optical axis (z -axis in Fig. 3). In this calculation, the preliminarily heated part on the backside was assumed to be illuminated by a laser with a constant diameter along the z -axis. Thermal radiation was neglected, and only heat conduction was considered because the thermal radiation was much smaller than the heat conduction [11]. The temperature $T(r, z, t)$ at

time t at a location with radius r and depth z was calculated utilizing the following two-dimensional heat conduction equation in the cylindrical coordinate system:

$$c\rho \frac{\partial}{\partial t} T(r, z, t) = \frac{\partial}{\partial z} \left[k \frac{\partial}{\partial z} T(r, z, t) \right] + \frac{1}{r} \frac{\partial}{\partial r} \left[rk \frac{\partial}{\partial r} T(r, z, t) \right] + \alpha(T)I(r, z, t) \quad (1)$$

where c is the specific heat, ρ the density, k the thermal conductivity, and $I(r, z, t)$ the laser intensity. The temperature dependence of these properties was not taken into account. $\alpha(T)$ is the absorption coefficient, which is set as

$$\alpha(T) = \begin{cases} 0, & T < T_1 \\ \alpha_p(T - T_1)/(T_p - T_1), & T_1 \leq T \leq T_p \\ \alpha_p, & T > T_p \end{cases} \quad (2)$$

where α_p is the maximum absorption coefficient reached at temperature T_p and T_1 is the temperature at which glass starts to absorb light. A wavelength of $\lambda = 1064$ nm was used to calculate the absorption coefficient, which is the wavelength used in the case of a fiber fuse [10], because there is no data for green light. The initial and boundary conditions were set as

$$T(r, z, t)|_{t=0} = \begin{cases} T_0, & z < z_{kb} \\ T_p, & z = z_{kb} \end{cases} \quad (3)$$

$$\frac{\partial}{\partial r} T(r, z, t)|_{r=r_{ib}} = 0, \quad \frac{\partial}{\partial z} T(r, z, t)|_{z=0, z=z_{kb}} = 0 \quad (4)$$

where T_0 is the room temperature, z_{kb} the location of the initially heated part, which is the surface of the glass on the opposite side to the laser source, and r_{ib} is the value of r at the boundary of the calculated region, in which the Neumann boundary conditions were applied. Regarding the laser parameters, a Gaussian energy distribution was set in the r direction at $z = 0$ μm :

$$I(r, 0, t) = \frac{2P}{\pi(w/2)^2} \exp\left(\frac{-2r^2}{(w/2)^2}\right) \quad (5)$$

where P is the laser power and w the spot diameter. The Beer–Lambert law, which represents the attenuation of laser intensity, was applied to the space between $z = z$ and $z = z + \Delta z$ [13]:

$$I(r, z + \Delta z, t) = I(r, z, t) \exp(-\alpha(T)\Delta z) \quad (6)$$

where z is the mesh width. Heat equation (1) was solved by an explicit finite-difference method using the following values: $r = 1 \text{ } \mu\text{m}$, $z = 1 \text{ } \mu\text{m}$, $t = 10^{-7} \text{ s}$, $i = 200$, $k = 1500$, $w = 36 \text{ } \mu\text{m}$, $P = 7.5\text{--}20 \text{ W}$, $\alpha_p = 560 \text{ cm}^{-1}$, $T_0 = 293 \text{ K}$, $T_l = 1973 \text{ K}$, and $T_p = 2273 \text{ K}$.

2.1.4 Results and discussion

2.1.4.1 In situ observation of the heated spot

The formation of a modified zone 1 mm away from the absorbent material was observed at various laser powers, and Fig. 4 shows typical results. The beam irradiation direction is from left to right in the figures. Figs. 4(b), (d), and (f) show images captured 500 μs after Figs. 4(a), (c), and (e), respectively. In these photographs, white emission was observed at the tip of the modified zone that moved toward the light source (to the left in the figures). Diagonal striped patterns were observed in the white emission because the background image was subtracted from the original image to reduce the interference fringes produced by the illumination. The white emission mainly resulted from thermal radiation, not from the scattered light of the Ar-ion laser, because the laser beam was filtered. At a power of 7.5 W, as shown in Fig. 4(a), two white emissions were observed. These two emissions were also observed for the case of a fiber fuse [14]; however, the reason for the existence of two emissions has not yet been clarified. The emission on the left became longer toward the right-hand side with increasing power and became connected to the emission on the right-hand side (Fig. 4(c)) to form an elliptical shape (Fig. 4(e)). Note that the white emission did actually become longer, and the increased length was not an artifact due to multiple exposures. Because the exposure time was set at 1 μs and the modification speed was approximately 200 mm/s, the heated spot shifted $\sim 0.2 \text{ } \mu\text{m}$ in each frame, a much smaller distance than the length of the white emission. Stripes were observed around the white emission. These stripes are considered to result from the change in the refractive index.

The contrasting shades indicated by arrows in Fig. 4(b) did not change after a certain time, which means that they were the interface of the permanently induced two-layered modified zone.

The characteristics of these two zones were revealed as follows [5]. The inner zone was modified by laser heating. The fictive temperature was estimated to be $\sim 1900 \text{ K}$. The etching rate and hardness were greater than those in the unmodified zone owing to the increased fictive temperature. The outer zone was modified by the tensile stress resulting from the densification

of the inner zone. In the outer zone, the etching rate was higher and the hardness was lower than those in the unmodified zone.

Thus, the permanently modified zone formed within 1 ms after the heated spot passed through the zone. When the power was 15 W, the permanently modified zone as above could not be identified from Fig. 4(f) because the large number of shades prevented the identification of the modified zone. However, after sufficient time passed, two shades were observed that were similar to those observed at 7.5 W. These patterns were caused by heating as well as by changes in the fictive temperature, and many shades were observed when the laser power was larger because more energy was provided. From the photographs, the diameter of the outer zone was found to be 47 μm at 7.5 W, 51 μm at 10 W, 60 μm at 15 W, and 62 μm at 20 W. These values were confirmed to be in accordance with those obtained by post observation using a microscope. At a power of 7.5 W, periodic dots were observed in the center of the modified zone, which were voids. Voids were also reported for the case of a fiber fuse [10].

2.1.4.2 Amounts of light absorption and scattering on the heated spot

It was reported that the fusion of a fiber was caused by the increase in the light absorption with the increased temperature [9]. The laser beam in this study is expected to be absorbed at the heated spot if the mechanism of modification by CW-LBI is the same as that of the fiber fuse. The powers of beams A and B in Fig. 2(b) were set at 13 and 10 W, respectively.

Figure 5 shows the temporal behavior of the transmittance, which is normalized by the initial value. The moment when the illumination starts is set at 0 s. First, the illumination heated the absorbent material and then the glass in the vicinity of the illuminated spot started to absorb the light. The heated spot moved toward the light source along beam A. During this time (0–0.055 s), the transmitted laser power was constant because the glass did not absorb beam B. The transmitted laser power of beam B started to decrease (at ~ 0.055 s) when the heated spot reached the intersection of beams A and B. The heated spot then branched off and moved along beams A and B. The heated spot moved along beam B during 0.055–0.08 s, and the amount of transmitted laser power was $\sim 5\%$. Therefore, the remaining 95% of the laser beam was absorbed or scattered in the glass. Finally, absorption at the heated spot ceased because the heated spot became out of focus and the fluence at the point decreased to below the threshold fluence required to maintain the absorption [6]. The amount of transmitted laser power became constant

at ~20% (0.1 s). The reason that the amount of transmitted laser power did not return to 100% after the absorption had finished was that beam B was scattered by the voids or at the boundary of the modified zone.

Beam A was constantly focused on the backside of the glass. However, the glass in this part did not ablate but melted, similarly to the absorbent material, according to the post observation. This is considered to be because the fluence was insufficiently high to ablate the glass and absorbent material because the laser beam was scattered by the modified zones and voids.

During the absorption, scattered green light, which had the same color as the laser source, was also observed. Therefore, not only absorption but also scattering reduced the transmitted laser power. The scattering was assumed to be caused by the change in the refractive index and the formation of plasma. When the refractive index is changed by heating, the refractive index varies continuously with the temperature distribution; thus, there is no clear boundary. Therefore, scattering due to the change in the refractive index is not dominant. On the other hand, it is well known that reflection occurs as a result of plasma formation in glass [9]. Quantitative estimation of the amount of reflection is planned as future research.

Figures 6(a) and (b) respectively show the distributions of the temperature and the energy density absorbed by the glass at a power of 10 W when the maximum temperature is at a distance of 1 mm from the absorbent material ($z = 500 \mu\text{m}$). The maximum temperature was calculated to be 11500 K. The calculated temperature is believed to be higher than the actual temperature because the thermal radiation and temperature dependences of the properties, such as the specific heat and thermal conductivity of the glass, were neglected in the simulation.

Figure 7(a) shows the distributions of temperature and absorbed energy density along the z -axis (broken line in Fig. 6(a)), and Fig. 7(b) shows the temperature distribution at $z = 500 \mu\text{m}$ in the r direction (dotted line in Fig. 6(a)). As shown in Fig. 7(a), the temperature first rapidly increased to above ~11500 K and then decreased because of the attenuation of the laser beam in the high-temperature zone. As shown in Figs. 6 and 7(a), more energy is absorbed on the side of the light source in the high-temperature zone. The energy of the laser that was not absorbed in the high-temperature zone and approached the other side of the light source was calculated to be 0.02 W, which is 0.2% of the laser input. In contrast, in the experiment, it was measured to be ~5%, as shown in Fig. 5. Although the reasons for this difference have not yet been clarified, the deviation of the beam profile from the Gaussian profile, the instability of the beam, and

diffraction caused by the change in the refractive index due to the temperature distribution are considered to have caused the difference.

2.1.4.3 Evaluation of validity of calculated results

It was difficult to evaluate the validity of the calculated results directly by the comparison of temperatures because of the difficulty of measuring the actual temperature distribution. Therefore, the experimental and calculated results were compared using the modification speed, which was calculated from the high-speed-camera images obtained in the experiment. Figure 8 shows the relationship between the modification speed and power. At each power, the calculated result was ~200 mm/s higher than the experimental result.

Dianov et al. measured the radiation spectrum of a fiber fuse, confirmed that the spectrum is similar to that of a black body, and estimated the temperature by assuming the spectrum to be that of a black body [10]. They reported that the temperature increased from 6000 to 10500 K when the laser power was increased from 2 to 38 W. The mode field diameter, which was defined as the distance between points where the intensity falls to $1/e^2$ times the maximum value, was 4 μm . The mode field diameter corresponds to the spot diameter of a Gaussian laser beam, and their value of 4 μm was much smaller than 36 μm , the spot diameter in this report; therefore, the fluence was markedly different. It was also reported that at the same fluence, the peak temperature increased with decreasing mode field diameter. Hence, a simple comparison between our result and their result is inappropriate.

Therefore, the calculated temperature is discussed on the basis of the threshold fluence. The fluence of the illumination at a laser power of 10 W was calculated to be four times larger than the threshold fluence required to maintain the absorption reported in Ref. [6]. The maximum temperature was calculated to be ~11500 K in this study. On the other hand, in Ref. [10], the temperature was ~6000 K when the fluence was four times larger than the threshold required to induce the fiber fusing, smaller than the calculated value in this report. In Ref. [10], the temperature was estimated using the radiation spectrum, meaning that it was estimated by the summation of data for radiation from the heated spot, not that from the small region with the highest temperature. Therefore, the temperature of the highest point is believed to be higher than 6000 K.

It is inferred that the calculated temperature was larger than the measured value. This conclusion is in accordance with the result that the calculated speed of the heated spot was higher than the measured result as shown in Fig. 8. The reasons for this are considered to be that the thermal radiation was neglected, the reflection due to plasma formation was not considered, the actual transmittance was larger than the calculated transmittance, and properties such as the specific heat and thermal conductivity, which are dependent on temperature, were neglected.

