

Application of Nanoparticles Dispersed Polymer to Micropowder Blasting Mask

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Abstract—Improvements in micropowder blasting have been realized for rapid prototyping of channels in glass substrates. The technique presented in this study consists of laser patterning of Au nanoparticles dispersed polymer and micropowder blasting. The patterned polymer was utilized as a mask material for the subsequent mechanical removal of the glass by the micropowder blasting. Five different polymers were tested for the matrix material. Using a line and space mask pattern of 110 μm in width, fabricated channels were created in the glass with a maximum aspect ratio of 2.1. The validity of the micropowder blasting using Au nanoparticles dispersed polymer mask was confirmed; additionally, we demonstrated that the micropowder blasting technique with elevated polymer mask temperature was able to reduce erosion of the polymer mask. [1081]

Index Terms—Laser machining, nanoparticle, polymer mask, powder blast.

I. INTRODUCTION

POWDER blasting with microparticles (micropowder blasting) is a very promising technique for microfabrication in brittle materials such as glass, ceramics and silicon. This technique is faster and cheaper than other microfabrication processes and has been widely used in applications such as electrical device marking, flat panel display production, etc., [1]. These features make micropowder blasting using a patterned mask an attractive option in the field of microelectromechanical systems (MEMS) microfabrication [2]–[4]. We have developed a microfabrication technique that combines micropowder blasting with a mask having high erosion resistance, for use in high aspect ratio machining of brittle materials. In addition, a dry film [5] of negative resist based on polyurethane and electroplated metal masks [6] has also been used as a micropowder blasting mask. There has been a strong demand for a rapid prototyping technique for glass substrates for a micro total analysis system (μTAS). However, the methods described to date have always included a photolithography step, making them unsuitable for this purpose because the processing time is longer and processing costs are higher. If a mask material with high resistance to erosion and high aspect ratio patterning ability can be patterned without photolithography, it will be a very powerful and promising technique for the prototyping of μTAS with micropowder blasting.

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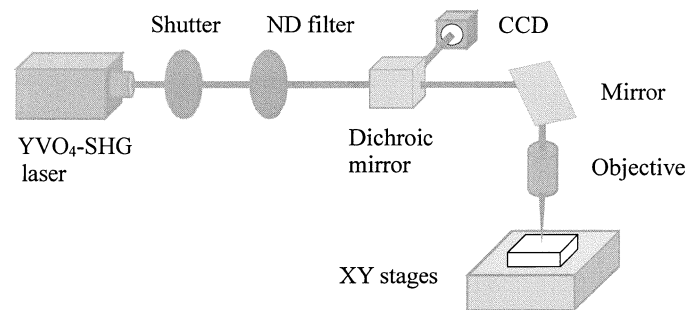


Fig. 1. Schematic diagram of laser microfabrication system.

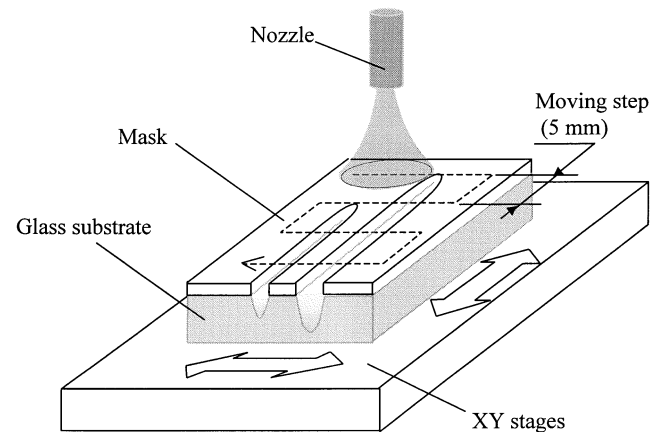


Fig. 2. Schematic diagram of the micropowder blasting process.

