Direct Nanomachining of Inorganic Transparent Materials Using Laser Plasma Soft X-Rays

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Abstract. We have investigated micromachining of a variety of materials by irradiation with laser plasma soft X-rays (LPSXs) at around 10 nm. The pulsed LPSXs were generated by irradiation of a Ta target in a vacuum chamber with Nd:YAG laser light at 532 nm, with a pulse duration of 7 ns, at a fluence of \( \sim 10^4 \) J/cm\(^2\). The LPSXs were focused on the surfaces of samples using an ellipsoidal mirror that is designed so that LPSXs at around 10 nm are focused efficiently. We found that quartz glass plates are ablated by LPSX irradiation at a typical rate of 48 nm/shot. Furthermore, the ablated regions have smooth surfaces with a roughness less than 10 nm after 10 shots of LPSX irradiation. It is demonstrated that quartz glass is machined with a lateral resolution higher than 100 nm. In addition to quartz glass, the LPSX processing can be applied to micromachining of a variety of materials such as Pyrex, CaF\(_2\), LiF, LiNbO\(_3\), Si and silicone.

1. Introduction —Nanomachining of Inorganic Transparent Materials—
Investigating interaction of intense soft X-rays with sold surfaces and resulting phenomena is still challenging, although extensive studies have been carried out on interaction of soft X-ray at intensities below ablation thresholds. Applying the interactions, one could expect direct light nanomachining of transparent materials at a precision as high as the diffraction limit of soft X-rays. Inorganic transparent materials, quartz in particular, are highly valued for their use in the fields of nanometric chemical analysis and chemical reactions in medicine and biotechnology, and optical materials such as gratings, photonic crystals and optical waveguides. More recently, imprint [1] and DNA sieving based on SiO\(_2\) nanomachining techniques [2] have attracted some interests. For practical applications, techniques with high precision and high productivity are in great demand for machining inorganic transparent materials.

So far, quartz glass micromachining has been achieved by techniques such as electron beam lithography [3], photo-lithography [4], focused ion beam etching [5]. Although nanomachining has been achieved by these techniques, they have the following difficulties. They include multiple and time-consuming process steps such as coating regists, patterning, development, selective etching, and removing the residual regists. And there are a limited number of materials for which etchants and resists are available. Practical applications require low-cost and high throughput techniques with which a variety of materials can be machined.
Compared to techniques mentioned above, photo-machining, i.e., direct laser machining, is one of the most promising techniques because of the precision, which is as high as the diffraction limit, that can be achieved, its suitability for mass-production, and because it is a direct single step process [6–14]. The photo-machining of transparent materials, however, suffer from the obvious difficulty of transferring photon energy of laser light to the materials because the materials are transparent. Moreover, photo-machining with a precision of $\sim 10$ nm requires soft X-rays.

In the present work, we have investigated one-step direct micromachining of a variety of materials using pulsed laser plasma soft X-rays (LPSXs) [15,16]. For this purpose, we designed an ellipsoidal mirror for focusing LPSXs at around 10 nm most efficiently. Applying the LPSX technique, we have investigated micromachining synthetic quartz glass, fused quartz glass, Pyrex, CaF$_2$, LiF, LiNbO$_3$, Si and silicone. Further, we have demonstrated quartz glass micromachining with a resolution higher than 100 nm.

2. Experimental

Figure 1 shows the experimental setup. Samples ($S$) were irradiated with LPSXs ($X$) in a vibration-isolated vacuum chamber (VIC International, Japan) at a pressure of $2 \times 10^{-4}$ Pa. For patterned irradiation, we used either a Ni grid with a mesh #2000 ($M$) or a WSi mask with 200-nm-pitch line-and-space patterns. The Ni was placed on the samples, as a contact mask. The WSi mask was fabricated by depositing a WSi layer with a thickness of 80 nm on samples using sputtering technique and patterned by electron beam lithography technique. After LPSX irradiation, the WSi mask was removed selectively by reactive ion etching technique.