2.1.4.4 Diameter of the modified zone

In the inner modified zone, the fictive temperature was ~ 1900 K [5]. According to Fig. 8, the heated spot moved at a speed exceeding 100 mm/s. Assuming that the fictive temperature was changed in the zone in which the temperature increased to above 1900 K, the diameter of the inner modified zone and that of the zone where the temperature was increased to above 1900 K should correspond. The actual diameter of the inner modified zone was compared with that of the calculated region in which the temperature increased to above 1900 K for each power. As shown in Fig. 9, the calculated region was ~ 45 μm in diameter, and the diameter increased slightly with increasing laser power. In the experiment, on the other hand, the diameter increased from ~ 35 to ~ 45 μm with increasing laser power from 7.5 to 20 W. At a larger laser power, the results correspond well; however, the difference between the results is greater at a smaller laser power. This was because, as mentioned above, the calculated temperatures were higher than the actual temperatures because the thermal radiation, reflection, the temperature dependence of the thermal properties, and other factors were neglected. At the same time, the region in which the temperature increased to above 1900 K was calculated to be smaller than that found experimentally, particularly when the total absorbed energy was small; therefore, the difference between the experimental and calculated results increased with decreasing laser power.

2.1.4.5 Explanation of the modification process

From these results, the modification process can be explained as follows. First, the heated zone in the glass absorbs the laser beam and is heated to ~ 11500 K. The glass in the neighborhood of the heated zone is also heated by thermal conduction, and the laser beam starts to be absorbed on the side of the light source. The opposite side to the light source is cooled because the

absorption in the heated spot reduces the laser power on the opposite side of the light source. As a result of repeated cycles of heating and cooling, the heated spot moves toward the light source. The cycle of heating and cooling finishes within ~ 1 ms at each point, quenching increases the fictive temperature of the glass, and the inner modified zone forms. Evaluation of the change in density and the stress distribution and clarification of the mechanism causing the formation of the outer modified zone are planned as future work.

2.1.5 Conclusions

The process causing the internal modification of glass by CW-LBI was investigated in this study, and the following results were obtained. In situ observation of the heated spot during the process clarified that the modification was induced within ~ 1 ms by rapid heating and quenching. The transmittance of the heated spot was $\sim 5\%$, and the remaining 95% of the laser power was absorbed or scattered during the process. The calculation revealed that the maximum temperature reaches ~ 11500 K, and that more laser energy is absorbed on the light-source side of the heated spot than on the other side. The calculated modification speed was larger than the experimentally obtained value, but the variation of the speed with the power was in qualitative agreement.

2.1.6 References

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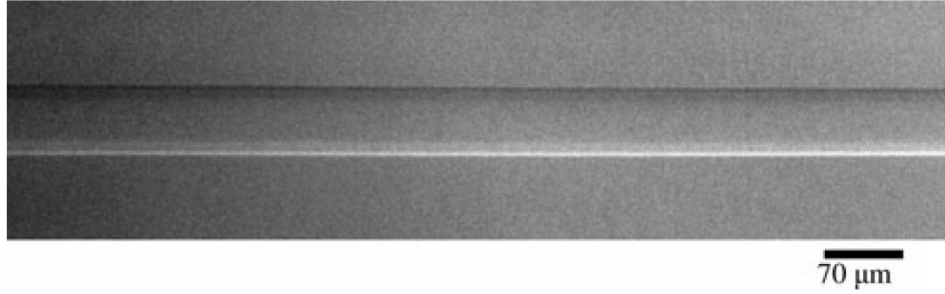


Fig. 1 Optical micrograph of transverse section of modified glass.

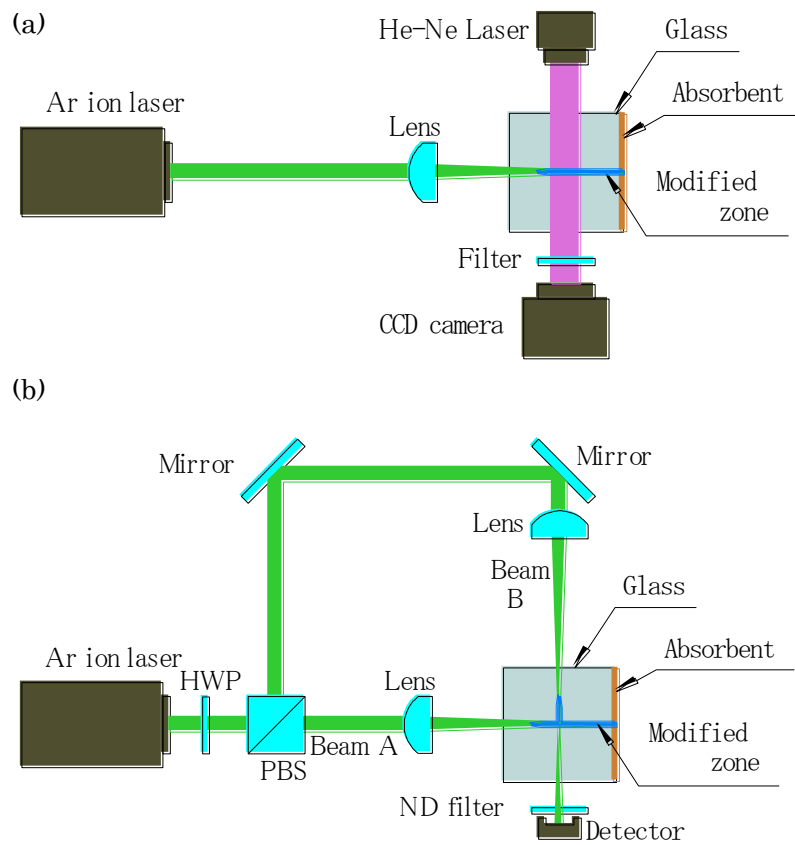


Fig. 2 Schematic drawing of experimental setup for (a) in situ observation and (b) measurement of transmitted laser power. HWP: half-wave plate, PBS: polarized beam splitter.

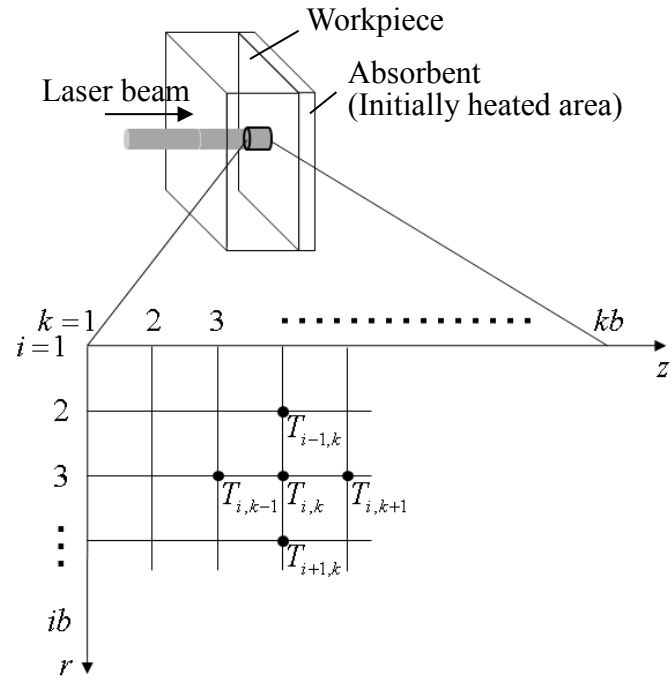


Fig. 3 Schematic drawing of the simulation model.

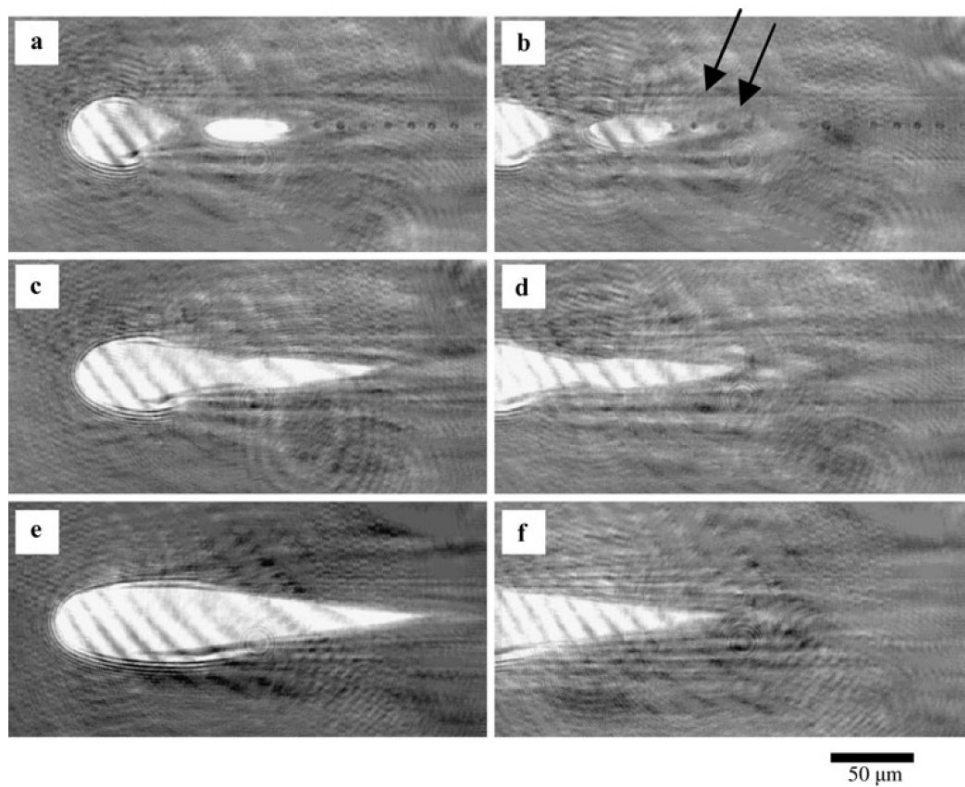


Fig. 4 Time-lapsed photographs taken during modification of glass. The laser power was (a), (b) 7.5 W, (c), (d) 10 W, and (e), (f) 15 W. The images in (b), (d), and (f) were taken 500 μ s after the images in (a), (c), and (e), respectively. The distance from the absorbent material was 1 mm.

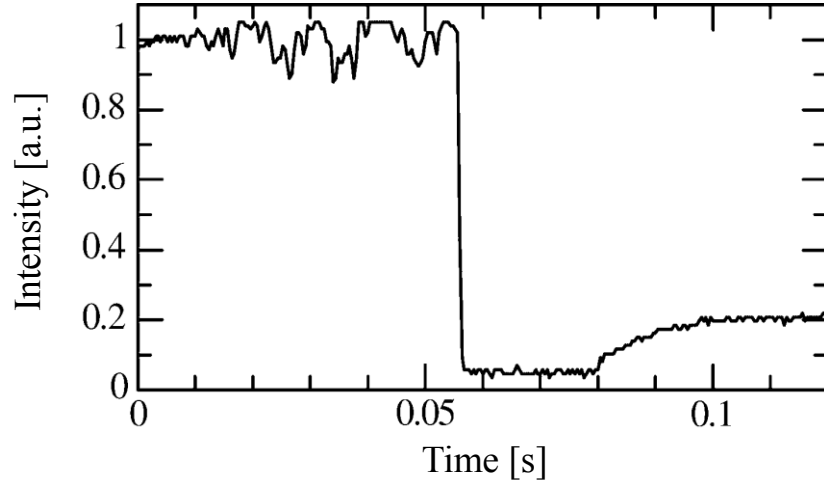


Fig. 5 Temporal behavior of transmittance of glass during CW-LBI.

