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## Direct micromachining of quartz glass plates using pulsed laser plasma soft x-rays

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We have investigated direct micromachining of quartz glass, using pulsed laser plasma soft x-rays (LPSXs) having a potential capability of nanomachining because the diffraction limit is  $\sim 10$  nm. The LPSX's were generated by irradiation of a Ta target with 532 nm laser light from a conventional Q switched Nd:YAG laser at 700 mJ/pulse. In order to achieve a sufficient power density of LPSX's beyond the ablation threshold, we developed an ellipsoidal mirror to obtain efficient focusing of LPSXs at around 10 nm. It was found that quartz glass plates are smoothly ablated at 45 nm/shot using the focused and pulsed LPSX's. © 2005 American Institute of Physics. [DOI: 10.1063/1.1882750]

Inorganic transparent materials are highly valued for their use in the fields of nanometric chemical analysis and chemical reactions in medicine and biotechnology, and for optical materials such as gratings, photonic crystals, and optical waveguides. Recently, we have developed a single-step technique used in micromachining quartz glass plates for these applications (x-ray–UV technique).<sup>1</sup> In the x-ray–UV technique, coloration and patterning are performed by the irradiation of quartz glass plates with laser plasma soft x-rays (LPSXs) from a pulsed Ta laser plasma, and the patterned area are ablated using pulsed 266 nm Nd:YAG laser light. The technique utilizes the high precision of the soft x-rays and the high fluence of conventional laser light. Although we have established a single step process using LPSXs and UV laser light, the following limitations still exist. The UV laser light must have a wavelength tuned to an absorption band induced by LPSX irradiation. Surface roughness is strongly affected by the UV laser beam quality. The technique can be applied only to transparent materials.

So far, quartz glass micromachining has been achieved by techniques such as electron beam lithography,<sup>2–5</sup> photo-lithography,<sup>6</sup> focused ion beam etching.<sup>7</sup> Although nanomachining has been achieved, the above techniques have the following difficulties. They include multiple and time-consuming process steps. And there are a limited number of materials for which etchants and resists are available. Compared to these techniques, photo-machining, (i.e., direct laser machining), is a promising technique because of its suitability for mass production and a direct single process. In addition, it can be applied to a wider range of materials which are able to absorb laser light. The photo-machining of transparent materials, however, requires additional photon absorbers such as excited defects in SiO<sub>2</sub>,<sup>8,9</sup> plasma exposed to transparent materials,<sup>10</sup> and photo-absorbing medium solutions.<sup>11,12</sup> Further, photo-machining with a precision of  $\sim 10$  nm requires soft x-rays, because precision is a function of the diffraction limit.

Although UV laser assistance is inevitable in the x-ray UV technique when the power density of LPSXs is low, it is preferable to machine materials using only LPSXs without assistance. At higher power densities of LPSXs, one can expect ablation of a variety of materials, including opaque as well as transparent materials, with a precision up to the diffraction limit of  $\sim 10$  nm.

In addition, one can expect smoother micromachining by use of only LPSXs, because beam quality of LPSXs can be higher than that of the original UV laser beam used for the LPSX generation as follows. During and after formation of plasma by laser irradiation, the plasma comes to thermal equilibrium and emits LPSXs. The thermalization process results in formation of a homogeneous x-ray emitting plasma.

In order to achieve ablation, one of the most crucial factors for ablation is the temperature of materials during a period of x-ray irradiation. The temperature depends on two competing processes, i.e., accumulation of absorbed x-ray energy and thermal diffusion of the energy into the un-irradiated region. When the material is heated beyond the boiling point, ablation can take place. At a fixed dose, pulsed x-rays with a higher peak power are suitable for ablation, because absorbed x-ray energy per unit time gets higher and hence higher temperature can be achieved. Furthermore, shorter pulsed x-rays are suitable for high-quality ablation because thermal diffusion length gets shorter.