TABLE I
THE CONDITION OF THE POWDER BLASTING

Material of the particle	SiC (GC#600)
Particle mean diameter	20 μm
Blasted pressure	0.30 MPa
Distance from the sample	100 mm
Amount of blasted	160 g/min
Nozzle diameter	8 mm
Stage moving speed	50 mm/s
Stage moving step	5 mm

We have developed a new polymer resist in which Au nanoparticles with a mean diameter of 3.4 nm are densely dispersed. Since this resist shows strong absorption in the visible wavelength region (about 530 nm), it can be processed using a focused Nd: YVO₄-SHG laser beam (CW, wavelength

TABLE II
MECHANICAL PROPERTIES OF THE POLYMER MASK MATERIAL

No.	AuPU1	AuPU2	AuPU3	AuPU4	AuEC	BF405
Matrix polymer	Acryl-PU Ureol 600	Acryl-PU 49-394-IM	PET-PU D7-880	PET-PU D7-885	EC	(Acryl-PU)
Au concentration [wt%]	17	17	17	17	17	-
Hardness [HS]	54	73	64	73	96	71
Tensile strength [MPa]	6.9	5.7	3	3.1	57.5	176
Tensile elongation [%]	217	60	80	44	50	200
Modulus 100% [MPa]	2.7	-	-	-	-	128
Peak temperature of E' [°C]	0.6	1.2	-20.2	-29.9	123.6	-25.0
Peak temperature of E'' [°C]	1.0	5.9	-16.1	-26.0	125.6	-23.1
Peak temperature of $Tan\delta (E''/E')$ [°C]	42.5	34.4	6.2	-10.9	138.1	0.3

PET-PU: polyester-Polyurethane, Acryl-PU: Acryl-Polyurethane, EC: Ethylcellulose

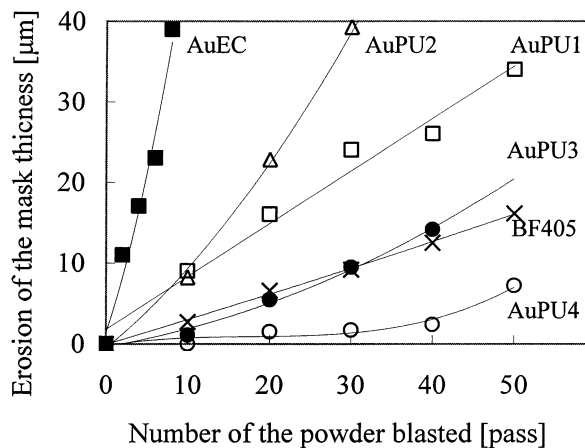


Fig. 3. Dependency of the mask thickness erosion on the number of the powder blasting passes using SiC microparticles (mean diameter of 20 μm).

of 532 nm, output power below 30 mW) [7]. One of the benefits of this fabrication technique is that a microscale channel and hole with high aspect ratio can be fabricated using a low power output laser without the need for a photolithography step.

In this paper, we report on the results of mechanical property measurements on the polymer mask, the erosion resistance of Au nanoparticles dispersed in the polymer mask by micropowder blasting, and the fabrication of glass substrate with this polymer mask.

II. EXPERIMENTAL PROCEDURES

A. Mask Materials

Five different polymers were used for matrix material: two polyester polyurethane (Burnock D7-880, D7-885, Dainippon Ink & Chemicals, Inc., Tokyo, Japan), two acryl polyurethane (Ureol 600, Kawakami Print, Co., Ltd., Hyogo, Japan; Acrylic 49-394-IM, Dainippon Ink & Chemicals, Inc., Tokyo, Japan) and ethylcellulose (Wako Pure Chemical Industries, Ltd., Osaka, Japan). Au nanoparticles with mean diameter of 3.4 nm (Perfect Gold, Vacuum Metallurgical Co., Ltd., Tokyo, Japan) produced by gas evaporation technique were used for nanoparticles. Au nanoparticles dispersed polyurethane