![Figure 1](image1.png)

The LPSXs ($X$) were generated by irradiation of a Ta target ($T$) with 532 nm Nd:YAG laser light with a pulse duration of 7 ns, at an energy of 700 mJ/pulse, at a fluence of $\sim 1 \times 10^4$ J/cm$^2$ using a focusing lens ($L$) with a focal length of 100 mm. It is a reasonable evaluation that the LPSX pulse has the same pulse duration of the Nd:YAG laser light pulse, on the time scale of a nanosecond [17].

The LPSXs were focused onto sample surfaces using an ellipsoidal mirror $E$, made of quartz glass and coated with a Au layer. We designed the ellipsoidal mirror so as to maximize power density of LPSXs on the sample surfaces. The power density depends on solid angle of the mirror $\omega$, 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 ellipsoidal mirror with $\psi = 120^\circ$, $f = 150$ mm and

![Figure 2](image2.png)

Figure 2. 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.
As $\theta$ increases, solid angle $\omega$ increases and hence total intensity of LPSXs incident to the mirror increases [18]. In contrast, as $\theta$ increases, reflectivity $R$ drastically decreases in the soft X-ray region around 10 nm. Figure 2 shows product of $R$ and $\omega/4\pi$, which is proportional to the power density of the LPSXs on the samples. Based on the result shown in Fig. 2, 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 samples efficiently. In order to machine large areas, samples were placed closer to the ellipsoidal mirror, than the focal point of the mirror so that the LPSX beam has a radius of 100 $\mu$m on the surface of the samples.

The X-ray emission spectrum of the Ta laser plasma and X-ray absorption spectrum of a thin SiO$_2$ film were measured using a time-resolved X-ray spectrometer. Details of the soft X-ray spectroscopy are given elsewhere [17,19]. It is confirmed that the Ta laser plasma emits LPSXs at wavelengths around 10 nm and that the SiO$_2$ film absorbs soft X-rays in that wavelength region. In the absorption spectrum of SiO$_2$ film, the $L_{\text{II,III}}$ and $L_4$ edges are observed at 100 eV and 150 eV, respectively. The $L_{\text{II,III}}$ and $L_4$ edges correspond to optical transitions of $2p$ and $2s$ core electrons in Si atoms to the bottom of the conduction band, respectively. Below the $L_{\text{II,III}}$ edge, optical transitions from valence band and the O 2$s$ core-like level to the continuum dominate. It is noted (a) that Ta laser plasma emit light even in the visible wavelength range as well as soft X-rays with photon energy up to 500 eV and (b) that the ellipsoidal mirror have effective focusing efficiency for soft X-rays with photon energy below $\sim$200 eV. Therefore, samples were irradiated with Ta plasma light in a range from visible wavelength to 200 eV.

3. Quartz nanomachining using laser plasma soft X-rays

Figure 3 shows a confocal microscope (Keyence Corp, VK-8510) image of a synthetic quartz glass plate (Tosoh Quartz Co., Ltd., ES grade), after 10 shots of LPSX irradiations at room temperature through square apertures of the Ni contact mask. It is clearly seen that square regions are ablated. The ablated area has a depth of 470 nm. Atomic force microscope observation revealed that the LPSX-irradiated regions have a root mean square roughness less than 10 nm. It is found that quartz glass plates can be smoothly ablated with a precision less than 10 nm, in the depth direction.

![Figure 3. A confocal microscope image of a quartz glass plate after irradiation of LPSXs through square apertures of a contact mask.](image)

In order to investigate lateral resolution, we fabricated a WSi contact mask with line-and-space patterns with a pitch of 200 nm on a quartz glass plate. Figure 4 shows an atomic force micrograph of the quartz glass plate, after a single shot irradiation with laser plasma soft X-rays and removing the WSi mask. In order to observe the nanostructures on the insulating quartz glass by scanning electron microscopy (SEM) more precisely, we replicated the structures to an ultra-thin UV-nanoimprint resin layer prepared on a conductive Si substrate. Figure 5 shows...
Figure 4. An AFM image of a quartz glass plate after a single shot irradiation with LPSXs through a 200-nm-pitch line-and-space contact mask.

