

# Generation of glass nanofibers from back surface of substrate using pulsed UV 355 nm laser

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**Abstract** We report a new phenomenon of generating glass nanofibers from substrates. A non-alkaline glass substrate was irradiated with a laser beam of 355 nm wavelength and a pulse width of nanosecond order while scanning the laser beam. This resulted in the generation of nanofibers from the back surface of the substrate. Scanning electron microscope images showed that the diameters of the nanofibers were of 100 nm order. The images also revealed that microparticles existed at the tips of the nanofibers. According to the investigation of the generation conditions, when the laser beam was focused below the top surface, particularly below the back surface, nanofibers were easily generated. By in situ monitoring, it was found that a region wider than the beam diameter ( $1/e^2$ ) on the surface was modified. Then, nanofibers were generated in the vicinity of the beam spot along with the ejection of microparticles. Compared with previously reported phenomena, in our process, it is more important for sufficient heat to have accumulated for nanofibers to form.

## 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. [7] reported the application of silica nanofibers fabricated by electrospinning for sensing. As other types of generating methods, lasers have been utilized by some researchers. Quintero et al. [8, 9] proposed a laser spinning method using a high-power CO<sub>2</sub> laser with a gas jet for elongating nanofibers. 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, we have found that a nanofibrous material was generated from glass substrates during a drilling experiment using a pulsed UV nanosecond laser. In this study, we investigate this phenomenon. First, the generated glass nanofibers were characterized. Then, we considered the generation process by setting up an optical system enabling in situ observation.

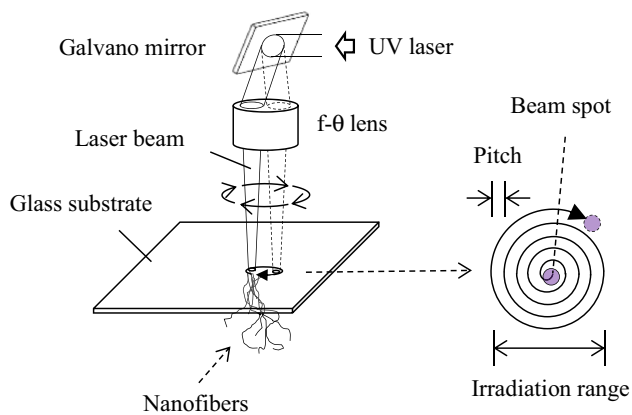
## 2 Experimental procedure

Figure 1 shows an overview of the internal optical system of the processing machine used (LDS-3000M, LTS Co., Ltd.). An oscillator emits a laser beam of wavelength

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

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  $\mu\text{m}$  through an  $f\text{-}\theta$  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  $\mu\text{m}$  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  $\mu\text{m}$ , and the range was set to 500  $\mu\text{m}$ . 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  $38 \times 10^{-7}/\text{K}$ . The sample was mounted on an X–Y stage via support pins.

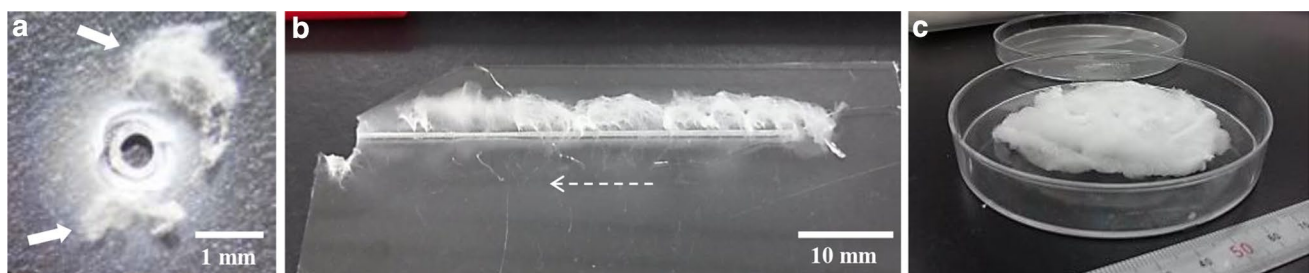
An optical system for in situ observation was also prepared. A UV laser beam emitted from an oscillator (AVIA355-4500, Coherent Inc.) was focused through an objective lens (magnification of 5, NA = 0.15; LU Plan

Fluor, Nikon). The beam diameter ( $1/e^2$ ) before the objective lens was 2.3 mm, as measured by the knife-edge method, which was used to calculate the beam diameter in each location along the direction of beam propagation. Using this value, the focused spot diameter and Rayleigh length were estimated to be 7.9 and 140  $\mu\text{m}$ , respectively, while the  $M^2$  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. We 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 Results and discussion