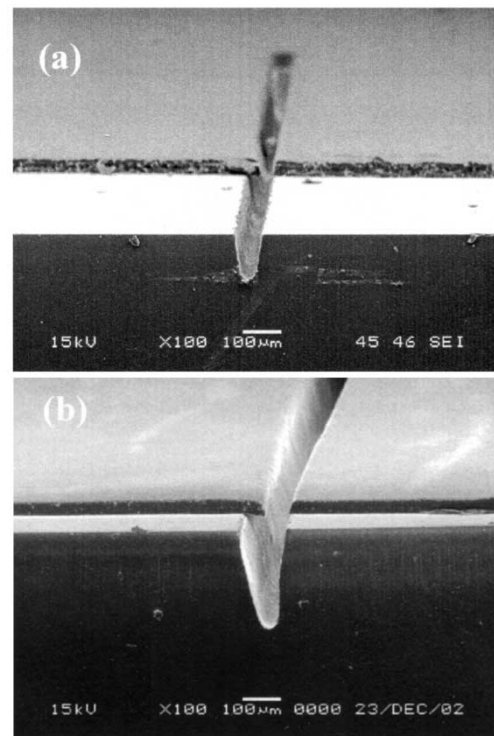


Fig. 4. SEM images of the fabricated channel using Au nanoparticles dispersed polyurethane (AuPU4) mask and 20 μm microparticle. The line opening width of the mask was 60 μm (a) and 110 μm (b). The number of the powder blasting was 30 passes.

(AuPU1–AuPU4) paste and ethylcellulose (AuEC) paste with an Au concentration of 17 wt% in the solid were prepared by mixing the polymer dissolved in the solvent with Au nanoparticles. In addition, a general powder blasting mask (Ordyl BF405, Tokyo Ohka Kogyo Co., Ltd., Tokyo, Japan) was tested as a reference mask material. BF405 is an elastic negative resist film with a thickness of 50 μm .

The mechanical properties (hardness, tensile strength, tensile elongation, modulus, dynamic viscoelasticity) of all materials were measured together with the erosion resistance for micropowder blasting. The dynamic viscoelasticity, the peak temperatures for the storage modulus (E'), loss modulus (E'') and loss

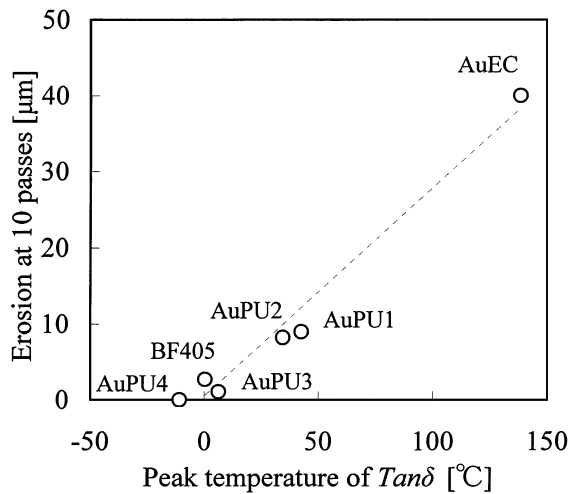


Fig. 5. Relationship between erosion by 10 passes of micropowder blasting and the peak temperature of $Tan\delta$.

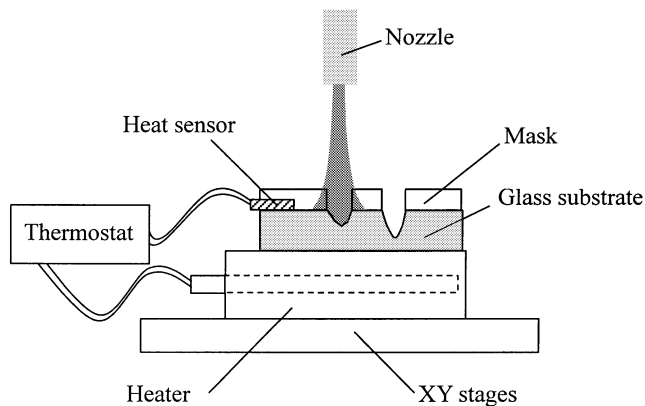


Fig. 6. Configuration of micropowder blasting system for controlling the mask temperature.

