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Investigating interactions of intense soft X-rays with solid surfaces and resulting phenomena is still challenging. One could expect material removal from the surfaces (ablation) caused by soft X-ray irradiation at a precision as high as the diffraction limit of the soft X-rays. The X-ray ablation technique could enable us to fabricate nano- and micro-structures on sufaces of even transparent materials such as silica glass, polymethylmethacrylate (PMMA) and polydimethyl-siloxane (PDMS), which are highly valued for their use in the fields of nanometric chemical analysis and chemical reactions in medicine and biotechnology.

For machining at high resolution, light with a short wavelength is preferable because of the diffraction limit. In the X-ray region, however, most of the materials have less optical absorption at shorter wavelengths, resulting in no energy transfer of the light to the materials, that is, no ablation. Therefore, photons in the range of 100 eV–1 keV are suitable for micromachining. So far, synchrotrons have been utilized for extensive studies on interaction of soft X-rays with inorganic materials such as silica glass. However, silica surfaces are etched at a low rate and the exposed surfaces are modified to Si-rich ones. In contrast, photo-etching of polymers has been realized. PMMA surfaces can be removed (etched) by X-ray irradiation without further chemical treatment. PMMA can also be etched by chemicals after X-ray irradiation, which is applied to fabricate micro-molds of PMMA and metals in the *Lithographie Galvanoformung und Abformung* (LIGA) process. In addition to synchrotrons radiation, soft X-rays from laser-produced plasma have been applied to PMMA ablation [1,2]. Barkusky *et al.* irradiated PMMA with focused laser plasma soft X-rays (LPSXs), using a Schwaltzschild objective that reflects X-rays at 13.5 \pm 1.0. Although they achieved high energy as high as 1 J/cm², X-rays out of the band were just absorbed by the objective.

In order to achieve a practical nano- and micromachining technique using LPSXs, we have developed a LPSX source and a focusing mirror for LPSX irradiation at high power density, and have investigated interactions of LPSXs with silica glass (SiO₂), PMMA, and PDMS at intensities beyond ablation threshold. Figure 1(a) shows the experimental setup. Tantalum plasma was generated by irradiation of a Ta target (*T*) with 532 nm Nd:YAG laser light (*Y*) with a pulse duration of 10 ns and a pulse energy of 500–800 mJ/pulse. The Nd:YAG laser was operated at 10 Hz and a single pulse was selected using a mechanical shutter. The laser-produced Ta plasma emits soft X-rays (*X*) around 100 eV (\simeq 10 nm), as shown in Fig. 1(b). The LPSX generation was carried out in a vacuum chamber (VIC International Inc.) at 2×10^{-4} Pa in order to avoid aborption of the generated LPSXs by air. The LPSXs have the same pulse duration as that of the Nd:YAG laser light. The LPSXs were focused onto a surface of silica (SiO₂) glass plates (*S*) using an ellipsoidal mirror (*M*) (Hidaka Kougaku Kenkyusho Co., Ltd.) that is made of silica glass and is coated with a Au layer on top of it. The mirror is designed so as to maximize power density of LPSXs at 100 eV on the surface of the samples [3]. As shown in Fig. 1(c), silica glass has optical absorption in the photon energy region. The details of the



Fig. 1. (a) Experimental setup for nano- and micromachining using laser plasma soft X-rays. (b) X-ray spectrum of light emission from laser-produced Ta plasma. (c) Absorption spectrum of a SiO_2 film with a thickness of 100 nm.



Fig. 2. Surface profiles of silica glass after laser plasma soft X-ray irradiation though (a) a Ni contact mask with square apertures with a window width of 8 μ m and (b) a WSi contact mask with a line and space pattern with a window width of 53 nm.

soft X-ray spectroscopy are given elsewhere [4, 5]. The power density of LPSX was roughly estimated to be 1×10^8 W/cm² from (a) conversion efficiency from pulsed Nd:YAG laser light at 532 nm to soft X-rays [6], (b) focusing efficiency [3, 7], and (c) area of cross section of LPSX beam on the samples, which was determined by geometry of the ellipsoidal mirror and samples [3]. The power density can be adjusted by keeping the samples away from the focal point of the LPSX beam.