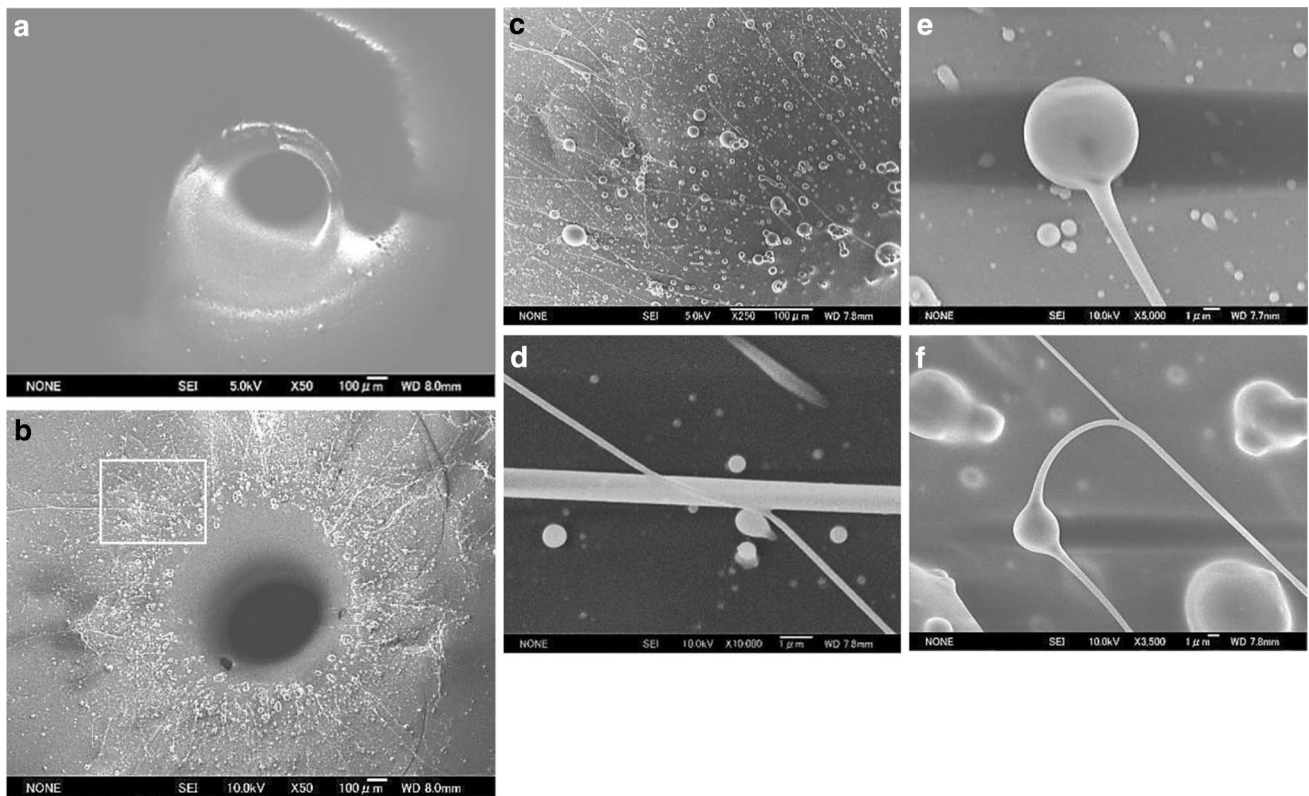
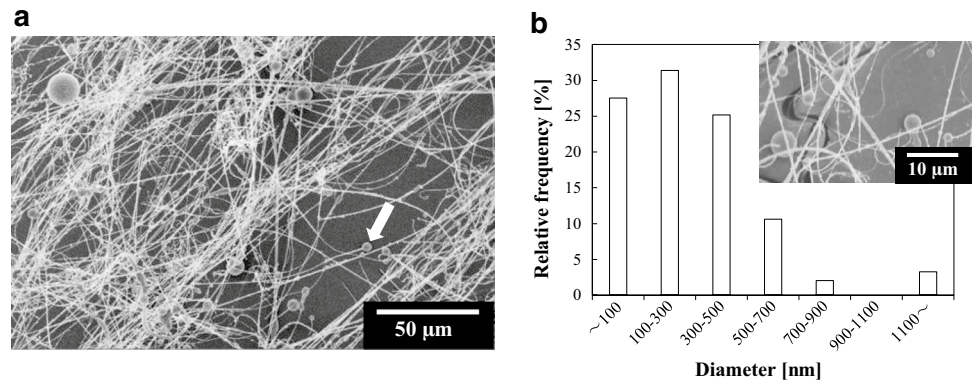
#### 3.1 Observation of generated nanofibers