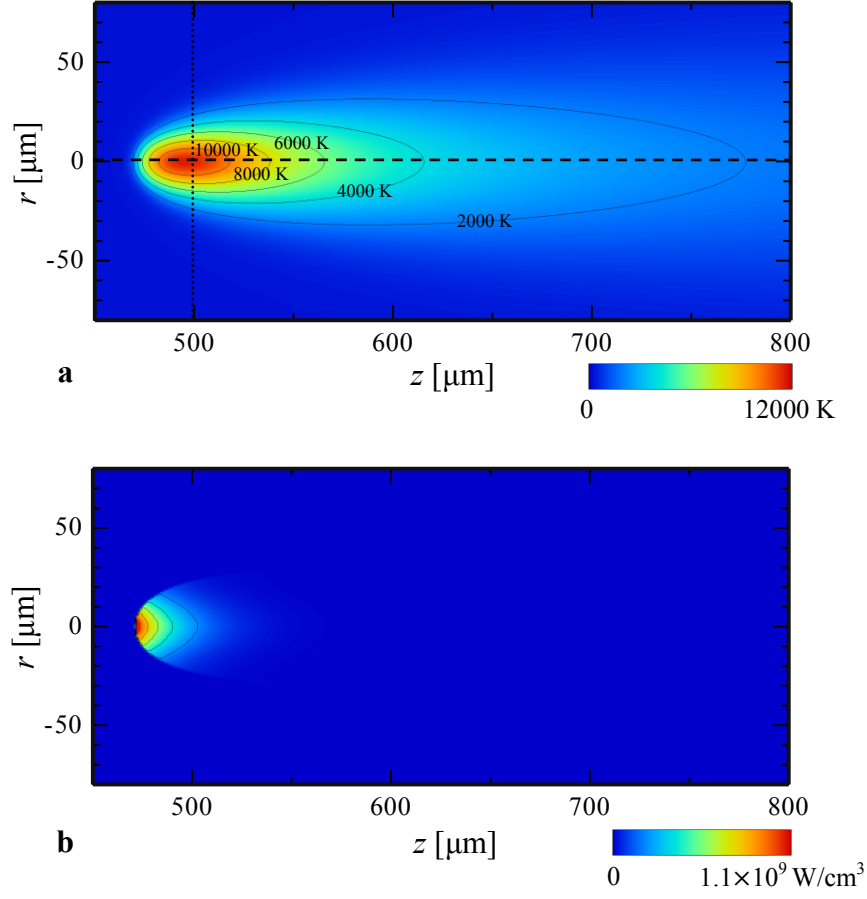


Fig. 6 Time-lapsed (a) temperature and (b) absorbed energy density distributions in glass during modification. The laser power was 10 W and the distance from the absorbent material was 1 mm. Contour lines were drawn every (a) 2000 K and (b) $2.0 \times 10^8 \text{ W/cm}^3$.

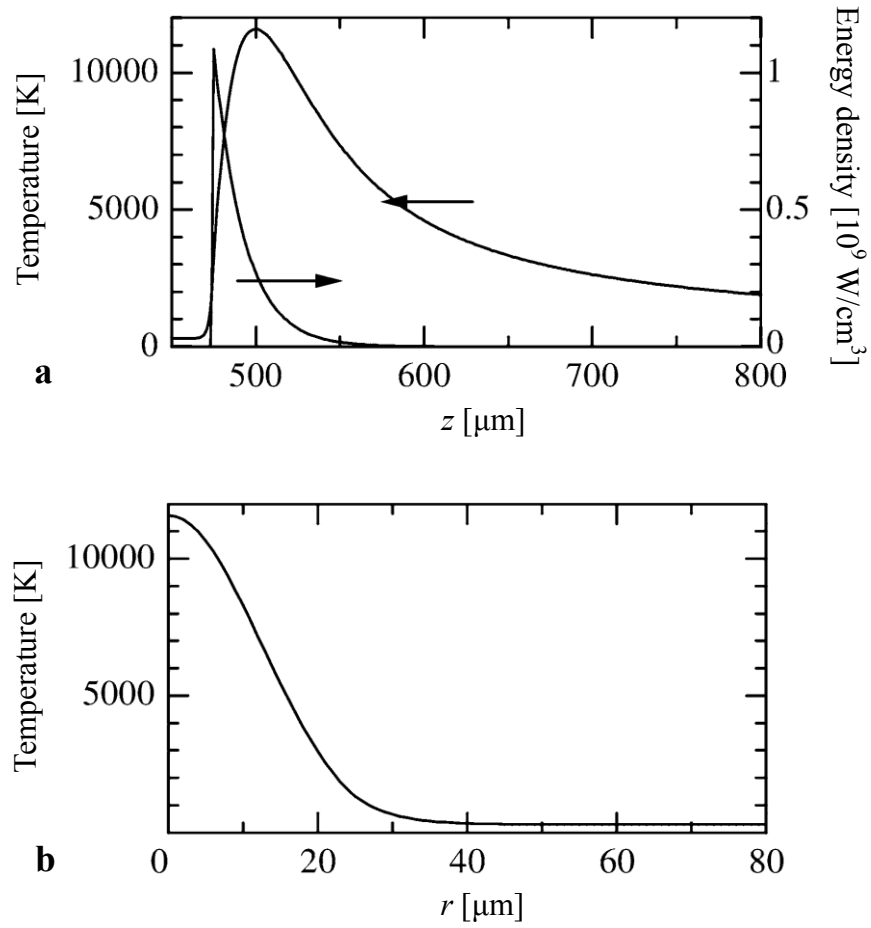


Fig. 7 Temperature distributions along (a) z -axis (broken line in Fig. 5) and (b) r -axis (dotted line in Fig. 5). The beam power was 10 W and the distance from the absorbent material was 1 mm.

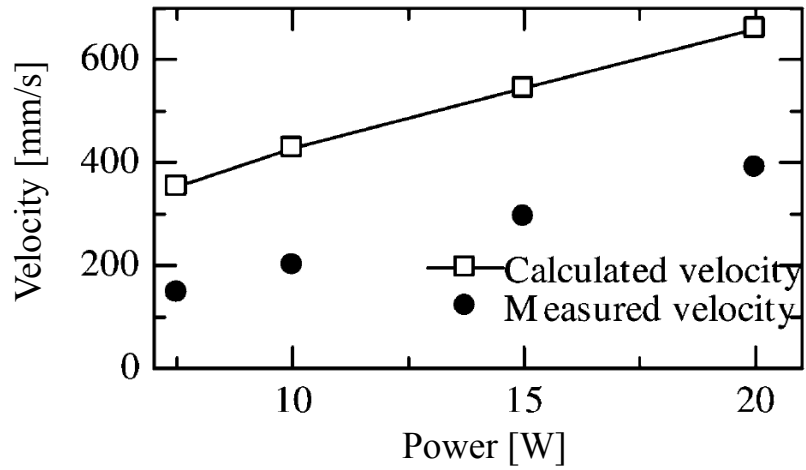


Fig. 8 Effect of power of laser beam on modification speed. The velocities were measured at a distance of 1 mm from the absorbent material.

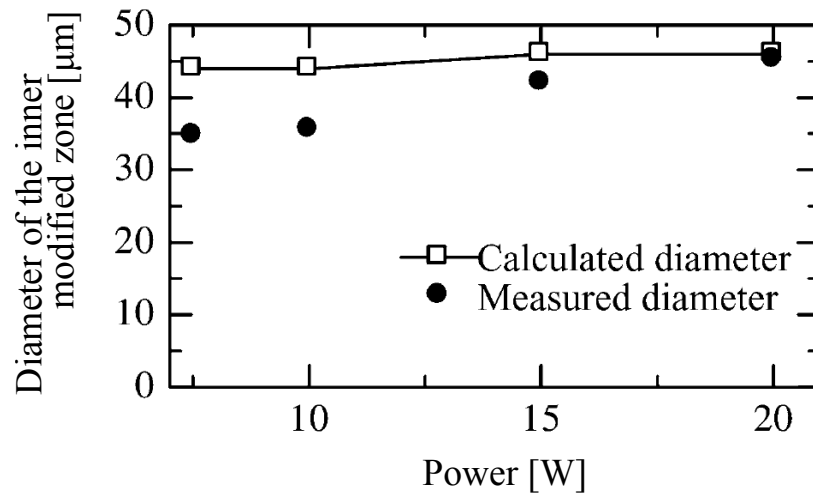


Fig. 9 Effect of power of laser beam on diameter of inner modified zone.

2.2 Phenomenon of metal particle implantation into borosilicate glass

2.2.1 Introduction

Light has the ability to move matter remotely [1]. Optical tweezers, which are commonly used in life science [2], control microscale objects, such as cells, in fluids. However, controlled objects must adhere to the surfaces of bases to maintain their position, which restricts three-dimensional applications. If laser manipulation is achieved in transparent solids, for example, a glass, the manipulated matter can be placed wherever in the glass, which is expected to be applied to the fabrication of optical devices and micro-electromechanical systems (MEMSs). Many research studies [3–5] on the fabrication of a waveguide in a glass have been conducted to achieve three-dimensional optical devices. However, such devices must be placed on the surface of the glass, which restricts three-dimensional device and high-density packaging.

It has been reported that microspheres are controlled in solids by local melting, that is, ice plates are melted locally by laser heating, and volume change during phase change generates fluid flow, which moves a polystyrene sphere [6]. The microspheres were controlled only two-dimensionally and the ice must be maintained below 0 °C.

In this research, the author proposes a new technique of manipulating a metal particle in borosilicate glass. A metal particle that is heated by laser illumination heats and softens the surrounding glass by radiation and conduction. A softened glass enabled metal particle migration. To obtain the metal particle, a metal film or foil was deposited on the back surface of the glass and illuminated with a laser through the glass. This new technique of placing metal particles in a glass expands the variety of the devices and increases the flexibility of design.

2.2.2 Experimental procedure

As shown in Fig. 1, the sample used is borosilicate glass with a thickness of 10 mm (Pyrex®, Corning 7440, Corning Inc.), which is placed on an X-Y-θ stage. A 1-μm-thick platinum - palladium film was deposited by sputtering using a 90 wt.% platinum and 10 wt.% palladium target on the glass sample, unless otherwise noted. Other metals, such as nickel, tin, tantalum, silver, copper and austenitic stainless steel (SUS304), were tested. Tantalum, tin and silver were deposited with a thickness of 1 μm. Copper, nickel and SUS304 foil with a thickness of 10 μm were placed on the glass sample and sandwiched with another glass plate to ensure good contact

between the sample and the metal foils. A CW laser beam (Ar ion laser, TSM-20, Coherent Inc.) oscillating with a single line at a wavelength of 514 nm was used to illuminate the film through the glass. The laser beam was focused on the platinum film by a convex lens with a focal length of 170 mm without any relative scanning motion of the laser focus during laser irradiation. Side-view shadowgraph images under white-light illumination were obtained to monitor the process in situ. A blue-IR cut filter (cutoff wavelength: 390 nm) was placed in front of a CCD camera to prevent the detection of scattered laser light and thermal emission.

To analyze the implanted particle, the glass was cut and polished to intercept the particle, then coated with carbon and observed with an energy-dispersive X-ray spectroscopy system (EDX, Link ISIS 300, Oxford Instruments Plc.) installed with a field-emission scanning electron microscopy system (FE-SEM, JSM-6301F, JEOL Ltd.).

2.2.3 Results and discussion

After laser irradiation was started, a bright emission was observed at the neighborhood of the platinum film, and then, the emission moved backward (toward the light source). Images of the bright emission are shown in Fig. 2. Figures 2(a)–(c) show the bright emission moving backward and a permanent modified zone in the area through which the bright emission passed. After laser irradiation (Fig. 2(d)), a black particle was observed in an area where the bright emission was observed.

