Quartz micromachining using laser plasma soft x rays and ultraviolet laser light

Tetsuya Makimura,[a] Shinjo Mitani, Youichi Kenmotsu, and Kouichi Murakami
Institute of Applied Physics, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan

Michiaki Mori
Applied Photon Research Group, Advanced Photon Research Center, Japan Atomic Energy Research Institute, 8-1 Umemidai, Kizu, Souraku-gun, Kyoto, 619-0215, Japan

Kiminori Kondo
Institute of Laser Engineering, Osaka University, Suita, Osaka 565-0871, Japan

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We have investigated a technique for micromachining inorganic transparent materials. In the technique, patterning and coloration are performed by the direct irradiation of materials with pulsed laser soft x rays and the patterned areas are ablated using ultraviolet laser light. The technique utilizes the high precision of the soft x rays and the high energy density of conventional laser light. For demonstration, we irradiated quartz plates with Ta laser plasma soft x rays. This results in generation of transient surface opaque layers that absorb more than 40% of the 266 nm Nd:YAG laser light. Applying the technique, quartz plates are found to be ablated smoothly at 85 nm/shots. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1782265]

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[1,2] and deoxyribonucleic acid (DNA) sieving based on SiO_2 nanomachining techniques[3,4] have attracted some interest. For practical applications, techniques with high precision and high productivity are in great demand for machining inorganic transparent materials.

Electron-beam patterning[5–8] is one of the approaches used in processing quartz on a nanometer scale. Direct write electron-beam lithography and subsequent reactive ion etching has been used to fabricate gratings[5] and lenses[6] in quartz substrates. Photolithography using photoregists is one of the most developed techniques. Bennion *et al.* demonstrated fabrication of a first-order Bragg grating in an optical fiber.[9] Fine structures in transparent materials can also be fabricated using focused ion beam etching. Albert *et al.* have demonstrated writing a grating on a silica substrate using focused ion beam implantation.[10] All these fabrication techniques includes a number of process steps such as coating regists, patterning, development, selective etching, and removing the residual regists. Although nanomachining has been done by these techniques, practical applications require low-cost and high throughput single step techniques with which a variety of materials can be machined.

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. The photo-machining of transparent materials, however, suffer from the obvious difficulty of transfering photon energy of laser light to the materials because the materials are transparent. Hence, machining transparent materials requires photon absorbers such as a defect state in SiO_2,[11,12] a plasma produced close to transparent materials,[13] and solutions containing photo-absorbing mediums.[14,15] Femtosecond laser light can be absorbed by transparent materials via a multiphoton process, and thereby machining such as ablation and modification can be performed.[16–19] Further, photo-machining with a precision of $\sim$10 nm requires soft x rays, although the intensity is not so high for machining.

Here, we report on a micromachining technique, in which patterning is performed by direct irradiation of quartz plates with laser plasma soft x rays and the patterned area is ablated by conventional UV laser light. The technique utilizes the high space resolution of soft x rays and the high energy density of conventional UV/visible laser light. It can be applied to the nanomachining inorganic transparent materials, without the above-mentioned difficulties. Applying the technique, we demonstrate micromachining quartz plates.

Figure 1(a) shows the experimental setup for the micromachining of transparent materials. Synthetic quartz glass plates (Q) (Toshiba Ceramics Co., Ltd., T-4040) were irradiated with laser plasma soft x rays (X) and UV laser light (Y_2) in a vacuum chamber at a pressure of 2×10^{-4} Pa. The temperature of the quartz plates was controlled in the range 18–295 K, using a He compressor unit.

The soft x rays (X) were generated by irradiation of a Ta target (T) with Nd:YAG laser light with a pulse duration of 7 ns and an energy of 800 mJ/pulse, at an energy density of $\sim1\times10^4$ J/cm^2 using a focusing lens (L_1) with a focal length of 10 cm. It is a reasonable evaluation that on a nanosecond time scale the pulse duration of the soft x rays is the same as that of the Nd:YAG laser light (Y_1).[20] The soft x rays were focused onto the quartz plates using an ellipsoidal mirror (M) (Hidaka Kougaku Kenkyusho Co., Ltd.), made from quartz and coated with Au.