Figure 2 shows photographs of the glass nanofibers generated by various types of beam scanning. Figure 2a 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. 2b. We also obtained a cluster of glass nanofibers of size  $\sim 50$  mm by continuous irradiation for approximately 30 min, as shown in Fig. 2c. Figure 3a shows a SEM image of the



**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

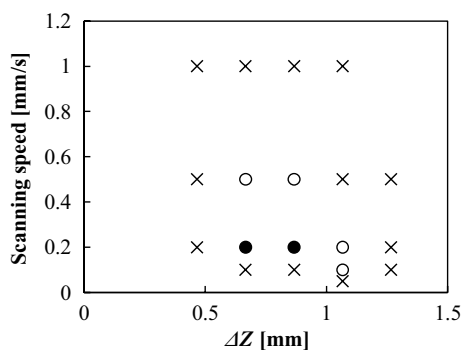


**Fig. 4** SEM images of the nanofibers generated around the irradiated zone. Overviews of **a** top and **b** back surface. **c** Magnified image of the *rectangular area* in **b**. **d** Intertwined part of nanofibers with diam-

eters of 810 and 160 nm. **e** Tip of nanofiber including a particle of 6.8  $\mu\text{m}$  diameter. **f** Particle of 2.8  $\mu\text{m}$  diameter in the middle of the nanofiber. This nanofiber also includes a branching point

nanofibers selected from a sample grown under the conditions of Fig. 2b. In the image, microparticles can be observed at the tips of the nanofibers (indicated by an arrow). We 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. 3b). Nanofibers with a diameter of <500 nm accounted for more than 80 % of the nanofibers. Moreover, we 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. 4a, only particles and no glass nanofibers can be observed on the top surface. According to Fig. 4b, a molten surface was formed adjacent to the hole. Further from the hole wall, many particles with nanofibers can be observed. Figure 4c shows a magnified image of the rectangular area in Fig. 4b. From the image, glass nanofibers appear to have been generated in the radial direction. Figure 4d shows two nanofibers intertwined together, the diameters of which were 810 and 160 nm. Figure 4e shows a microparticle of 6.8  $\mu\text{m}$  diameter at the tip of a nanofiber.



**Fig. 5** 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 are plotted as *open circle* and *times symbol*, respectively (or *filled circle* when a large number of nanofibers were observed). The incident power was  $\sim 2$  W

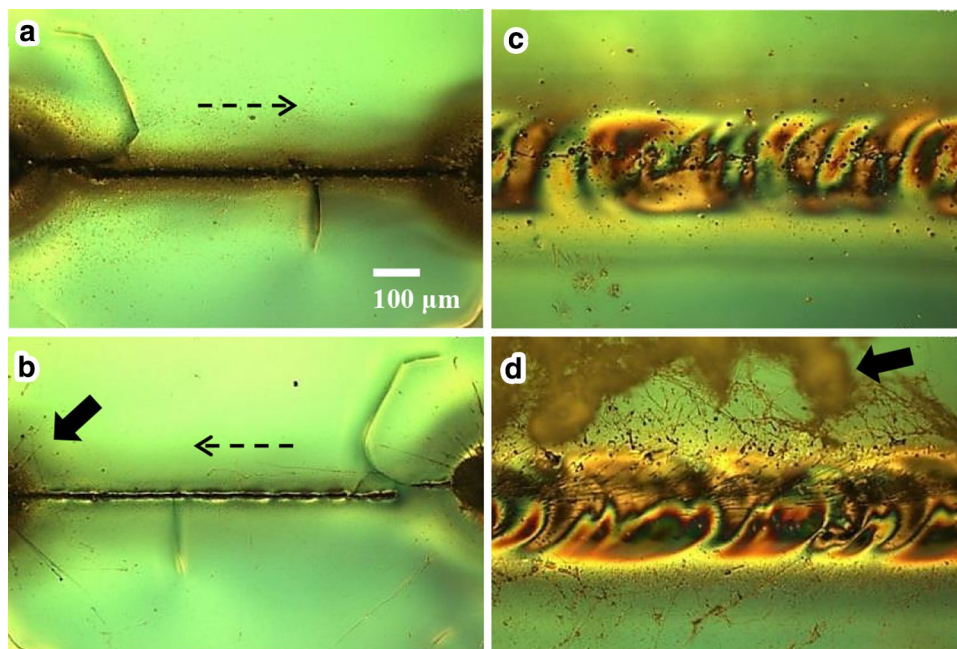
In some nanofibers, a microparticle was found in the middle of the nanofiber, as shown in Fig. 4f, in which the particle diameter is  $2.8 \mu\text{m}$ . We determined the composition of nanofibers and the glass substrate by EPMA as a reference, but we were unable to find a significant difference between them. We 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.