To reveal the black particle, the glass was cut, polished and observed with the EDX. Figure 3 shows the spectra of the particle and map results. The white circle observed in the secondary electron image (Fig. 3(a)) is the particle. The EDX spectra of the circle in Fig. 3(a) and the nonirradiated area are shown in Fig. 3(b). No peaks of silicon and oxygen, which are the components of the glass, were observed, but platinum and palladium peaks were observed from the particle. X-ray mapping results (Figs. 3(c) and (d)) indicate that the platinum particle and the glass show a clear boundary. Therefore, interestingly, the platinum particle was implanted into the glass. It is noteworthy that EDX analysis detects neither platinum nor palladium from the trajectory of platinum particle migration, that is, the permanent modified zone in Fig. 2. Heating and quenching by laser illumination cause refractive index change [7]; therefore, the trajectory of platinum particle migration is observed in Fig. 2.

After the particle implantation, the platinum film was observed from the back surface. No platinum film was observed in the area with a diameter of $\sim 300\ \mu\text{m}$. A part of the removed platinum was believed to be implanted into the glass. The glass was softened at its center with a diameter of $\sim 100\ \mu\text{m}$.

The particle migration was terminated at a certain point by defocusing and started again by increasing the laser power or focusing. The particle was able to migrate more than 7 mm in the glass by increasing the laser power without the scanning of the focal point. The threshold fluence for platinum particle migration was estimated by changing the laser power. The fluence was calculated from the beam profile and the laser power. As a result, the threshold fluence for the particle migration was almost constant at $0.3 \pm 0.06\ \text{MW}/\text{cm}^2$. Note that the fluence was the average fluence in the central area with a diameter of $5\ \mu\text{m}$ (same as the diameter of the particle). The average fluence in the laser spot ($1/e^2$ diameter, calculated to be $38\ \mu\text{m}$ at the focus) was calculated to be $0.15 \pm 0.03\ \text{MW}/\text{cm}^2$.

It is noteworthy that the particle migrated during the laser illumination, even after laser illumination was stopped. Figure 4 shows the particle migration observed in between laser illuminations. The particle stopped at a certain point after laser illumination was stopped (Fig. 4(a)). Laser illumination was started again (Fig. 4(b)) and the particle migrated again (Figs. 4(c) and (d)). No changes, except for a small bend, were observed at the point where the particle stopped, as indicated by an arrow in Fig. 4(e).

In addition, the direction of the particle migration was controlled by changing the direction of the laser beam, and the migration was always directed toward the light source. Therefore, the particle location was controlled by adjusting the beam fluence and direction. Figure 5 shows bent and curved modified zones formed in the trajectories of the platinum particles. The direction of the laser beam was changed after the illumination was stopped, and the illumination was started again. The direction of the particle migration was changed and a bent modified zone was formed (Fig. 5(a)). The direction of the migration was curved (Fig. 5(b)) by simultaneously increasing the laser power and gradually changing the direction of the laser beam.

The speed of the particle migration at the focal point, which was measured by changing the laser fluence, is plotted in Fig. 6. The migration speed increased with the fluence, and the maximum speed was $\sim 10\ \text{mm/s}$. When the fluence was higher than $\sim 0.95\ \text{MW}/\text{cm}^2$, the glass

itself absorbed the light, which is the same as the phenomenon indicated in references [8] and [9], and the particles did not migrate.

The diameter of the particles was controlled by changing the film thickness. The films with thicknesses of 0.1 μm and 5 μm were illuminated with the laser. The implanted particle is shown in Fig. 7. The diameters of the particles were $\sim 3 \mu\text{m}$ and $\sim 50 \mu\text{m}$ when the thicknesses of the deposited films were 0.1 μm and 5 μm , respectively.

Migration force was considered. Optical trapping is known as the force caused by light, and the trapping force is generated as the counterforce of the light [10]. A platinum particle reflects laser light. Therefore, the force is applied in the direction of the light progression, which is the counter direction of the particle migration. Photophoretic force also induces the migration of particles, and its direction depends on the particle size. When the wavelength is about twice as large as the particle diameter, the direction is against the light progression, because the excitation of surface plasmons heats the back surface more [11]. In our case, the particle with a diameter of 3–50 μm migrates toward the light source, which cannot be explained by photophoresis. On the other hand, fluid flow in ice with local melting by laser illumination and freezing has been reported. The water flow in molten ice in the direction of laser scanning is generated by the volume change induced by repetitive melting and freezing [6]. In contrast, when gel is used [12] instead of ice, the fluid flow is directed against the movement of the heated spot, because the gel expands upon heating. In our case, the specific volume of the glass is increased by heating. Hence, the flow direction is against the movement of heated platinum particles. This direction is the counter direction of the particle migration; therefore, the migration force cannot be explained on the basis of fluid flow. The moving force for the particle migration has not been identified.

Other kinds of metals, such as nickel, tin, tantalum, silver, copper and austenitic stainless steel (SUS304), were tested. As a result, nickel and SUS304 were implanted in the same manner as platinum. However, tantalum, tin, silver and copper were not implanted. Figure 8 shows the thermal conductivities and melting points of the implanted metals, which are below 1 W/cm $\cdot$ K and ranged from 1500 to 2200 K, respectively.

The author supposes that the temperature at the laser spot governs the difference, because the implanted metals have similar melting points and thermal conductivities. Hence, numerical calculations were performed to estimate the temperature. To describe a two-dimensional model

of the temperature increase in the cylindrical coordinates r and z in a rectangular area, the author employs the heat conduction Eq. (1) in the following forms [13]:

$$\rho c \frac{\partial}{\partial t} T(t, r, z) = k \left[\frac{\partial}{\partial z^2} T(t, r, z) \right] + \frac{1}{r} \frac{\partial}{\partial r} \left[r k \frac{\partial}{\partial r} T(t, r, z) \right] + Q(t, r, z) \quad (1)$$

Here, z is the coordinate along the optical axis, r is the radial coordinate, c is the specific heat, k is the thermal conductivity, ρ is the density of the metals and Q is the heat flux. The radiation intensity I is calculated as a Gaussian profile with a spot radius of 20 μm , which is measured by a knife edge technique. The author assumed that the laser energy is completely absorbed on the surface because absorption depths of the metals are small. The heat flux is expressed as

$$Q = \begin{cases} \frac{\partial}{\partial z} (1 - R) I(r) & (z = 0) \\ 0 & (z \neq 0) \end{cases} \quad (2)$$

Here, R is the reflectivity of the metal films/foils. The average fluence in the $1/e^2$ spot is set at 0.15 MW/cm^2 . The initial temperature T_0 is 293 K. The author assumed the absence of heat sinks on the metal surface, because thermal conductivities of the air and glass are ten times less than those of metals. The area with a radius of 800 μm is calculated. The temperature at the boundary is set constant at T_0 . These equations are solved by a finite-difference method at a uniform r and z mesh.

Figure 9 shows that the calculated temperatures increase at the center of the laser spot. The temperatures of platinum, nickel, SUS304, tantalum and tin exceeded their melting points within 0.01 s, whereas those of silver and copper did not exceed their melting points even after 1s.

When a platinum film was used, the results were categorized into the following three types in terms of an increase in laser power. i) No change was observed in the glass. ii) Metal particles were implanted. iii) The glass itself absorbed the laser beam and was modified in the same manner as that indicated in references [8] and [9]. The threshold fluences in the $1/e^2$ spot for ii) and iii) were $\sim 0.15 \text{ MW}/\text{cm}^2$ and $\sim 0.2 \text{ MW}/\text{cm}^2$, respectively. When tantalum, silver and copper films/foils were used, only glass absorption was observed with increasing laser power. Compared with the platinum film, the metals with higher thermal conductivities, such as silver and copper, required higher fluences to melt. As a result, the threshold fluence for metal

implantation was higher than that for glass absorption; therefore, glass absorption was believed to occur before metal implantation. Tantalum was not implanted, although it was heated at temperatures higher than its melting point. The absorption of glass increased with temperature [14]; therefore, the threshold fluence for glass absorption was reduced to less than the threshold for the implantation at the melting point of tantalum. The tin film was evaporated and no changes were observed. This result indicates that the tin melted before glass softening and absorption.

2.2.4 Conclusions

The author has shown that platinum, nickel and SUS304 particles can be implanted in borosilicate glass by laser irradiation. The metal particles heated by laser illumination softened the surrounding glass. Glass elements were not detected from the metal particles and no metals were detected in the trajectory of the migration. The platinum particles with diameters of ~ 3 to ~ 50 μm were implanted at speeds up to 10 mm/s. The threshold fluence required for platinum particle migration was 0.3 MW/cm^2 . Further studies are necessary to clarify the driving force for the particle migration.

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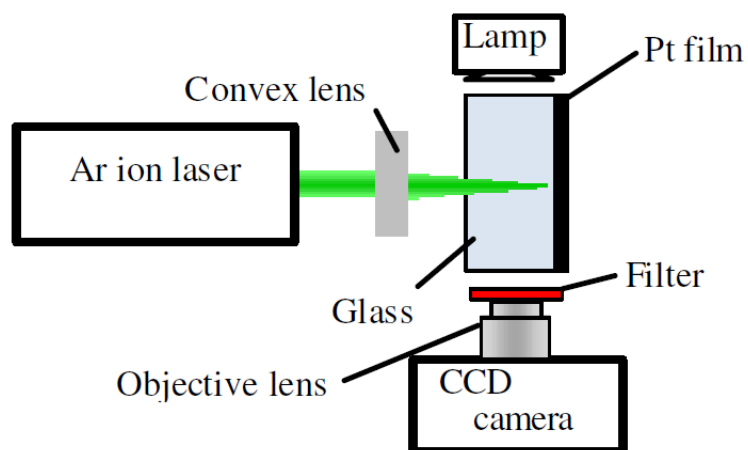


Fig. 1 Illustration of experimental setup.

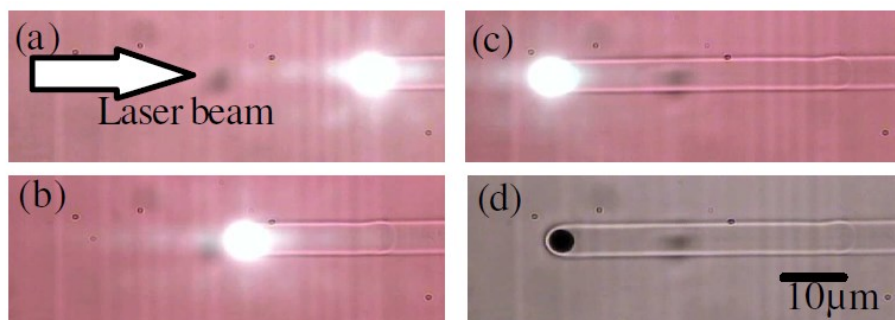


Fig. 2 Images of radiation from heated platinum particle. (a)-(c) Bright emission moving toward light source during laser irradiation and (d) platinum particle located in area where bright emission was observed (c). Laser power was 4.2 W.

