Laser-Assisted Nanoimprint on Glass Materials and Its Mechanism

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Nanostructured glass is expected to be used for various applications such as optical devices, electronic devices, biological devices, micro reactors and solar cells because glass materials have many advantages such as optical properties, electrical properties, gas barrier properties, chemical resistance, weathering resistance, hardness and biocompatibility. Thermal nanoimprinting is one of the major methods used to fabricate nanostructures on glass materials. However, conventional thermal nanoimprinting has technical issues like long cycle time and low energy efficiency. Laser-assisted nanoimprinting (LANI) is one of the highest-throughput and highest-energy-efficient replication techniques. Glass is pressed by a Ni mold, and a laser is irradiated on the mold to generate heat. Thus, the glass melts by conductive heating to immediately fill the mold's structures. In this study, we successfully demonstrated the replication of a 1.5-µm-pitch (650-nm-depth) line and space structure onto aluminosilicate glass by spot laser irradiation. Furthermore, a 5-µm-pitch (3-µm-depth) line and space structure was also replicated onto aluminosilicate glass. The result suggested that the maximum depth of structure to replicate by LANI is approximately a few microns.

1. Introduction

Fabricating nanostructures onto materials is a widely known method for creating functionalized surfaces with uses such as light management, flow management, super water repellent, surface area maximization and so on. Glass is a commonly used material for many devices because of its advantageous physical properties. Thus, nanostructured glass is expected to be applied to high-functioning devices. Lithography is one of the most common methods to fabricate nanostructures onto glass materials. Lithography can make precision structures; however, it shows relatively low-throughput because of batch-processes. In addition, toxic chemicals are used in the process. Since nanoimprint technology was developed by Chou et. al [1], many studies have been done on glass materials [2, 3]. Conventional thermal nanoimprinting is also a well-used method for thermoplastic materials and several studies have been reported about its use on glass. However, conventional thermal nanoimprinting has technical issues like long cycle time and low energy efficiency because it needs to heat and cool the whole of the mold and glass materials. In this study, we demonstrated a high throughput imprinting method on glass materials by using laser irradiation.

2. Laser-Assisted Nanoimprint

In this section, we describe the concept of this study. Laser-assisted nanoimprinting (LANI) is one of the highest throughput and highest energy efficient replication techniques [4]. A laser is irradiated from the backside of the glass material and onto the surface of the mold which immediately generates heat, and heat conduction partially melts the glass material. Thus, nanostructures are replicated onto the glass surface. Fig. 1 shows a process comparison of fabricating nanostructures onto glass including LANI. Compared with current processes such as lithography and conventional thermal molding, LANI provides a simpler process which can expect higher throughput. In previous research, Sato et al. used a quartz mold and with a DLC film layer applied on top as a light-absorption layer [5]. In this study, we applied Ni to the mold as a replication and light-absorption layer because it is easy to handle and costs less.

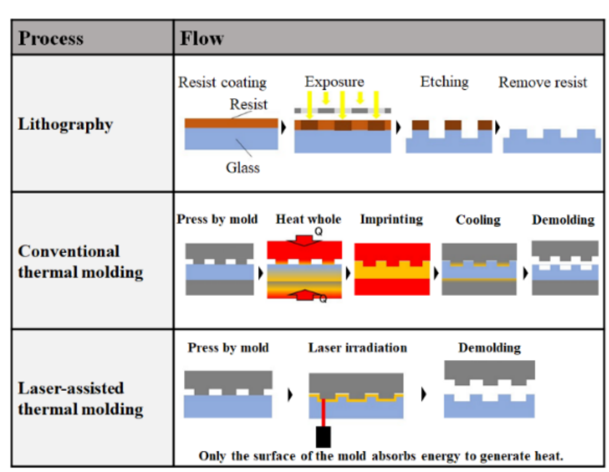

Fig. 1 Comparison of fabrication process of nanostructures on glass.