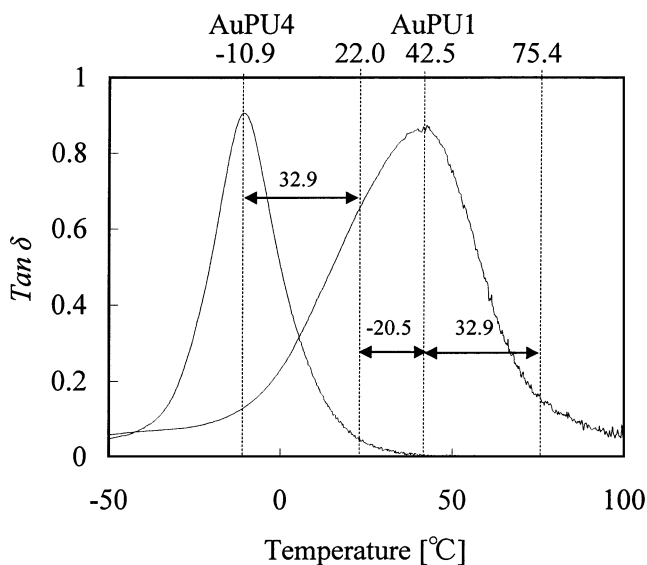


Fig. 7. Dependency of loss tangent ($Tan\delta = E''/E'$) of AuPU1 and AuPU4 on the temperature.

tangent ($Tan\delta = E''/E'$) were measured by Dynamic Mechanical Analysis (DMA). Sheets with a thickness of 2 mm were

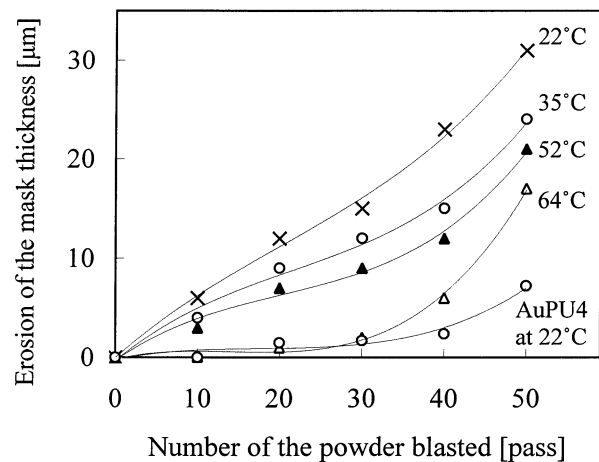


Fig. 8. Dependency of AuPU1 mask thickness erosion on the number of powder blasting passes. The temperature of the mask was 22, 35, 52 and 64 °C.

prepared using molding techniques in order to measure the mechanical properties of all polymer masks. For measurement of the erosion along the thickness direction, another sample was prepared by coating a glass substrate with 30 μm of paste using an applicator, and baking at 80°C for 30 min. As pinholes in the mask will cause defects in the glass substrate after powder blasting, coating was carefully operated to minimize these pinholes. In the case of using thinner resist than 30 μm , a lateral erosion rate of the mask was high and the processed channel in a glass had a lower aspect ratio. On the other hand, for the thicker resist, the channel with high aspect ratio cannot be also fabricated in the glass, because the mask pattern with a large depth cannot be processed by laser beam, or particle for powder blasting was accumulated in opening of the mask pattern. These samples were also utilized for the machining of the glass using the patterned paste as a mask for the micropowder blasting. A powder blasting system (Microblaster MB1, Shinto Brator Co., Ltd., Nagoya, Japan) using a silicon carbide (SiC) microparticle with a mean diameter of 20 μm was utilized in this study.