In the present work, we have investigated quartz glass micromachining by direct irradiation with only LPSXs. The key device for the micromachining is an efficient focusing soft x-ray mirror, which we have newly designed for the micromachining.

Figure 1 shows the experimental setup for the micromachining. Synthetic quartz glass plates (*Q*) (Tosoh Quartz Co., Ltd., ES grade) were irradiated with pulsed LPSXs (*X*) in a vacuum chamber at a pressure of  $2 \times 10^{-4}$  Pa, using a focusing ellipsoidal mirror (*E*). To permit patterning, a Ni grid with a mesh #2000 (*M*) was placed on the quartz glass plates, as a contact mask.

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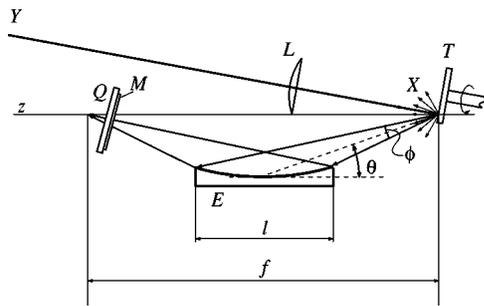


FIG. 1. The experimental setup for micromachining quartz glass plates (Q) using pulsed LPSXs (X).

The LPSXs (X) were generated by irradiation of a Ta target (T) with 532 nm Nd:YAG laser light with a pulse duration ( $\tau$ ) of 7 ns, with an energy ( $E$ ) of 700 mJ/pulse, at a fluence of  $\sim 1 \times 10^4$  J/cm<sup>2</sup> using a focusing lens (L) with a focal length of 10 cm. The Ta laser plasma emits soft x-rays, as shown in Fig. 2(a). The detail of the soft x-ray spectroscopy is given elsewhere.<sup>13,14</sup> It is noted that the Ta laser plasma emits light at wavelength in vacuum-ultraviolet, ultraviolet, and visible light regions. It is a reasonable evaluation that the LPSX pulse has the same duration of the Nd:YAG laser light pulse, on the time scale of a nanosecond.<sup>13</sup>

The LPSXs were focused onto the quartz glass plates using the ellipsoidal mirror (E) (Hidaka Kogaku Kenkyusho Co., Ltd.), made of quartz glass and coated with a Au layer. Au is a material that has a high reflectivity in the soft x-ray region around 10 nm.<sup>15</sup> In order to improve the adhesion of the Au layer to the quartz glass substrate, the substrate was first coated with a Cr layer.

We designed the ellipsoidal mirror so as to maximize power density of LPSXs on the surface of the quartz glass plates. The power density depends on the visual angle of the mirror  $\phi$ , and grazing angle of LPSXs incident to the mirror  $\theta$ , if angle of ellipsoid of revolution about rotating axis ( $\psi$ ), distance between focal points ( $f$ ) and mirror length ( $l$ ) along rotation axis ( $z$ ) are fixed. In the present work, we used an

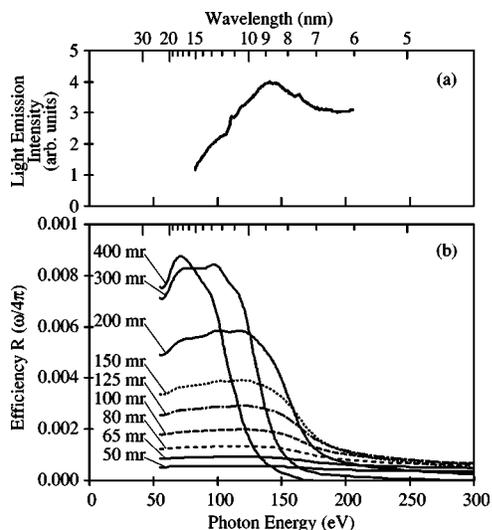


FIG. 2. (a) Light emission spectrum of a Ta laser plasma. (b) Focusing efficiency  $R \times (\omega/4\pi)$  of ellipsoidal mirrors with given grazing incident angles  $\theta$ , as a function of photon energy of soft x-rays incident to the mirrors.