3. Experimental Details

We prepared three kinds of glass material which have different glass transition temperature (T_g); optical glass A (T_g: 288℃, 1.3 mm thick), optical glass B (T_g: 498℃, 1.5 mm thick) and aluminosilicate glass (T_g: 604℃, 1.3 mm thick). The mold material is made of Ni at 250μm thick. The patterns on the mold are 1.5-μm-pitch line and space (L:S = 1:1, height: 750 nm) and. 30-μm-pitch line and space (L:S = 2:3, height: 15 μm). Fig. 2 shows a schematic of the sample holder. The Ni mold, glass sample, silicone rubber sheet and a quartz plate as a support layer are sandwiched by metal holders. A pressure of 4 MPa is applied by screws. The upper metal plate has an open window to pass the irradiating laser. We used a fiber laser (λ = 1070 nm, gaussian beam) for this demonstration. The absorbance of the Ni mold was 30% for the laser's wavelength. The spot diameter is 150 μm at the focal point. The irradiation power can be set to 25 – 500 W. The glass size for each trial is 10 mm * 10 mm. First, we observed the molten mark which is formed by spot laser irradiation. A Ni mold without any structures was set and its surface roughness was Sa = 0.3 μm. Table 1 shows the irradiation conditions for each glass sample. The irradiated energy density was 32 and 43 kW/cm^2 for optical glass A, 134 and 161 kW/cm^2 for optical glass B, 161 and 215 kW/cm^2 for aluminosilicate glass. Energy density less than 134 kW/cm^2 was tuned by defocusing. The spot laser was irradiated for 2, 4, 6, 8, 10, 12, 14, 16, 18 and 20 ms. The molten mark on the glass was observed by a confocal laser scanning microscope (OLS4500, OLYMPUS Corporation). Second, we demonstrated nanoimprinting on aluminosilicate glass by LANI. Fig. 3 shows the detail of the structures on the Ni molds by SEM (SU-8000, Hitachi High-Tech Corporation) and AFM (NanoNavi L-trace, Hitachi High-Tech Corporation). Table 2 shows the process conditions. The irradiated energy density was 161 kW/cm^2 and its spot diameter was 150 μm. The spot laser was irradiated for 2, 4, 6, 8, 10, 12, 14, 16, 18 and 20 ms for nano-structure imprinting and 10, 12, 14, 16 and 18 ms for micro-structure imprinting. The imprinted structures on the glass were observed by SEM and AFM.

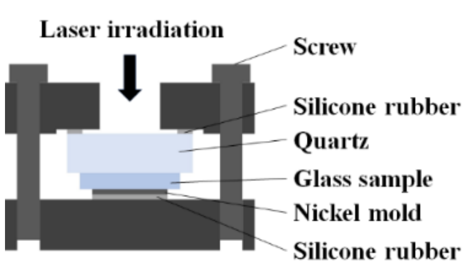

Fig. 2 Schematic of sample holder.

	Optical glass A		Optical glass B		Aluminosilicate glass	
Energy density [kW/cm2]	32	43	134	161	161	215
Spot diameter [μm]	650	485	150	150	150	150
Irradiation time [ms]	2, 4, 6, 8, 10, 12, 14, 16, 18, 20					

Table 1 Spot laser irradiation for molten mark observation

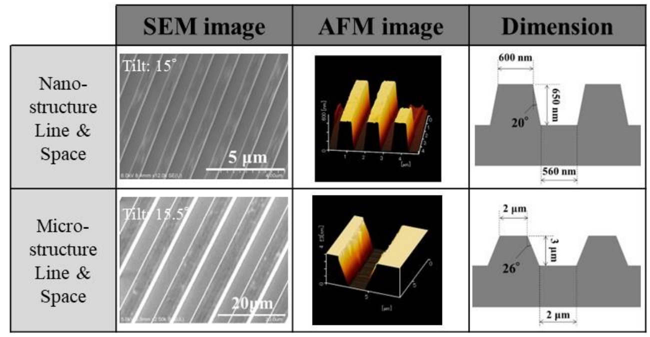

Fig. 3 Tiny structures of Nickel mold

Nickel mold	Nano-structure	Micro-structure
Energy density [kW/cm2]	161	
Spot diameter [μm]	150	
Irradiation time [ms]	2, 4, 6, 8, 10, 12, 14, 16, 18, 20	10, 12, 14, 16, 18