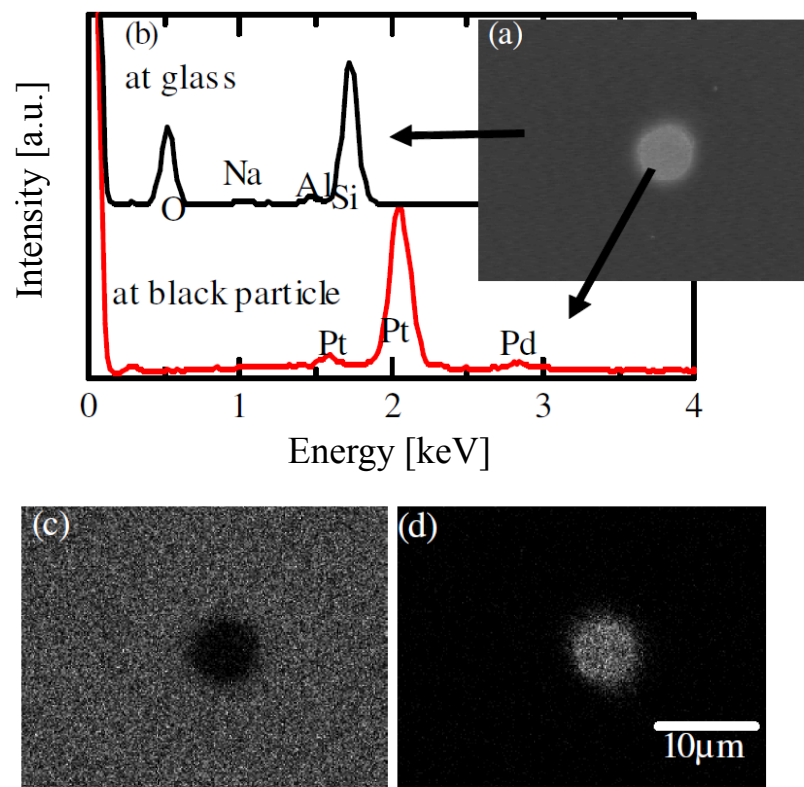


Fig. 3 SEM micrographs, EDS analysis results and X-ray maps of cross section of particle: (a) secondary electron micrograph, (b) EDS analysis results and X-ray maps of (c) Si and (d) Pt.

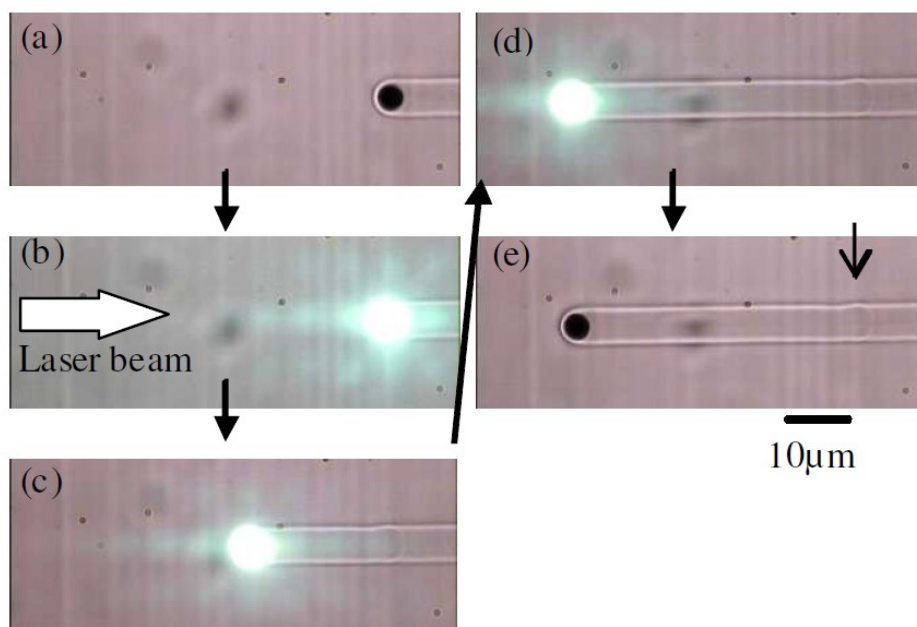


Fig. 4 Images of platinum implantation in between laser illuminations. Laser power was 4.2 W.

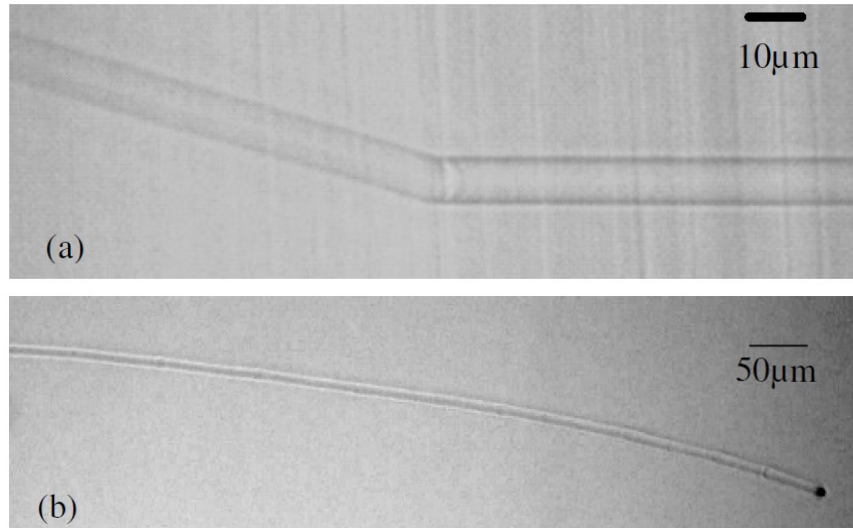


Fig. 5 Micrographs of modified zones: (a) bent with 20° and (b) curved modified. Laser power was 4.2 W.

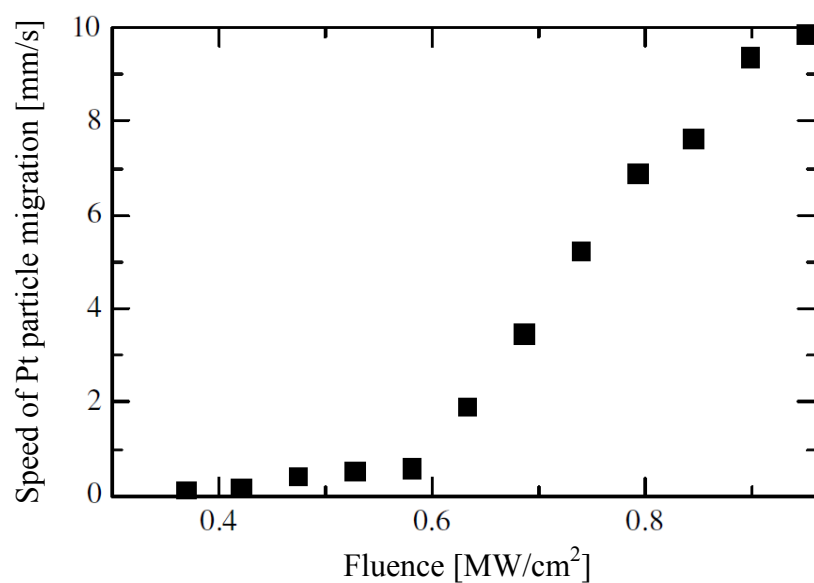


Fig. 6 Speeds of platinum particle migration under laser illumination at various fluences at focus.

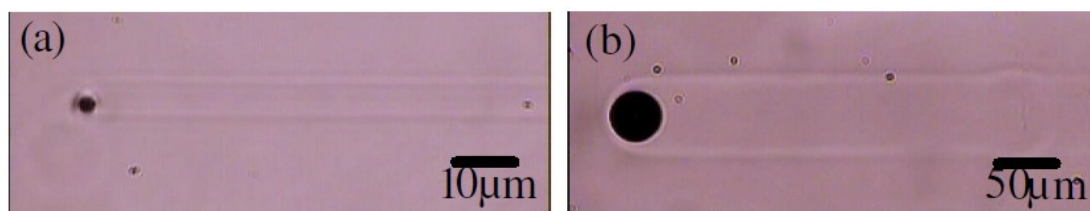


Fig. 7 Micrographs of platinum particles with different diameters implanted into glass. Thicknesses of deposited platinum films: (a) 0.1 μm and (b) 5 μm. Laser powers were (a) 5 W and (b) 1.8 W.

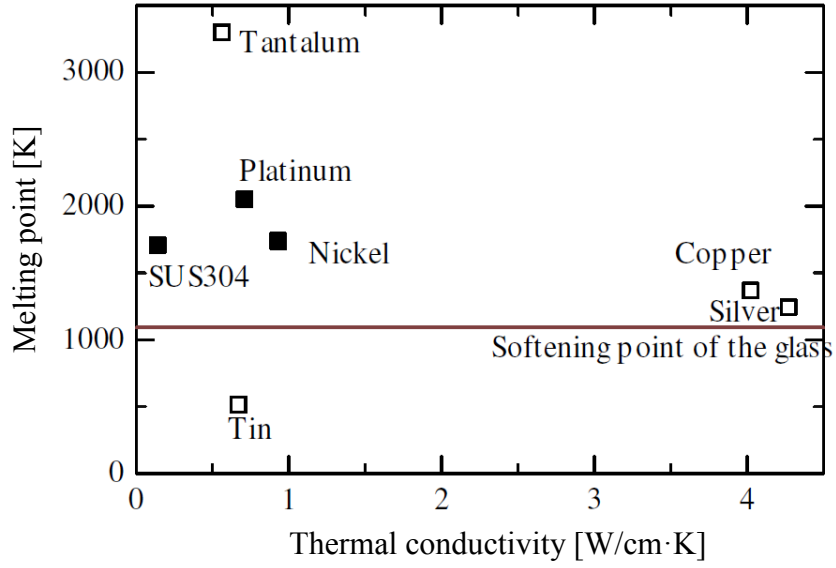


Fig. 8 Properties of metals for absorbent. Thermal conductivity vs melting point. ■: metals implanted into glass and □: metals not implanted into glass.

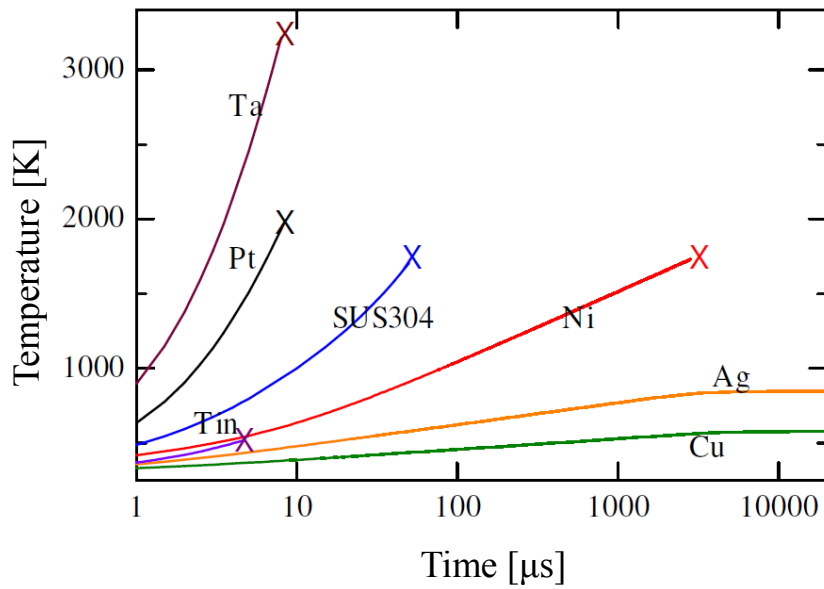


Fig. 9 Calculated temperatures at the center of heated spot. The thicknesses of the Ta, Pt, Tin and Ag films were 1μm, and those of SUS304, Ni and Cu foils were 10μm. × : melting temperatures.

Chapter 3

Glass nanofiber production by laser spinning

3.1 Generation of glass nanofibers from back surface of thin glass substrates

3.1.1 Introduction

Nanofibrous materials have been studied for various applications because of their small diameter and high aspect ratio, leading to their unique characteristics [1],[2]. In particular, glass nanofibers have great potential as materials for optical components [3], catalysts [4],[5], medical use [6], sensors [7], and other devices because of the optical, chemical, and physical advantages of glass materials. The industrial use of these nanofibers, nevertheless, has not progressed as expected because the methods used to generate them have major drawbacks. Several methods have been proposed. The electrospinning was developed and can also be used to generate glass nanofibers by preparing a sol-gel precursor [1],[5],[7]. Kameoka et al. reported the application of silica nanofibers fabricated by electrospinning for sensing [7]. As other types of generating methods, lasers have been utilized by some researchers. Quintero et al. proposed a laser spinning method using a high-power CO₂ laser with a gas jet for elongating nanofibers [8],[9]. Venkatakrishnan et al. proposed a method of generation using a high-repetition-rate femtosecond laser [10],[11]. To enable a variety of applications of glass nanofibers, precise control of their shape, composition, and the location of their generation as well as improved production efficiency are necessary.