### 3.2 Investigation of generation conditions

Using a line-scanning optical system for in situ observation, we 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 Sect. 3.1, nanofibers were generated. Thus, we chose the laser focusing location as one parameter. Figure 5 shows the dependence of nanofiber generation on the laser focusing location and scanning speed at a power of  $\sim 2$  W.  $\Delta Z$  denotes the focusing location considering the refractive index of the substrate, where 0 mm was defined as the top surface, and positive values correspond to below the top surface. In this experiment, when nanofibers and no nanofibers were observed on the back surface after irradiation, we plotted the conditions as a circle and times symbol in Fig. 5, respectively (or a filled circle when a large number of nanofibers were observed). Figure 6 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 speeds 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  $27 \mu\text{m}$ , which is almost equal to the laser spot size on the top surface of  $35 \mu\text{m}$ . 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 Sect. 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,

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



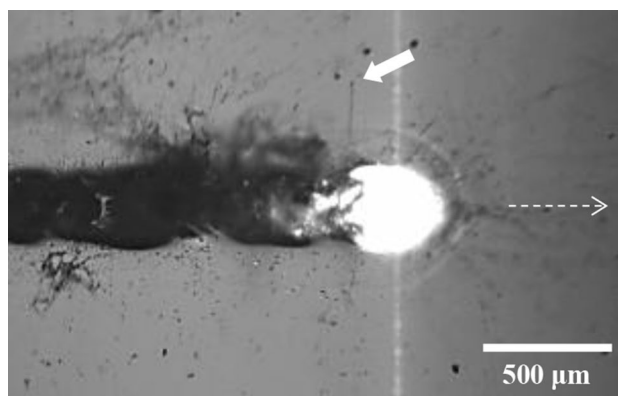
at a scanning speed of 0.2 mm/s, the image shows stable nanofiber generation with a modified region of width  $\sim 240$   $\mu\text{m}$ . After irradiation, a glass surface was formed instead of grooves. At a scanning speed of 1.0 mm/s, the glass was modified in a region with a width of  $\sim 140$   $\mu\text{m}$ . However, no nanofibers were observed.

To carry out a more direct investigation, we conducted in situ observation using a CCD camera. Figure 7 shows an image captured under the conditions of Fig. 6c, d. The CCD focus was adjusted to the top surface. In the image, a white region can be observed, which is considered to be a molten pool resulting in heat radiation, the width of which is  $\sim 360$   $\mu\text{m}$ . 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 Fig. 6d, the original points of nanofiber generation on the molten surface were mainly located in the region, which had a width of one-quarter of the modified width. This value was larger than the beam diameter ( $1/e^2$ ) on the surface of 28  $\mu\text{m}$ . 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.

### 3.3 Consideration of generation process

On the basis of the above results, we 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  $\text{CO}_2$  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, we 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  $\text{CO}_2$  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. [12], 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  $\text{CO}_2$  laser), leading to energy absorption on most of the top surface. On the other hand, in our process, the light transmittance of our material



**Fig. 7** Image captured in the 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

was  $\sim 90$  % at a wavelength of 355 nm at room temperature [13]. We measured the amount of transmitted light under the condition of Fig. 6c, d, which was about 0.5 W for an incident laser power of  $\sim 2$  W. Thus,  $\sim 75$  % of the laser energy was absorbed. Therefore, we 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, it is necessary for the molten region to reach the back surface for nanofibers to form.

In Fig. 6a, b, unstable generation was observed. We 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. 6d), the amount of the stage motion increases, which enables to prevent the laser pulse from penetrating 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. We consider 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 the ejection of particles from the substrate, it is considered that nanofibers were formed when the viscosity, which is dependent on the temperature, became a 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.

#### 4 Conclusions

We reported glass nanofiber generation using a pulsed UV laser. We 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.

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