Table 2 Spot laser irradiation for replication

4. Result and Discussion

4.1 Molten mark observation

Fig. 4 shows the results of the molten mark on the glass surface after laser irradiation. The results show that longer irradiation time makes a larger mark, and a higher input energy is needed to initiate molten flow on the glass surface as the glass's T_g gets higher, otherwise lower T_g glass is difficult to manage thermal fractures. On the other hand, the molten mark becomes dome-shaped when irradiated for a longer time.

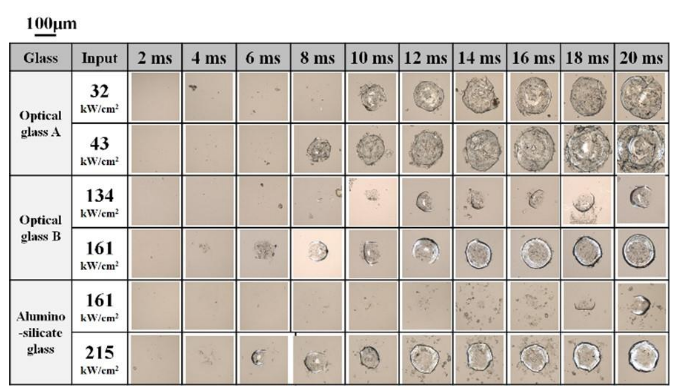

Fig. 4 Formed molten mark on glass surfaces by spot laser irradiation.

Fig. 5 shows an SEM image of the surface of a dome-shaped molten mark (aluminosilicate glass, 215 kW/cm^2, 20 ms irradiation). It doesn't show any mound and becomes thermally fractured along its boundary with the surrounding glass. Fig. 6 shows the formation mechanism of the molten mark. To get a good enough imprinting, the glass surface needs to achieve molten flow in order to fill the mold. However, if the glass surface is over-heated, the molten area expands to the inside of the glass forming a dome-shaped molten mark. Soon after laser irradiation is finished, the molten part is quickly cooled and shrinks creating local strain which cause thermal fracture around it. To complete precise imprinting without any thermal fracture, process conditions should be decided to prevent the forming of dome-shaped molten marks.

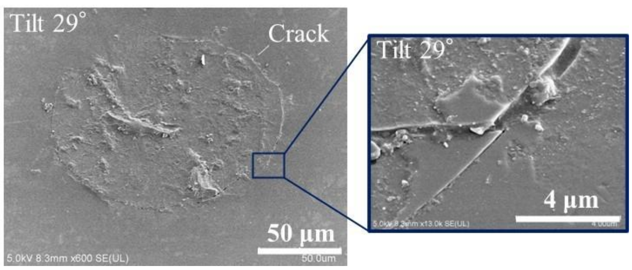

Fig. 5 SEM image of dome-shaped molten mark (aluminosilicate glass, 215 kW/cm^2, 20 ms irradiation)

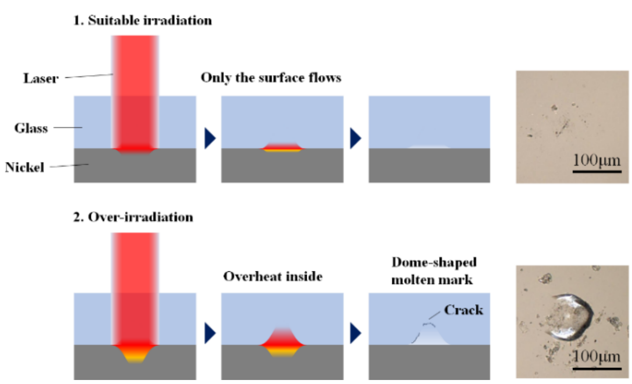

Fig. 6 The forming mechanism of a molten mark.