Recently, the author has found that a nanofibrous material was generated from glass substrates during a drilling experiment using a pulsed UV nanosecond laser. In this study, the author investigates this phenomenon. First, the generated glass nanofibers were characterized. Then, the author considered the generation process by setting up an optical system enabling in situ observation.

3.1.2 Experimental procedure

Figure 1 shows an overview of the internal optical system of the processing machine used (LDSD-3000M, LTS Co., Ltd.). An oscillator emits a laser beam of wavelength 355 nm and pulse width 40 ns. The power was set to 10-20 W and the frequency was set to 100 kHz. The laser beam was focused to a spot with a diameter of approximately 20 μm through an f- θ lens (focal length of 103 mm) mounted on a Z stage. The location of the focus was determined by searching for the minimum spot size by irradiating aluminum-coated glass with multiple spots, each shifted by 100 μm along the irradiation direction. The location of the focus considering the refractive index of the sample substrate was set at 0.3 mm below the top surface. The beam was scanned along a spiral path at a speed of 300 mm/s using a galvano mirror. The irradiation pitch was set to 1-3 μm and the range was set to 500 μm . A non-alkaline glass substrate (OA-10G, Nippon Electric Glass Co., Ltd.) of 0.5 mm thickness was used as the workpiece owing to its relatively low thermal expansion coefficient of 38×10^{-7} /K. The sample was mounted on an X-Y stage via support pins.

An optical system for in situ observation was also prepared. A UV laser beam emitted from an oscillator (AVIA355-4500, Coherent Inc.) was focused through an objective lens (magnification of 5, NA = 0.15; LU Plan Fluor, Nikon). The beam diameter ($1/e^2$) before the objective lens was 2.3 mm, measured by the knife-edge method to calculate beam diameters in each location along a direction of beam propagation. Using the value, the focused spot diameter and Rayleigh length were estimated to 7.9 μm and 140 μm , respectively, while M^2 factor was neglected. LED light with a wavelength of 627 nm was used for illumination, and wavelengths of less than 600 nm were filtered using an optical filter. The author also used an acrylic plate to protect the LED light module from the transmitted UV laser light. A CCD camera and a plano-convex lens (focal length of 100 mm) for adjusting its focus were set coaxially to the incident beam. The transmitted laser power was measured by a detector (LM-10HTD, Coherent Inc.) to evaluate the energy absorbed during nanofiber generation. The optical system was surrounded by an acrylic box to eliminate the effect of the air flow. The same non-alkaline glass was used for the substrate, but its thickness was reduced to 0.2 mm owing to the relatively low laser power. Generated nanofibers were characterized by a scanning electron microscope (SEM; Superscan 440W, Shimadzu Corp.) and a field-emission scanning electron microscope (JSM-6705F, JEOL Ltd.).

3.1.3 Results and discussion

3.1.3.1 Observation of generated nanofibers

Figure 2 shows photographs of the glass nanofibers generated by various types of beam scanning. Figure 2(a) shows glass nanofibers generated from the back surface around a drilled hole. Upon changing the irradiation conditions, it was found that when the irradiation range was increased, nanofibers were not generated. When spiral scanning was combined with linear scanning using the X-Y stage, aligned glass nanofibers were generated along a line, as shown in Fig. 2(b). The author also obtained a cluster of glass nanofibers of size ~ 50 mm by continuous irradiation for approximately 30 minutes, as shown in Fig. 2(c). Figure 3(a) shows a SEM image of the nanofibers selected from a sample grown under the conditions of Fig. 2(b). In the image, microparticles can be observed at the tips of the nanofibers (indicated by an arrow). The author also sampled moderate number of nanofibers to measure the diameter distribution. The diameters of the nanofibers were primarily of 100 nm order (as shown in Fig. 3(b)). Nanofibers with a diameter of less than 500 nm accounted for more than 80% of the nanofibers. Moreover, the author observed the area around the drilled hole to clarify the generation process. Figure 4 shows SEM images of the (a) top and (b) back surface around the hole. As shown in Fig. 4(a), only particles and no glass nanofibers can be observed on the top surface. According to Fig. 4(b), a molten surface was formed adjacent to the hole. Further from the hole wall, many particles with nanofibers can be observed. Figure 4(c) shows a magnified image of the rectangular area in Fig. 4(b). From the image, glass nanofibers appear to have been generated in the radial direction. Figure 4(d) shows two nanofibers intertwined together, the diameters of which were 810 nm and 160 nm. Figure 4(e) shows a microparticle of 6.8 μm diameter at the tip of a nanofiber. In some nanofibers, a microparticle was found in the middle of the nanofiber, as shown in Fig. 4(f), in which the particle diameter is 2.8 μm . The author also determined the composition of nanofibers and the glass substrate by EPMA as a reference, but the author was unable to find a significant difference between them. The author also investigated raman spectra of the glass substrate and nanofibers. These spectra showed similar peaks. Further investigation of the structures and compositions will be part of our future research.

3.1.3.2 Investigation of generation conditions

Using a line-scanning optical system for in situ observation, the author investigated the effect of the primary laser parameters on nanofiber generation. When the laser focus was set below the top surface in the experiment in 3.1.3.1, nanofibers were generated. Thus, the author chose a laser focusing location as one parameter. Figure 5 shows the generation condition on the laser focusing location and scanning speed at a power of ~ 2 W. ΔZ shows the focusing location considering the refractive index of the substrate, when 0 mm was defined as the top surface, and plus value was set below the top surface. In this experiment, when nanofibers and no nanofibers were observed on the back surface after irradiation, the author plotted the conditions as a circle and cross in Fig. 5, respectively (or a filled circle when a large number of nanofibers were observed). Figure 6, for example, shows optical micrographs of the surfaces of substrates after beam scanning. The upper and lower rows show the top and back surfaces, respectively and results are shown for $\Delta Z = 0.67$ mm and scanning speed of (a), (b) 0.1 mm/s and (c), (d) 0.2 mm/s. No nanofibers were generated on the top surface under both conditions. At a scanning speed of 0.1 mm/s, the glass substrate was ablated to a width of 27 μm , which is almost equal to the laser spot size on the top surface of 35 μm . Under this condition, glass nanofibers were not generated on the back surface. Note that this condition resulted in a region of unstable generation where the glass was sometimes widely modified, as shown at the edge of the image (indicated by the arrow), where several nanofibers were observed. The reason for the unstable generation is discussed in 3.1.3.3. On the other hand, at a scanning speed of 0.2 mm/s and above, the glass substrate was modified in a region wider than the spot size and showed a beadlike morphology instead of an ablated surface. In particular, at a scanning speed of 0.2 mm/s, the image shows stable nanofiber generation with a modified region of width ~ 240 μm . After irradiation, a glass surface was formed instead of grooves. At a scanning speed of 1.0 mm/s, the glass was modified in a region with a width of ~ 140 μm . However, no nanofibers were observed.

To carry out a more direct investigation, the author conducted in situ observation using a CCD camera. Figure 7 shows an image captured under the conditions of Figs. 6(c) and (d). The CCD focus was adjusted to the top surface. In the image, white region can be observed, which is considered to be a molten pool resulting in heat radiation, the width of which is ~ 360 μm . The laser beam spot was located at the center of the molten pool. Nanofibers were generated around the white region on the back surface. In the Fig. 6(d), the original points of nanofiber generation

on the molten surface were mainly located in the region, which is the one-fourth of the modified width. This value was larger than the beam diameter ($1/e^2$) on the surface 28 μm . From careful observation of the image, microparticles were found to be located at the tips of the nanofibers (indicated by an arrow). A cluster of nanofibers was also observed after scanning the laser beam.

3.1.3.3 Consideration of generation process

On the basis of the above results, the author considered the generation process. Several mechanisms have been reported for similar generation processes. First, in the laser spinning process [8], a supersonic gas jet (Ar gas) with a high-power CO_2 laser is utilized. This process is similar to our process in that glass nanofibers are generated from the back surface of glass substrates. However, in our process, it is considered that the microparticles themselves drive nanofiber formation. Thus, the mechanism is different from that in Ref. 8. Moreover, in our process, the glass nanofibers remain attached to the substrate. Thus, the author can conclude that the glass nanofibers were directly grown from the substrate.

As another process, the generation of a fibrous material when irradiating silica glass with a CO_2 laser has been reported [12]. Nanofibers were generated from the top surface, but the process was similar to ours in that the driving energy was only provided by a laser beam. In Ref. 13, the mechanism of nanofiber generation was explained to be due to melt-pool formation and fiber ejection from the melt around the irradiated area. According to another report, this process occurs when a high-repetition-rate femtosecond laser is utilized [10]. However, in Ref. 10, the absorption coefficient of the workpiece subjected to laser irradiation was relatively high (for example, $2.16 \times 10^{-4} \text{ m}^{-1}$ in the case of irradiating silica with a CO_2 laser), leading to energy absorption on most of the top surface. On the other hand, in our process, the light transmittance of our material was $\sim 90\%$ at a wavelength of 355 nm at room temperature [13]. The author measured the amount of transmitted light under the condition of Figs. 6(c) and (d), which was about 0.5 W for an incident laser power of ~ 2 W. Thus, $\sim 75\%$ of the laser energy was absorbed. Therefore, the author can assume that an increase in the absorption coefficient occurred as a result of irradiation. This finding is also supported by the in situ observation. In fact, there is a time lag (0–0.5 s) between the start of irradiation and the time at which the glass starts to absorb the light. This is probably because the glass was first heated around the laser spot, then the

temperature rise affected the absorption coefficient. Moreover, in our process, it is necessary for the molten region to reach the back surface for nanofibers to form.

In the Figs. 6(a) and (b), unstable generation was observed. The author considered the following to be a possible reason for the phenomenon. First, the material was removed to a width, which was almost same size of the laser spot. Then, due to repetitive action of the laser pulses, the glass around the irradiated area was gradually heated, resulting in melting and nanofiber generation. After this state continued along the scanning direction of $\sim 200\ \mu\text{m}$, the melting finished. This is probably because the scanning speed is low, that is, the laser irradiates almost same location in each pulse (stage motion of 4 nm in each), causing that the pulse energy penetrates through the substrate owing to material removal. On the other hand, when the scanning speed is 0.2 mm/s (as shown in Fig. 6(d)), the amount of the stage motion increases, which enables to prevent from the laser pulse to penetrate through the substrate. Thus, the molten state remains, resulting in stable generation of nanofibers.

Also, in the case of beam scanning along a spiral path, it is assumed that a larger molten region compared with the laser spot size is formed. This is in accordance with the fact that if the irradiation range increases, nanofibers are not generated, probably because under laser irradiation, the outer part around the center of the irradiated area is cooled. The author considers that if the power is increased in the line scanning system, the laser power will be saturated. However, by rapidly moving the laser beam, the efficient generation of glass nanofibers may be possible.

After ejection of the particles from the substrate, it is considered that nanofibers were formed when its viscosity, which is dependent on the temperature, became preferable value. The reason why glass nanofibers were only generated from the back surface is still not clear. More precise analysis of the generation conditions will be part of our future research.