Figure 5. A SEM image of nanostructures on photocurable resin. The nanostructures were fabricated by UV nanoimprint method using the quartz glass template shown in Fig. 4.

the SEM image of the replicated nanostructures. These results have demonstrated that a quartz glass plate can be machined with a resolution higher than 100 nm. With X-ray imaging optics, direct photo-machining with a precision less than ~100 nm should be achieved.

Further, in order to achieve nanomachining, it is important to demonstrate that quartz glass can be ablated by LSPX’s at a short wavelength such as 10 nm, because precision is limited by the diffraction limit. For that purpose, we filled the vacuum chamber with Ar gas, which can be used as a band pass filter. Figure 6 shows transmittance spectra of Ar gas at given pressures. Ar gas absorbs photons at 20–40 eV even at pressures below 50 Pa and photons higher than 40 eV at pressures higher than 50 Pa, effectively. Open circles in Fig. 7 shows ablation rate of quartz glass in Ar gas, as a function of Ar gas pressure. In Fig. 7, transmittance of Ar gas at 20 eV and 100 eV are also shown by curves (a) and (b), respectively. It is found that quartz glass is ablated in Ar gas even at pressures higher than 50 Pa, at which LPSXs in the region of 20–40 eV are eliminated. Therefore, it can be concluded that only LPSXs with photon energies higher than 40 eV (~30 nm) can ablate quartz glass.

It is difficult to explain the results obtained here by only thermodynamic processes. In the case of quartz glass, LPSXs are absorbed in a surface layers with a thickness of ~100 nm. Because thermal diffusion length during LPSX irradiation (= 7 ns) is roughly estimated to be 80 nm, the LPSXs energy is accumulated in the same region without significant heat diffusion [16]. Therefore, the accumulated energy density (30 kJ/cm³) is estimated to be of the same order as the evaporation energy of SiO₂ (76 kJ/cm³). Thus, 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 shown in Fig. 5, however, quartz glass is machined more precisely than heat diffusion length. Therefore, processes other than thermodynamic process contribute ablation of quartz glass by LPSX irradiation.

4. Micromachining of a variety of inorganic materials
We irradiated a variety of materials with LPSXs and measured ablation depth as a function of the number of LPSX irradiation shots. It is found that the depth is proportional to the shot number for CaF₂, LiF, SiO₂ (quartz glass) and LiNbO₃, having ablation rates of 80 nm/shot, 70 nm/shot, 50 nm/shot and 40 nm/shot, respectively. This indicates that ablation is intrinsic
to interaction of LPSXs with the materials but not with surface specific states such as surface contaminations or surface cracks before LPSX irradiation. In addition, we have ascertained that Si, silicone and pyrex are machined by LSPX processing. It should be noted that a variety of materials can be machined by LSPX processing.

5. Conclusion
We have investigated micromachining of a variety of materials by direct soft X-ray irradiation, using LPSXs at around 10 nm. The pulsed LPSXs were generated by irradiation of a Ta target in a vacuum chamber with Nd:YAG laser light at 532 nm, with a pulse duration of 7 ns, at a fluence of $\sim 10^4 \text{J/cm}^2$. The LPSXs were focused on the surfaces of samples using an ellipsoidal mirror that is designed so that LPSXs at around 10 nm are focused efficiently. We found that quartz glass plates are ablated by LPSX irradiation at a rate of 48 nm/shot. Furthermore, the ablated regions have smooth surfaces with a roughness less than 10 nm after 10 shots of LPSX irradiation. It is demonstrated that quartz glass can be machined with a lateral resolution higher than 100 nm. In addition to quartz glass, the LPSX processing can be applied to micromachining of a variety of materials such as Pyrex, CaF$_2$, LiF, LiNbO$_3$, Si and silicone. With X-ray imaging optics, direct photo-machining with a precision less than $\sim 100$ nm should be achieved.

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