4.2 Replication by spot irradiation (Nano-structure L/S)

Fig. 7 gives a summary of the replication results for the nano-structure Ni mold. The vertical line shows the actual absorbed energy by the Ni mold's surface calculated from a set energy density [kW/cm^2], laser irradiation time [ms] and the measured absorbance of the Ni mold at $\lambda = 1070$ nm (30%). The "○" marker indicates that the nanostructure is imprinted without any thermal fracture. The areas in the red-square are where dome-shaped molten marks are confirmed based on section 4.1. Fracture defects are observed in the red-squared process conditions. This means dome-shaped molten marks led to thermal fracture because of thermal stress during quenching.

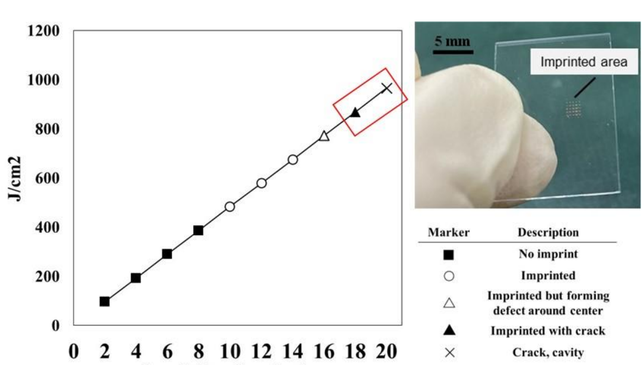

Fig. 7 Result of imprinting of Nano-structure L/S.

Fig. 8 shows SEM images (i) and AFM images (ii) of the imprinted surfaces on aluminosilicate glass with a laser power density of 161 kW/cm^2. The SEM images show irradiation time of 10, 12, 14, 16, 18 and 20 ms. The structure with a size of 1.5-µm-pitch is replicated well from 10 ms to 14 ms. But 16 ms and 18 ms are shown forming defects around the center and thermal fracture is confirmed at 18 ms and 20 ms. When quenching during the LANI process, a large thermal expansion coefficient causes the glass to store a huge local strain, which readily causes thermal fracture. The AFM images are of irradiation times of 10, 12, 14, 16 ms which do not have any thermal fracture. Imprinted structures show horn-shaped depression along the edge of the convex pattern from 10 ms (a) to 14 ms (c). 16 ms (d) does not show horn-shaped depression but the imprinted pattern is lost. Fig. 9 shows SEM images of the Ni mold with nanostructures after laser irradiation (161 kW/cm^2, 16 ms). It shows that the tiny structures are lost due to the laser irradiation. This is the reason why the imprinted structure (e, Fig. 8) is lost. Fig. 10 describes the filling rate of the imprinted structure which is calculated by the cross-sectional area of the measured number shown in Fig. 8 (ii). The ratio is slightly increasing between 10 ms and 14 ms, however, it jumps up from 14 ms to 16 ms dramatically. This suggests that the temperature of a glass is high enough to fill the concave structure easily. As we discussed in section 4.1, dome-shaped molten marks occur after 18 ms of laser irradiation because the irradiated part of the glass is heated too much, thus 16 ms gives the ideal temperature (soften enough to imprint nano-structure line and space) to the glass for imprinting.