3.1.4 Conclusions

The author reported glass nanofiber generation using a pulsed UV laser. The author observed that nanofibers with a diameter of 100 nm order were generated from the back surface of substrates. By in situ observation, a molten region was observed around the irradiated area. Investigation of the generation conditions showed that nanofibers were generated when sufficient laser-induced heat was accumulated. The generation of nanofibers from the back

surface of a glass substrate is advantageous in terms of their collection owing to the reduced direct interaction with the laser beam.

3.1.5 References

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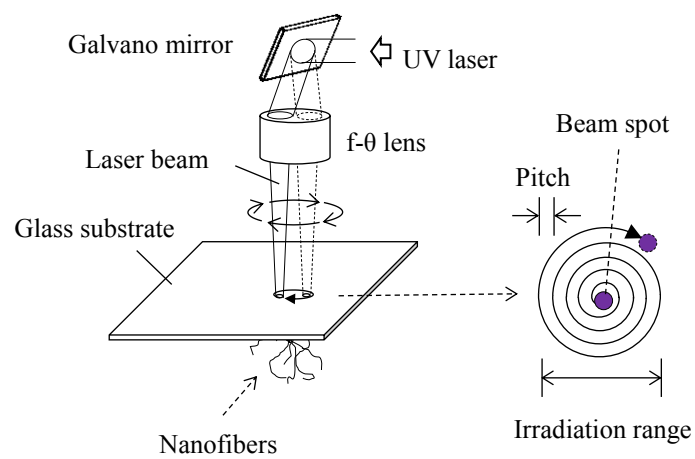


Fig. 1 Schematic image of the optical system set up for nanofiber generation using a glass substrate. The focused beam was scanned along a spiral path.

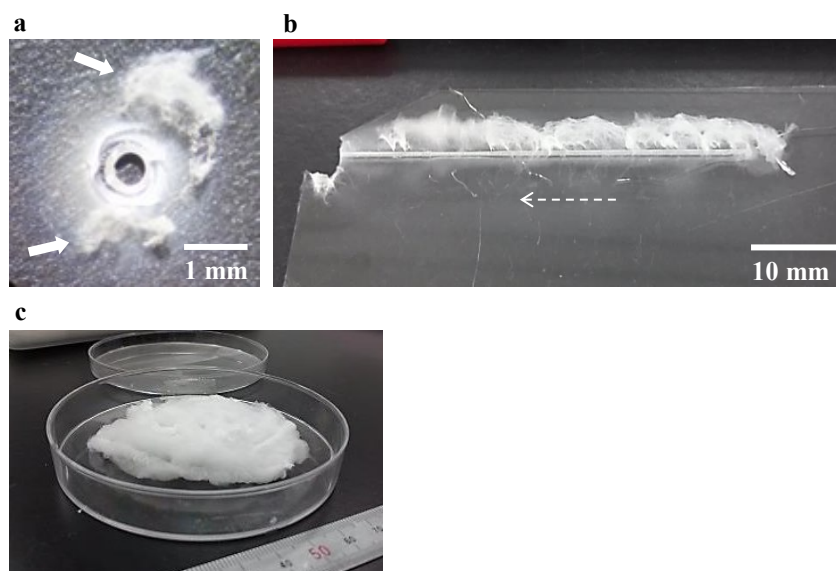


Fig. 2 Photographs of (a) nanofibers generated during drilling (indicated by the arrows), (b) nanofibers generated from a glass substrate by combining spiral scanning and line scanning (in the direction of the broken arrow), (c) cluster of nanofibers.

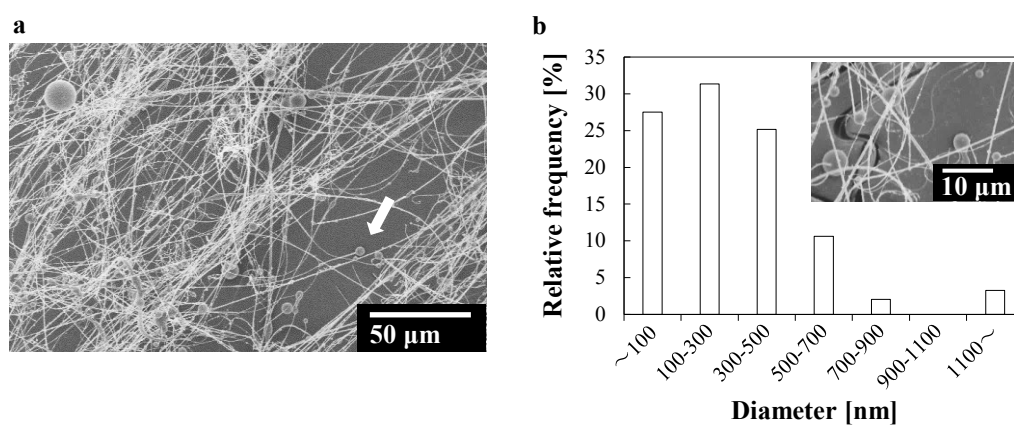


Fig. 3 (a) SEM image of the generated nanofibers and (b) diameter distribution of the nanofibers shown in the inset image.

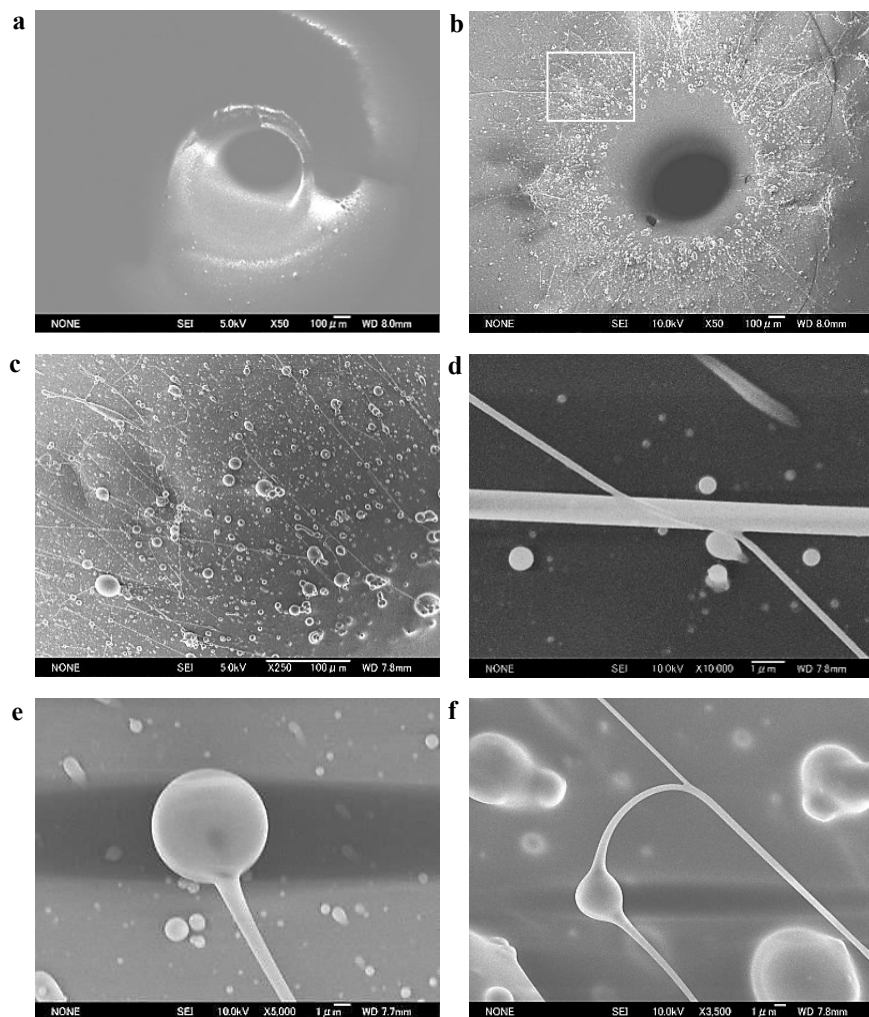


Fig. 4 SEM images of the nanofibers generated around the irradiated zone. Overviews of (a) top and (b) back surface. (c) Magnified image of the rectangular area in (b). (d) Intertwined part of nanofibers with diameters of 810 nm and 160 nm. (e) Tip of nanofiber including a particle of 6.8 μm diameter. (f) Particle of 2.8 μm diameter in the middle of the nanofiber. This nanofiber also includes a branching point.

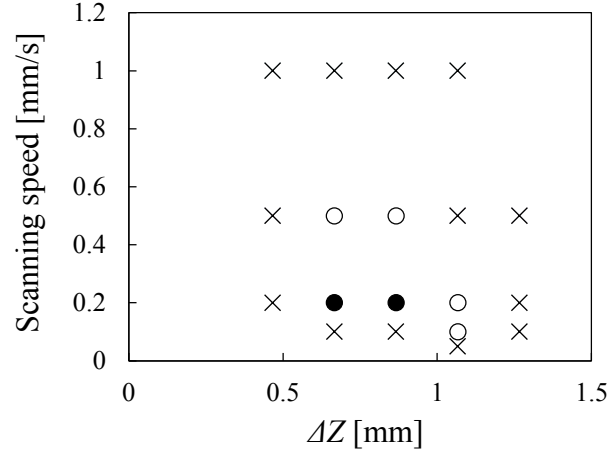


Fig. 5 The Dependence of nanofiber generation on the focusing location and scanning speed. When nanofibers and no nanofibers were observed on the back surface after irradiation, the conditions were plotted as $\circ$ and $\times$, respectively (or $\bullet$ when a large number of nanofibers were observed). The incident power was ~ 2 W.

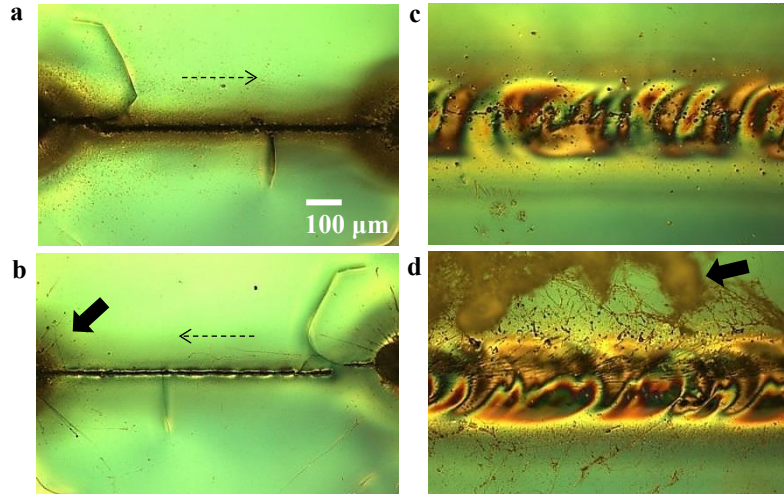


Fig. 6 Micrographs of glass substrates. The upper and lower rows show the top surface and back surface, respectively. The beam was scanned at a speed of (a)(b) 0.1 mm/s and (c)(d) 0.2 mm/s. The incident power was ~ 2 W. The focusing position was 0.47 mm below the bottom surface. Broken arrows show the scan directions.

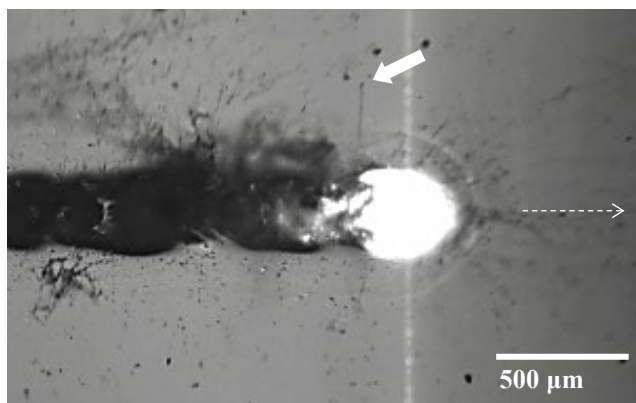


Fig. 7 Captured image in vicinity of the molten spot. The arrow shows a microparticle at the tip of a glass nanofiber. The laser beam was scanned in the direction of the broken arrow.