Figures 1(b) and 1(c) show the light emission spectrum of the Ta laser plasma and the absorption spectrum of a SiO_2

[a]Electronic mail: makimura@ims.tsukuba.ac.jp

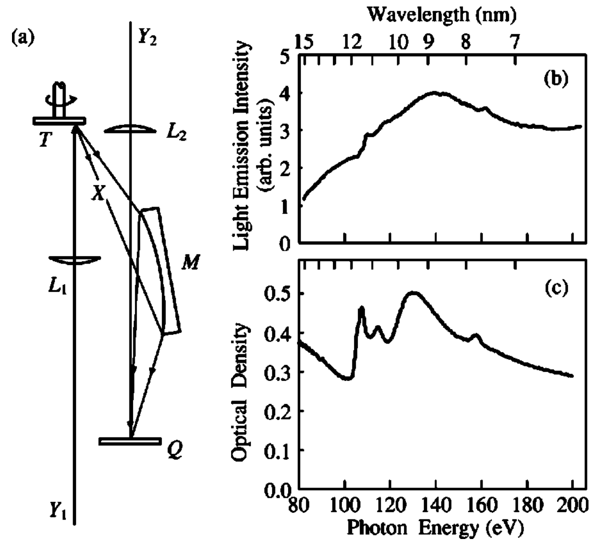

FIG. 1. (a) The experimental setup for micromachining quartz plates (Q) using laser plasma soft x rays (X) and UV laser light (L_2). (b) Light emission spectrum of a Ta laser plasma in the soft x-ray region. (c) Light absorption spectrum of a SiO_2 film in the soft x-ray region.

film with a thickness of ~100 nm, in the soft x-ray region. Details of the soft x-ray spectroscopy are given elsewhere.[20,21] It is noted that the Ta laser plasma emits light at wavelength at around 10 nm and that the SiO_2 film absorbs light in that wavelength region.

In addition to soft x rays, the quartz plates were irradiated with 266 nm Nd:YAG laser light (Y_2), using a lens (L_2) with a focal length of 50 cm. The 266 nm UV light has a pulse duration of 7 ns and an energy density of $\sim 1\ \mathrm{J/cm^2}$. The UV light pulse was delayed with respect to the soft x-ray pulse using a delay generator.

Figure 2 shows an optical microscope image of a quartz plate after four sets of irradiation with soft x rays and UV laser light with a delay of 7 ns at 18 K. For patterning, a Ni grid with a mesh #2000 was placed on the quartz plates as a contact mask. It can be clearly seen that the patterned regions are smoothly ablated. The ablated area was inspected using a confocal microscope (Keyence Corp, VK-8510 and VK-9500) and was found to have a depth of 450 nm and a root mean square value less than ~30 nm. The root mean square value is the same as the limit of the microscope. The depth of

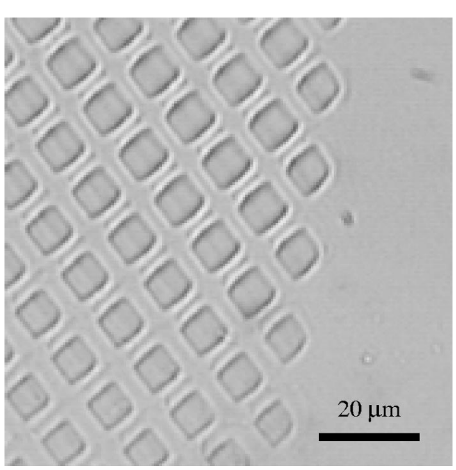

FIG. 2. An optical microscope image of a quartz plate after irradiation with laser plasma soft x rays and UV laser light.

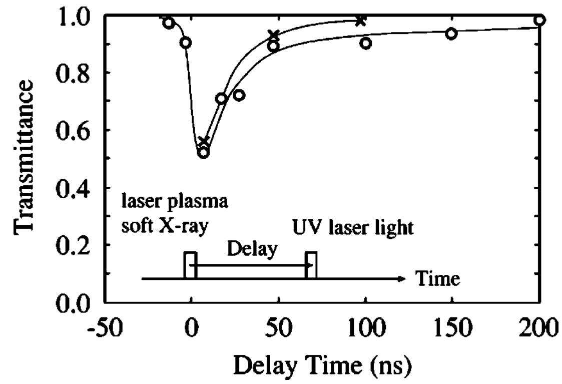

FIG. 3. Transient transmittance at 266 nm as a function of the delay between the 266 nm laser pulse and laser plasma soft x-ray pulse. The transmittance was measured at 295 K (×) and 18 K (∘).

the ablated area is proportional to the number of sets of irradiation, and the ablation rate in the range of 1–10 sets was measured and found to be 85 nm/set. The steepness at the edge of each pattern is less than 1 μm, which is the detection limit of the confocal microscope.

For *in situ* monitoring, we measured the intensity of transmitted 266 nm laser light. Figure 3 shows the transmittance as a function of the delay of the 266 nm laser pulse from the laser plasma soft x-ray pulse, at quartz plate temperatures of 18 K (∘) and 295 K (×). We found that transient light absorbing states are produced by soft x-ray irradiation of the quartz plates. The states decay on a timescale of 100 ns, depending on the temperature. It is remarkable that more than 40% of the UV laser light is absorbed at a delay of 7 ns even at room temperature, as shown by crosses in Fig. 3. The result shows that it is possible to perform machining at room temperature.