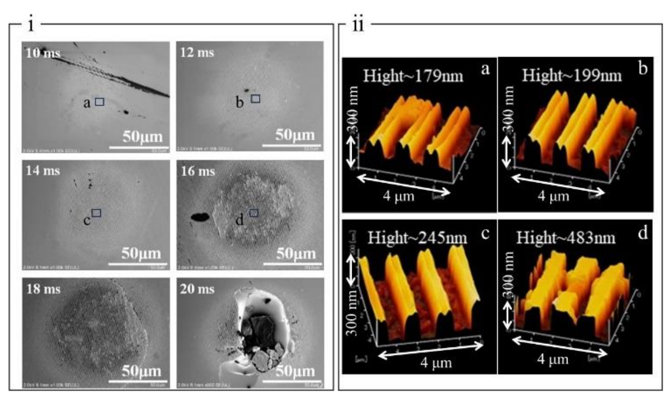

Fig. 8 SEM images of the imprinted glass surface.
i: SEM image ii: AFM image

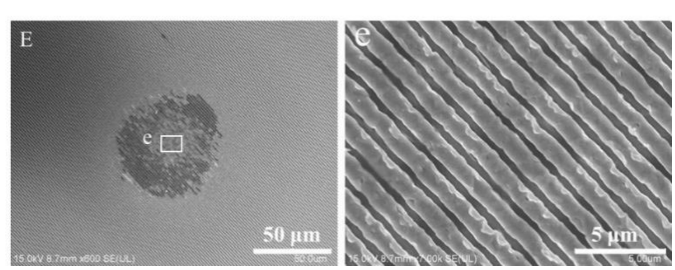

Fig. 9 Ni mold with nano-structure line and space after laser irradiated (161 kW/cm^2, 16 ms)

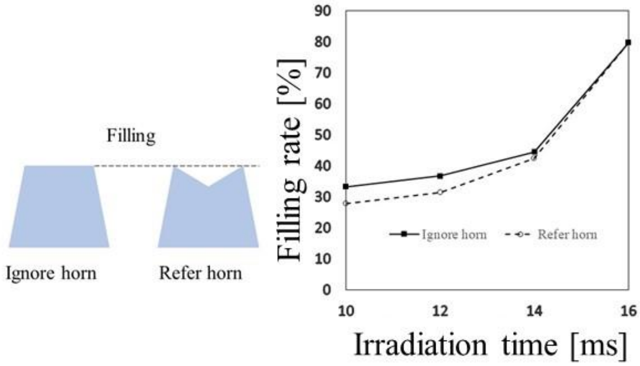

Fig. 10 Filling rate of imprinted nano-structure line and space

4.3 Replication by spot irradiation (Micro-structure L/S)

Fig. 11 shows iii; SEM images of imprinted aluminosilicate glass where the laser irradiation time is from 10 ms to 18 ms and iv; AFM images of imprinted aluminosilicate glass where the laser irradiation time is from 12, 14 and 18 ms. Only 18 ms shows thermal fracture and with the result being the same as that of nano-structure imprinting. Almost all marks were observed on the convex part of the Ni mold. SEM images (iii) show a flow mark of glass along the pressed (or touched) part by the Ni mold. The AFM images (iv) show that the flow marks are horn-shaped (a and b) before they start forming the convex pattern (c).

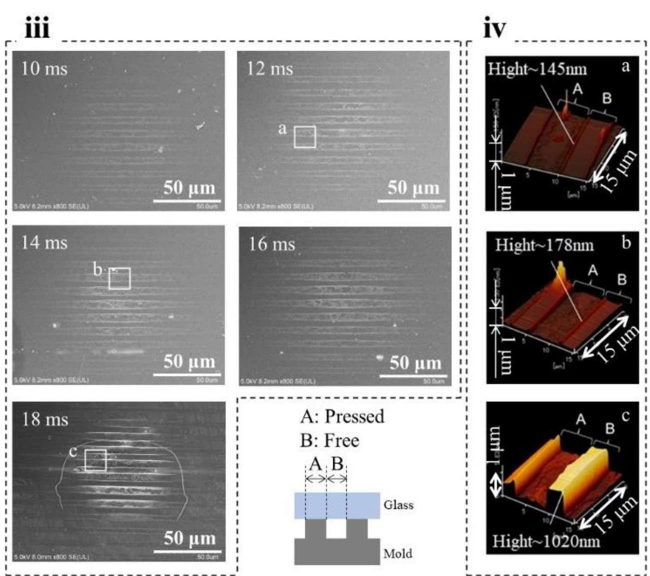

Fig. 11 SEM images (iii) and AFM images (iv) of imprinted aluminosilicate glass (Micro-structure L/S)