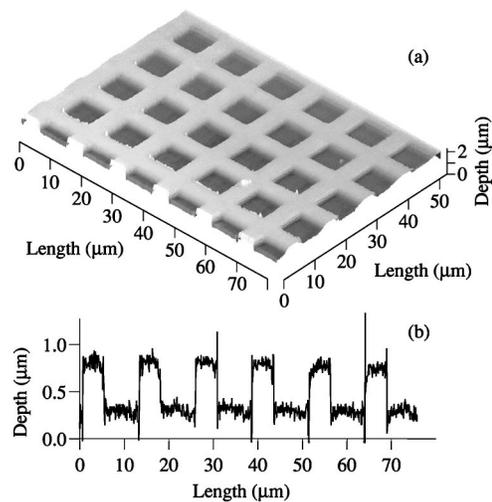


FIG. 3. (a) A confocal microscope image of a quartz glass plate after irradiation of LPSXs through square apertures in a contact mask. (b) A cross sectional profile of the machined quartz glass plate.

ellipsoidal mirror with  $\phi=120^\circ$ ,  $f=150$  mm, and  $l=80$  mm.

As  $\theta$  increases, solid angle  $\omega(\phi, \psi)$  increases and hence total intensity of LPSXs incident to the mirror increases. In contrast, as  $\theta$  increases, reflectivity  $R$  drastically decreases in the soft x-ray region around 10 nm. The reflectivity  $R$  in the soft x-ray region as a function of photon energy and grazing angle is available in the literature.<sup>15</sup> Figure 2(b) shows product of  $R$  and  $\omega/4\pi$ , which is proportional to the power density of the LPSXs on the quartz glass plates. Note that  $R$  is normalized to unity for total reflectance. Based on the result shown in Fig. 2(b), the ellipsoidal mirror is designed to have a grazing angle at  $\theta=200$  milliradians at the center, in order to focus LPSXs at around 10 nm on quartz glass plates efficiently.

In order to machine large areas, the quartz glass plates were placed closer to the ellipsoidal mirror, than the focal point of the mirror so that the LPSX beam has a radius ( $r$ ) of 200  $\mu\text{m}$  on the surface of the quartz glass plates.

The ablated area was observed using a confocal microscope (Keyence Corp, VK-8510). Figure 3(a) shows a three-dimensional image of a quartz glass plate after 10 shots of LPSX irradiations. It is clearly seen that square regions are ablated. Figure 3(b) shows a cross-sectional profile of the machined quartz glass plate. The ablated area has a depth of 470 nm and a root mean-square roughness less than  $\sim 30$  nm. This root mean square value is the same as the limit of the microscope. It is found that quartz glass plates can be smoothly ablated with a precision less than 30 nm, in the depth direction. The steepness at the edge of each pattern is less than 1  $\mu\text{m}$ , which is the detection limit of the confocal microscope.

Figure 4 shows ablation depth as a function of the number of LPSX irradiation shots. The depth is proportional to the shot number, and the ablation rate is 45 nm/shot. It is found that the ablation is intrinsic to interaction of LPSXs with the material but not with surface specific states such as surface contamination.

Assuming that ablation is caused by the heating of the quartz glass plates beyond the boiling point, this is mainly governed by two competing processes occurring during LPSX irradiation, i.e., accumulation of LPSX energy and heat diffusion to the un-irradiated region.

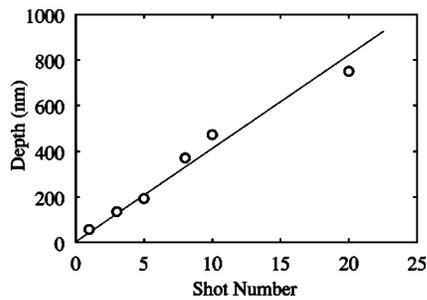


FIG. 4. Ablation depth as a function of the number of LPSX irradiation shots.