B. Laser Processing

Fig. 1 shows the configuration of the laser microfabrication system using an Nd:YVO₄-SHG laser (58GC42, CW, wavelength of 532 nm, Melles Griot, Inc., Carlsbad, CA, USA) which has a wavelength near the plasmon resonance absorption peak for Au nanoparticles. The system is small and low-cost since the output power of the laser is 23 mW and the cooling laser device is unnecessary.

The laser beam was focused on a polymer mask with an objective lens with a magnification of 10 and a numerical aperture of 0.25. The patterns were directly drawn on the polymer mask by controlling the laser beam position with programmable moving XY stages. The intensity of the irradiated laser beam was adjusted within the range from 1 to 23 mW using an ND filter. The movement speed of the XY stages was set at 0.5 mm/s. The calculated diameter d of the focused laser beam was 10 μm and the incident angle 2θ was 6×10^{-4} rad. In this study, mask patterns of width 60 and 110 μm in width were fabricated by moving the XY stages in steps of 2.5 μm , since the diameter of the focused laser beam spot was small in comparison with the required line width. In the case of writing the line pattern

of 100 μm in width and 10 mm in length using this laser processing condition, it took about 13 min ($20 \text{ s} \times 40 \text{ step} = 800 \text{ s} = 13.3 \text{ min}$) to complete the mask pattern. From our previous study [7], we have confirmed the processed depth and width depend on laser processing condition and Au concentration of the mask. Hence, this processing time can be shortened by a faster movement speed with higher intensity of irradiated laser beam and a higher Au concentration mask.

C. Micropowder Blasting

Table I shows the conditions under which micropowder blasting was carried out. The SiC microparticles with a mean diameter of 20 μm were accelerated from the nozzle (diameter of 8 mm) toward the sample with high-pressure airflow and an incident angle of 90° . In order to process the entire surface of the glass substrate, the substrate was scanned repeatedly hereafter each scanning session is referred to as a "pass" by the XY stages with the constant velocity and a moving step shown in Fig. 2. When the glass substrate coated with the patterned polymer mask was hit by the SiC microparticles, it was machined in the open areas of the polymer mask due to the difference in the erosion rate between the polymer mask and the exposed glass substrate. The processed glass was immersed in water to remove the mask after powder blasting. We didn't clean a processed glass substrate in this work, because microparticles and mask debris were not observed in the channel. In order to clarify the dependency of polymer mask erosion along the thickness on the number of passes, the thickness of the mask was measured with a profile meter (Alpha-Step 500, KLA-Tencor Co., San Jose, CA) after the powder blasting. The fabricated channels in the glass substrate were observed using the patterned polymer mask with scanning electron microscopy (SEM).

III. RESULT AND DISCUSSION

A. Mechanical Properties of the Polymer Mask Material

Table II shows the mechanical properties of the polymer mask material. BF405 showed a comparatively high tensile strength and tensile elongation, and a low peak temperature of $T_{\text{an}\delta}$. The peak temperatures of E' , E'' and $T_{\text{an}\delta}$ were highest for AuEC, and lowest for AuPU4.

B. The Erosion of the Mask

Fig. 3 shows the dependency of the erosion of mask thickness on the number of passes. AuPU4 (polyester polyurethane) showed the best erosion resistance and its erosion value was 0.4 times lower than that of BF405 at 50 passes.