The energy density of absorbed UV light is estimated to be comparable to the evaporation of SiO_2, as follows. Because the penetration depth of soft x rays at 10 nm is ~100 nm, 50% of the UV light at $1\ \mathrm{J/cm^2}$ is absorbed in the 100 nm surface layer. Therefore, the energy density of absorbed UV light is $50\ \mathrm{kJ/cm^3}$, which is comparable to that for evaporation: $SiO_2\,(\mathrm{solid}) + 76\ \mathrm{kJ/cm^3} \rightarrow Si\,(\mathrm{gas}) + 2O\,(\mathrm{gas})$.

The micromachining process can be explained by two models, depending on the power density of the laser plasma soft x ray on the surface of the quartz plates. One is the x-ray exciton model that is applicable at low energy densities and the other is melting model that is applicable at high energy densities.

In the x-ray exciton model, irradiation of transparent materials with soft x rays results in formation of self-trapped excitons (STE),[22,23] as illustrated in Fig. 4. The self-trapped excitons localize themselves in a small region comparable to the lattice constant. In addition, the self-trapped excitons absorb light in the UV or visible range, due to transitions from the lowest state (E) to excited states (E^*).[24–26] Self-trapped excitons in amorphous SiO_2 have a continuous absorption band in the photon energy region above 3 eV, with a large absorption component at around 5 eV.[26] Hence, a Nd:YAG laser at 266 nm (4.6 eV) is suitable for energy transfer via the self-trapped excitons in SiO_2.

In the melting model, the surface layer is melted when the quartz plates are irradiated with laser plasma soft x rays. The irradiation results in the formation of highly excited

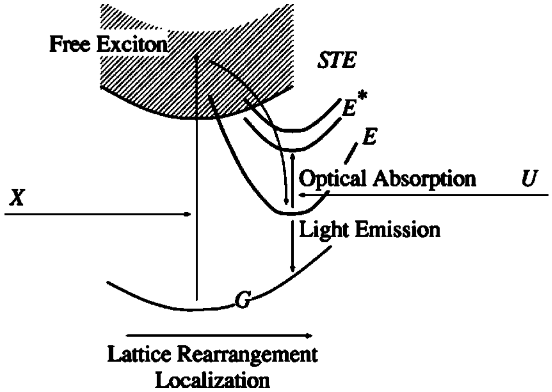

FIG. 4. Proposed x-ray exciton technique for micromachining inorganic transparent materials.

electron-hole pairs, which relax into lower states by energy dissipation to lattice vibrations. Thus, the temperature of the lattice increases beyond the melting point. The molten layer is opaque in the UV and visible regions because the band gap disappears.[20] The UV laser light is absorbed by the liquid SiO_2 layer.

Sugioka *et al.* reported a vacuum ultraviolet (VUV)-UV multiwavelength technique for micromachining quartz plates.[11] Compared to their technique, the x-ray–UV technique in the present work have the following potential capabilities for nanomachining quartz plates. The diffraction limit is much shorter and hence we can expect micromachining with higher precision up to 10 nm in the lateral direction. Total intensity of absorption induced by soft x ray is the same as that induced by VUV laser light. But, in the x-ray–UV technique, absorbers are generated in the thinner surface layers because the soft x rays have a penetration depth of $\sim$100 nm. This will enable us nanomachining quartz plates in the depth direction.

They proposed that UV laser light is absorbed by defects in SiO_2 excited by VUV laser light, in their VUV–UV technique.[11] In our x-ray–UV technique, it might be possible that the defects that are excited by soft x-ray irradiation absorb 266 nm laser light. In this case the average distance between the defects should be much less than 30 nm, e.g., 3 nm, because the surface roughness of the machined regions is less than 30 nm. Then the defect density should be 10^{20} cm^{-3}, which can be found in only heavily damaged or doped SiO_2. Therefore, it is rather possible that absorbers which are more intrinsic to the material, i.e., excitons or molten layers, are generated by soft x-ray irradiation.

In conclusion, we have investigated micromachining quartz plates using laser plasma soft x rays together with UV laser light. In the micromachining technique, patterning and coloration are performed by the direct irradiation of quartz plates with laser plasma soft x rays and the patterned areas are ablated using UV laser light. The method utilizes the high precision of the soft x rays and the high energy density of the UV laser light. It is found that more than 40% of 266 nm Nd:YAG laser light is absorbed by the surface opaque layers that are generated by irradiation of Ta laser plasma soft x rays. We have demonstrated that quartz plates are smoothly machined by irradiation of the soft x rays and the 266 nm laser light, at 85 nm/shot. With further development of x-ray imaging optics, machining with a precision as high as the diffraction limit, that is, 10 nm, should be achieved.

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