The energy density of the LPSXs can be estimated by the fluence of the LPSXs and the penetration depth. The fluence of the LPSXs on the quartz glass plate  $F$  can be estimated from  $F = E\eta(\omega/4\pi)R/(\pi r^2)$  where  $E$ ,  $\eta$ ,  $\omega$ , and  $R$  are the energy per pulse of Nd:YAG laser used for LPSX generation, a conversion efficiency of the Nd:YAG laser light to the LPSXs, the solid angle of the ellipsoidal mirror and reflectivity of the ellipsoidal mirror, respectively. As described above,  $E = 700$  mJ/pulse. From the geometric parameters described above,  $\omega = 0.12$ . According to the literature,  $R = 60\%$  at around 10 nm. The conversion efficiency  $\eta$  could be 10% at maximum, because the reported conversion efficiency for a Ta target is 0.3% /eV at 13 nm<sup>16</sup> and the ellipsoidal mirror used in the present work is capable of focusing LPSXs in a spectral region  $100 \pm 20$  eV, at least. Compared to the reported efficiency, the conversion efficiency in the present work might be lower because LPSX generation has not yet been optimized. Consequently, the fluence  $F$  can be estimated to be  $0.3$  J/cm<sup>2</sup>.

The penetration depth  $l$  of LPSXs is related to the absorption cross sections  $\sigma_x$  ( $x = \text{Si}$  and  $\text{O}$ ) by

$$1/l = N_A(\sigma_{\text{Si}} + 2\sigma_{\text{O}})/(M_{\text{Si}} + 2M_{\text{O}})\rho,$$

where  $N_A$  is Avogadro's number,  $M_x$ 's are the atomic weights, and  $\rho$  is the density of amorphous SiO<sub>2</sub>. The cross sections are obtained from the reported mass absorption coefficients<sup>15</sup> by  $\mu_x = N_A/M_x\sigma_x$ . Thus, the LPSXs at around 10 nm are estimated to penetrate 100 nm into the quartz glass plates. Hence, the energy density of absorbed soft x-rays  $\varepsilon (= F/d)$  is  $\sim 30$  kJ/cm<sup>3</sup>.

The heat diffusion length is given by  $\sqrt{D\tau}$ , where  $D$  and  $\tau$  are the thermal diffusivity and the pulse duration of the LPSXs, respectively.  $D$  is  $8.5 \times 10^{-7}$  m<sup>2</sup>/s at 300 K and monotonically decreases up to the melting point. Unfortunately,  $D$  beyond the melting point is unknown, to our knowledge. The heat diffusion length can be roughly estimated to be less than 77 nm during the LPSX irradiation.

Consequently, most of the LPSX energy absorbed by the surface layers of the quartz glass plates is accumulated in the surface layers without significant heat diffusion during LPSX irradiation. Because the accumulated energy density (30 kJ/cm<sup>3</sup>) is of the same order as the evaporation energy

of SiO<sub>2</sub> (76 kJ/cm<sup>3</sup>), quartz glass plates certainly can be heated to high temperature and may be ablated by heat accumulation via the absorption of pulsed and focused LPSXs.

As another ablation mechanism, it is possible that quartz glass plates are ablated by bond breaking. The LPSX irradiation may cause photo-dissociation of SiO<sub>2</sub> via processes such as direct photo-excitation of the bonding electrons or a Feibelman-Knotek process.<sup>17</sup>

With further development of x-ray imaging optics, machining with a precision as high as the diffraction limit of 10 nm, should be achieved.

In conclusion, we have investigated quartz glass micro-machining using pulsed LPSXs. In order to achieve high power density of the LPSXs on the surface of quartz glass plates, we have developed an ellipsoidal mirror to efficiently focus LPSXs at around 10 nm. We found that quartz glass plates are smoothly ablated at 45 nm/shots by irradiation with the pulsed LPSXs focused using the mirror.

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