C. Machining of Glass Substrate

Utilizing the sample coated with AuPU4, which showed the highest erosion resistance, line patterns of width 60 and 110 μm in width were patterned with an irradiated laser beam power of 23 mW, followed by the machining of glass substrate by 30 passes of powder blasting. The channel fabricated on the glass substrate had an aspect ratio (depth/width) of 1.7 (for a width of 60 μm) and 2.1 (for a width of 110 μm) as shown in Fig. 4. In the case of processing of a glass substrate using line pattern of

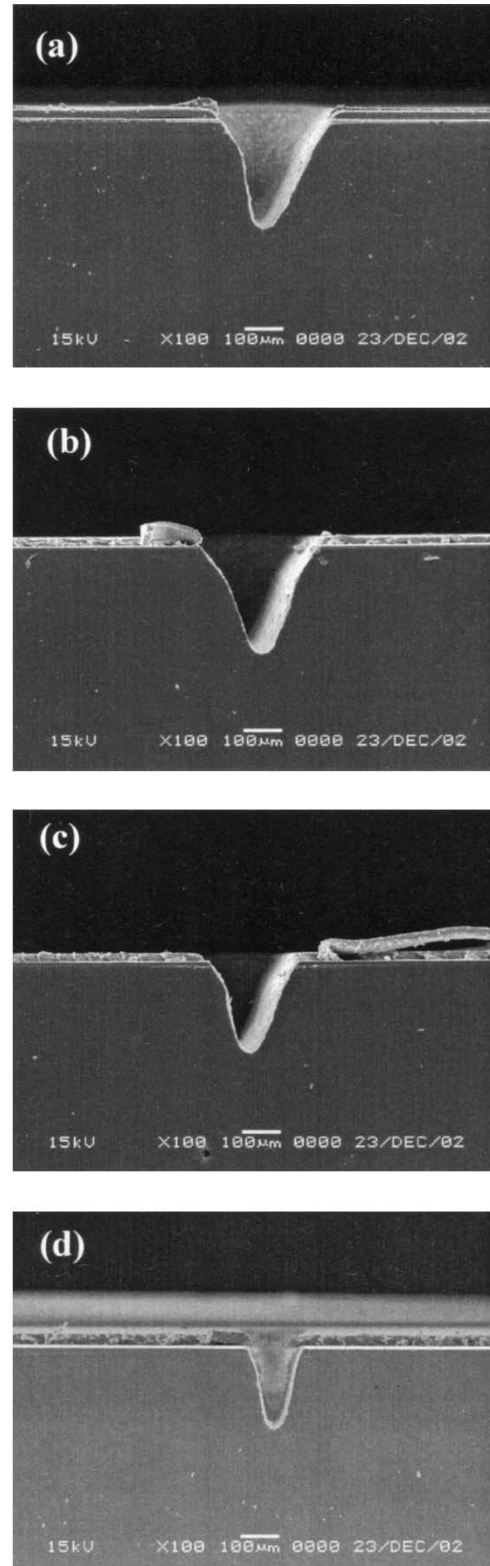


Fig. 9. Cross sections of the fabricated channel on the glass substrate using AuPU1 mask with control of the mask temperature (a) 22 $^\circ\text{C}$, (b) 35 $^\circ\text{C}$, (c) 52 $^\circ\text{C}$, and (d) 64 $^\circ\text{C}$, respectively. Line width of the mask was 60 μm .

110 μm in width, the processed channels depth and aspect ratio in the glass ranged in variation from 161 μm to 246 μm , and from 1.6 to 2.1, respectively. This variation will be reduced by optimization of powder blasting condition (particle size, blasted

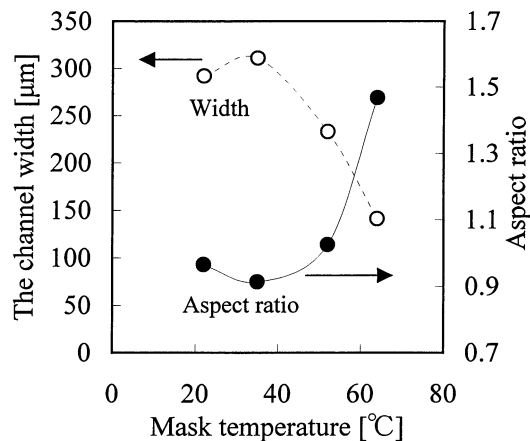


Fig. 10. Relationship between the channel width and aspect ratio of the fabricated channel on the glass substrate and the mask temperature. The line width of the mask was 60 μm .

pressure and so on). These results confirm the validity of the micropowder blasting technique using Au nanoparticles dispersed polyurethane.