3.2 In situ observation of the nanofiber generation process

3.2.1 Introduction

Nanofibers have been widely focused as prospective, functional materials [1]. Particularly, glass nanofibers have been expected because of their characteristics as non-organic materials, and several applications have been proposed such as catalysts, medical use, or sensing devices [2–4]. For its future applications, investigation and development of fabrication method are inevitable. Also, it is necessary to develop methods for controlling nanofibers. At a moment, electrospinning and melt blowing, which have been used in fabrication of polymer nanofibers, are candidates for mass-production. In addition, the production of nanofibers using lasers has been reported: Markillie et al. showed that excimer laser irradiation to glass caused fiber generation, with a diameter of 3 μm [5]. Venkatakrishnan et al. reported that high-repetition-rate femtosecond laser irradiation to glass induced nanofiber generation [6]. Because glass melting occurs in both the processes, elucidation of the nanofiber generation helps us to understand glass processing using pulsed lasers.

The author found that nanofibers were generated from glass plates using a pulsed UV 355 nm laser [7]. The diameters of the fibers were in the order of 100 nm. The unique points in the method presented this paper is that nanofibers were generated from the back surface, which is convenient for efficient collection of nanofibers. For industrial application of this method in the future, elucidation of the nanofiber generation is highly important.

In this study, the author observed the dynamics of glass during laser irradiation to observe the glass melting and fiber generation using a high-speed camera. The observation showed the behavior of inner glass and melt ejection. The author discussed the pressure applied on the glass surface at which molten glass was ejected based on the speed of melt ejection.

3.2.2 Experimental procedure

Figure 1 shows a schematic drawing of the optical system. The laser beam propagated from the lower to upper direction. A UV laser beam emitted from an oscillator (AVIA355-4500, Coherent Inc.) was focused through an objective lens (magnification of 5, NA = 0.15; LU Plan Fluor, Nikon). An oscillator emits a laser beam of wavelength 355 nm and pulse width 40 ns. The power was set to ~ 2.5 W and the frequency was set to 25 kHz. The beam diameter ($1/e^2$) before the objective lens was 2.3 mm, measured by the knife-edge method. The focusing location was

set at +0.8 mm from the lower surface, and scanning speed 0.2 and 0.5 mm/s. A non-alkaline glass substrate (OA-10G, Nippon Electric Glass Co., Ltd.) of 0.2 mm thickness, which was mounted on an X-Y-Z stage, was used as the workpiece. A high-speed camera (FASTCAM SA-Z, Photron Ltd.) with the optical filter and LED with a wavelength of 627 nm was prepared to observe the phenomenon in the direction of the cross section. The frame rate was set at 50,000 and 300,000 fps and the exposure time 1/100,000 s and 1/4,030,200 s, respectively. Nanofibers were also observed using a scanning electron microscope (SU3500, Hitachi High-Technologies Corp.).

3.2.3 Results and discussion

3.2.3.1 Observation of the generated nanofibers

By the optical system shown in Fig. 1, glass nanofibers were generated from the upper surface (i.e. back surface) of the glass. Figure 2 shows a SEM image of a part of nanofibers. The diameters were in the range of 50–300 nm. The image also includes a tip of nanofibers, which has a spherical shape. The diameter was $\sim 1\ \mu\text{m}$.

3.2.3.2 Investigation of the generation process

Figure 3 shows images during the ejection of nanofibers captured by a high-speed camera. The images in Fig. 3(a) and those in Fig. 3(b) were captured at the frame rate of 50,000 fps and 300,000 fps, respectively. In Fig. 3(a), voids with a diameter of 40 μm were observed in the glass. The voids propagated in the upper direction after laser irradiation and shrunk until the next laser irradiation. The lower side of the voids opened to the air, which can be considered by seeing the plasma shape. When the upper side of voids approached the back surface, nanofibers were generated as shown in the image at $\Delta t = 160\ \mu\text{s}$ in Fig. 3(a). After that, these voids were closed probably because of the surface tension. Then, light absorption started from the lower side of the glass plate. Nanofibers were generated by every ~ 7 pulses, which means that generation rate was $\sim 3,600$ fibers/s. In Fig. 3(b), in which images were captured at a higher frame rate, ejection of glass melt was observed. The images at $\Delta t = 3.3\ \mu\text{s}$ and $6.6\ \mu\text{s}$ showed nanofibers clearly. The locations of the nanofibers were marked as broken lines. In this picture, two fibers connected with each other on the top were formed. By comparing the distance of the two broken lines with the interval time, the ejection speed was calculated as 51.7 m/s (Note that

the moving distance of 12.8 μm during the camera exposure time can be neglected compared with that of the two broken lines). From the other observation in the same laser irradiation condition, the speed of the fiber ejection was in the range of 10–100 m/s.

3.2.3.3 Discussion of generation process of nanofibers

Here, the author discusses the generation process of nanofibers based on the observation by a high-speed camera. Figure 4 represents a schematic of the proposed process. At the early stage of laser irradiation, laser beam is irradiated from the lower surface of a glass plate and the glass around irradiation area was melted. Then, by the successive irradiation, voids are formed in the molten region and extend to the upper surface of the glass plate. The thin layer of the molten glass is expected to be pushed from the lower to upper side of the glass plate, i.e., laser propagation direction. Finally, molten glass is ejected from the glass plate, and nanofibers are formed as the result of cooling of ejected molten glass. After the ejection of molten glass, voids are closed by melt flow and its surface tension.

The possible driving force to induce the ejection of molten glass is recoil pressure, which has been reported in the laser processing of metals [8]. Here, the author estimated the pressure when a molten glass is ejected by considering the relationship between pressure and momentum of ejected glass. The author assumed that molten glass with its mass of m was ejected at the velocity of v when the pressure of p was applied on the surface of a molten glass of the specific area of A during the time of t . If the author considers that the momentum of ejected melt is equal to that by the pressure on the surface of molten glass, the author can make the following equation:

$$p \cdot A \cdot t = m \cdot v \quad (1).$$

Here, the author assumed that the area A was considered as the void diameter, 40 μm , and the time t , equals to the pulse width, 40 ns. The mass of the ejected glass was calculated using the glass density of 2.5 g/cm^3 and diameter of the sphere on the tip, 1 μm , as observed in the SEM image shown in Fig. 2. In reality, molten materials are not spherical during ejection, but here, the author used the volume after cooling of ejected glass. Using eq. (1), p was calculated as 1.3 MPa. Chen et al. [9] estimated that the recoil pressure value should be around 0.1–1.0 MPa

when laser fluence is 1.0×10^{10} W/cm². The value estimated by Chen et al. is close to the estimated value in this study. One difference between ours and Chen et al. is the pulse width. From the other observation, when the void closed after the melt ejection, the lower side of the void was closed earlier than the upper side (also, depicted by Fig. 4). It is because the glass around the upper side of the void was ablated with each pulse, which caused widening of the void on the upper side. On the other hand, the lower side is only heated because of the defocusing, which leads to gradual closing.

3.2.4 Conclusions

The author observed the nanofiber generation from the back surface of a glass plate by a pulsed UV laser irradiation. First, glass was molten, and then, voids were formed in the glass plate. The voids propagated toward the back surface. After the voids reached the back surface, molten glass was ejected from the surface at a speed of ~ 50 m/s. The author considered that one possibility of the driving force was recoil pressure. The shrinkage of voids was observed after ejection of molten glass, which may be induced by the surface tension.

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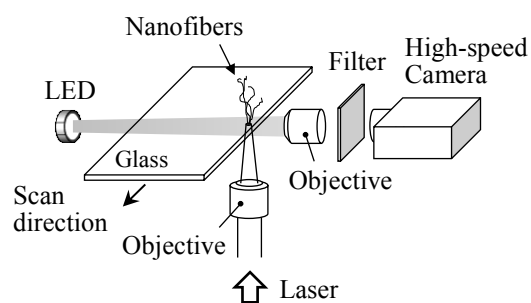


Fig. 1 Schematic drawing of the optical system for in situ observation. Laser beam propagated from the lower to upper direction. Nanofibers were generated from the upper surface of the glass plate.



Fig. 2 SEM image of the generated nanofibers. The arrow points a tip of nanofibers.

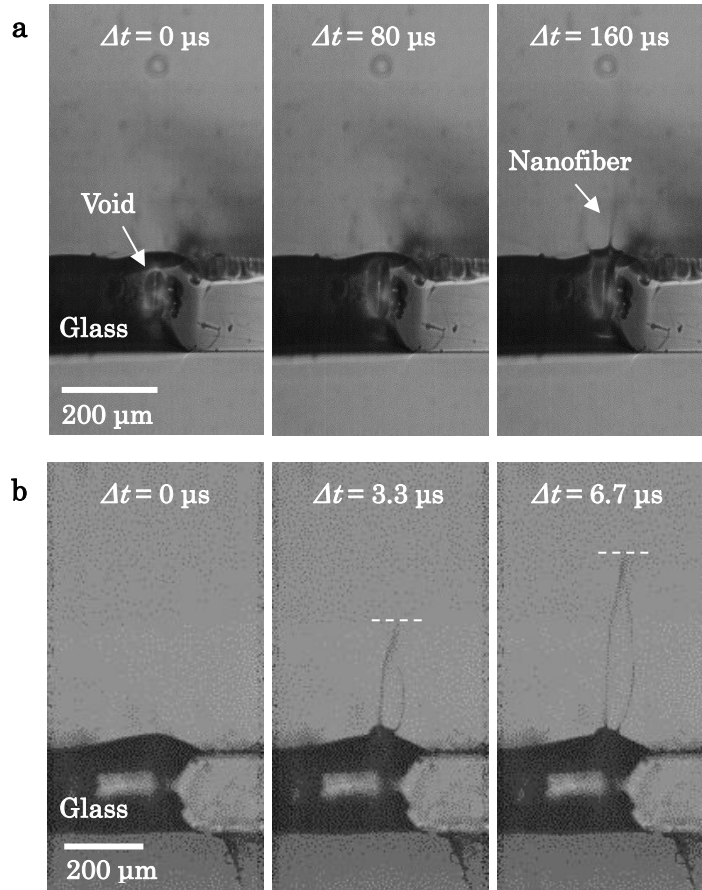


Fig. 3 Images captured by a high-speed camera. (a) Images were captured at 50,000 fps, and (b) at 300,000 fps, respectively. Broken lines in the figs.(b) represent the locations of the front of ejected glass.

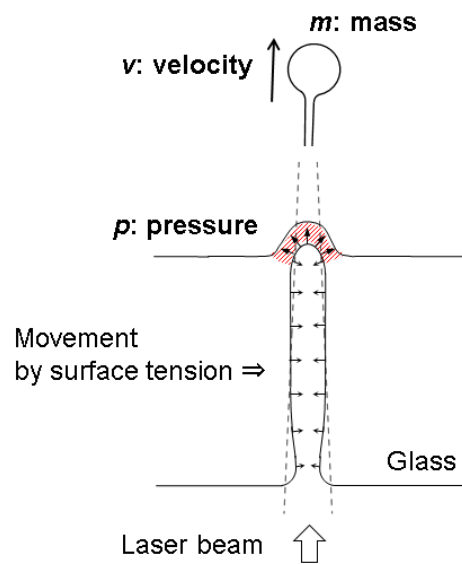


Fig. 4 Schematic drawing of the melt ejection process.

Publication List

Chapter 1

H. Hidai, S. Itoh, H. Tokura, S. Nagasawa, S. Tachikawa,
High-aspect-ratio microdrilling with UV laser ablation I - Drilling holes with an aspect-ratio of
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Sho ITOH