Figure 2(a) shows a confocal laser microscope (Keyence, VK-8510) image of silica glass after LPSX irradiation through a Ni contact mask with square apertures with a width of 8 μ m. The LPSX-irradiated regions are removed and square holes are observed. The surface is ablated at 47 nm/shot at 3 \times 10⁷ W/cm² and surface roughness R_a is 1 nm after 10 shots of LPSX irradiation. The ablation depth is proportional to shot number of LPSX irradiation at rates of 0.1–150 nm/shot. It is remarkable that high-quality micromachining at high rates can be achieved using the LPSX technique.

In order to fabricate nanostructures on silica glass, a WSi line-and-space mask was fabricated on a silica plate by the electron beam lithography technique. The WSi mask had windows with a width of 53 nm and a ptich of 175 nm. After LPSX irradiation through the windows of the WSi contact mask, the WSi mask was removed by the selective ion etching technique. Figure 2(b) shows a cross section of the nano-trenches fabricated on the silica glass plate, observed using a scanning electron microscope. We have demonstrated that nanostructures can be fabricated by the LPSX technique.

The thermal diffusion length during the 10-ns LPSX pulse is estimated to be 80 nm while the fabricated nanostructures have finer features. The result indicates that ablation from a silica surface occurs faster than the thermal diffusion. In order to clarify the ablation process, we performed mass spectroscopy for species ejected from silica surface by LPSX irradiation [8]. We found that silica glass is broken into atomic species and that 1–15% of the species are ionized. Most of the ions are generated during LPSX irradiation before ejection from silica surface, because ionization caused by interactions with photons in the soft X-ray region in the gas phase is almost prohibited. Therefore, the ablation is possibly caused by Coulomb repulsion of ionic species that are generated by LPSX irradiation. This enables us to fabricate nanostructures on silica surfaces using even nanosecond LPSX pulses. In the infrared, visible and ultravilet regions, lasers with shorter pulse durations are often requied to realize micromachining at higher resolution as the resolution is limited by thermal diffusion lengths during laser pulses.

Recently, we found that silica glass can be ablated using LPSX in a narrow range of 6–25 nm. The LPSX was obtained using a Zr filter with a thickness of 100 nm that is transparent in the chosen spectral region. Compared to the wide band LPSX without any Zr filter, the narrow band LPSXs have an advantage that higher resolution can be achieved during LPSX irradiation. Further, it is essential to irradiate materials with LPSXs at sufficiently high power densities for the purpose of micromachining. Hence, it is advantageous to use X-ray optics with a glancing angle of incident such as an ellipsoidal mirror. The optics with glacing angle can focus LPSXs in a wide photon-energy range. Imaging optics with glancing angles such as a Wolter mirror would be preferable for practical use.

In addition to silica glass (SiO₂), the micromachining technique using LPSXs is applicable to a variety of materials such as Pyrex and Al_2O_3 , PMMA [9] and PDMS. By applying the PMMA ablation using LPSXs, syncrotrons could be replaced by laser-produced plasma sources in the LIGA process. This would enable us to fabricate micro components made of polymers and metals in a practical way. The PDMS ablation could be applied to medicine and biotechnology because of its biocompatibility. Micro-structures at high aspect ratio such as through-holes could be fabricated using LPSXs.

In conclusion, we have investigated a practical nano- and micromachining using LPSXs. It is found that silica glass is ablated at rates of 0.2–150 nm/shot. At the same time, high quality micromachining can be achieved. Typically, suraface roughness R_a is 1 nm after 10 shots of LPSX ablation at a rate of 47 nm/shot. Furthermore, it is demonstrated that 50 nm trenches are fabricated using LPSXs. The LPSX technique would provide a practical way for fabricating micro total analysis systems, micro fludic devices, MEMS devices.

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