D. Temperature Control of the Polymer Mask

Careful observation of the relationship between erosion resistance by micropowder blasting and the mechanical properties of the polymer mask materials revealed that the erosion of the polymer mask material strongly depended on dynamic viscoelasticity, specifically, on the peak temperature of T_{and} . Fig. 5 shows the relationship between erosion by 10 passes of micropowder blasting and the peak temperature of T_{and} . The erosion decreased in proportion to the decrease in peak temperature of T_{and} for the polymer mask material. Hutchings *et al.* studied the relationship between the erosion resistance of an elastomer by particle impact and its mechanical properties, concluding that erosion increases with a decrease in rebound resilience [8]. Since rebound resilience, which involves the absorbed energy in an elastomer, shows a minimum at the peak temperature of T_{and} , it is expected that erosion resistance will improve when the temperature difference between the peak temperature of T_{and} (T_1) and the processing polymer mask temperature (T_2) is increased ($\Delta T = T_2 - T_1$).

In order to confirm this speculation, powder blasting was conducted while controlling the temperature of AuPU1 mask. Since the T_{and} peak temperature of AuPU1 is 42.5°C, which is above room temperature, it is possible to increase ΔT for AuPU1 by heating the mask material. Fig. 6 shows the configuration for this experiment. The temperature of the polymer mask was controlled at a constant value with a thermostat and the heat sensor was inserted between the glass substrate and the polymer mask.

The AuPU4 has a ΔT of 32.9 °C as shown in Fig. 7, assuming that the process is carried out at a room temperature of 22°C. This is the maximum ΔT among the materials shown in Table II. As both AuPU1 and AuPU4 have same ΔT of 32.9 °C, we expected to observe comparable erosion resistance if we set the processing temperature of AuPU1 to 75.4°C. The experiment was carried out with AuPU1 at a temperature of 64 °C because the possible maximum temperature was limited due to cooling by the airflow blown from the nozzle.

Fig. 8 shows the thickness erosion of the AuPU1 mask as a function of both the number of powder blasting passes (from 0 to 50) and the mask temperature (from 22 to 64°C). The erosion of the AuPU1 mask decreased with increasing temperature, and its erosion values at 64°C and 50 passes were 1.1 and 2.4 times lower than those of BF405 and AuPU4 at 22°C. These results confirm that the erosion resistance of the mask can be improved by increasing the ΔT of the polymer mask.

The validity of the proposed idea was verified by fabricating microchannels in the glass. The channel profile was determined by measuring the width and depth with SEM. Fig. 9 shows cross-sections of the fabricated channel on the glass substrate using AuPU1 mask and controlling the mask temperature from 22 to 64 °C. As anticipated, the fabricated channel width and aspect ratio showed a strong dependency on the mask temperature, and showed maximum and minimum, respectively, at a mask temperature of 35 °C. The aspect ratio increased with an increase in mask temperature above 35 °C, and showed a decrease of about 1.5 times at a mask temperature of 64 °C, as shown in Fig. 10.

IV. CONCLUSION AND FUTURE WORK

In the application of Au nanoparticles dispersed polymer for the micropowder blasting mask, it was confirmed that an Au nanoparticles dispersed polyurethane (AuPU4) mask has a high erosion resistance. A channel with an aspect ratio of 2.1 on the glass substrate was successfully fabricated using an AuPU4 mask.

We also conclude that erosion is strongly correlated with the dynamic viscoelasticity of the mask and that the new technique of performing powder blasting while controlling the mask temperature was successful; the erosion resistance of the polymer mask was improved by this technique.

The laser processing conditions of the polymer mask and the powder blasting conditions will be optimized in future work, and its application of this technique to rapid prototyping of μTAS will be examined.

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