Fig.12 shows the mechanism of replication. (1) A glass and a structured Ni mold are sandwiched in a metal holder. (2) A laser is irradiated, and the Ni mold absorbs energy to generate heat. (3) The glass is heated by the convex part of the Ni mold by conductive heat transfer, then the heated part of glass starts to melt and flow along the convex part. (4) Molten glass flows and merges, while the convex part sinks into the glass due to applied pressure. (5) The merged molten glass enlarges and makes a droplet. However, the imprinted structure is only a few microns in height at the highest point (AFM image of c in Fig. 11). This suggests that LANI has a size limitation for replicating structures on aluminosilicate glass of approximately a few microns in height before thermal fracture.

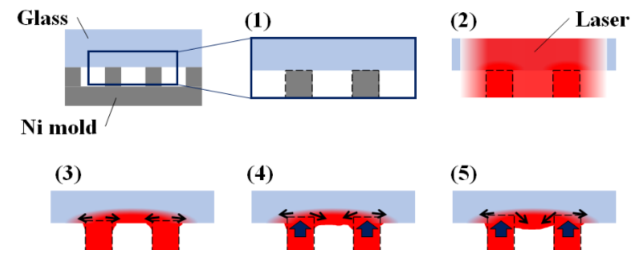

Fig. 12 Mechanism of replication by LANI on glass.

5. Conclusions

We demonstrated laser-assisted nanoimprinting on glass materials. First, we observed a molten mark on optical glass A (T_g; 288 °C), optical glass B (T_g; 498 °C) and aluminosilicate glass (T_g; 604 °C) using spot laser irradiation to find suitable process conditions for replication. A dome-shaped molten mark causes thermal fracture in the glass due to thermal shrinking. Second, we imprinted nano-structure lines and spaces onto aluminosilicate glass by LANI at 161 kW/cm^2. Imprinting was done without thermal fracture on the glass from 10 ms to 16ms. Imprinted structures were detected by SEM and AFM. The filling rate was dramatically increased between 14 ms and 16 ms but the imprinted structure was lost at 16 ms because the structure on the Ni mold was lost. This suggests that lower melting point glass or higher melting point mold will serve the LANI process better. Third, micro-structure lines and spaces were replicated onto aluminosilicate glass. The maximum height of the replicated structures was only a few microns, despite the maximum depth of the mold being 3 µm. This suggests that the maximum depth possible to replicate by LANI is limited to around a few microns. Further experiments will need to be conducted with structures of various sizes and other glass materials to expand on the discussion on the mechanisms of LANI.

REFERENCES

1. Chou, S. Y., Krauss P. R. and Renstrom P. J., "Imprint of sub-25nm vias and trenches in polymers," Appl. Phys. Lett., vol. 67, No. 21, pp.3114-3116, 1995

2. Y. Hirai, "Nano fabrication for Glass material by Nanoimprint," NEW GLASS, Vol. 25, No. 2, pp. 1-6, 2010

3. Takahashi, M., Sugimoto, K. and Maeda, R., "Nanoimprint of Glass Materials with Glassy Carbon Molds Fabricated by Focused-Ion-Beam Etching," Japanese Journal of Applied Physics, Vol. 44, No. 7B, pp. 5600-5605, 2005.

4. Nagato, K., Takahashi, K., Sato, T., Choi, J., Hamaguchi T. and Nakao, M., "Laser-assisted replication of large-area nanostructures," Journal of Materials Processing Technology, 214, pp. 2444-2449, 2014

5. Sato, T., Nagato, K., Choi, j., Hamaguchi, T. and Nakao, M., "Laser-assisted imprinting of nanostructured glass," In; Proceedings of 11th IEEE International Conference on Nanotechnology (IEEE NANO), pp.1-4, 2011